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## User's Manual for PANDA II: A Computer Code for Calculating Equations of State

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## User's Manual for PANDA II: A Computer Code for Calculating Equations of State

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### Abstract

PANDA is an interactive computer code that is used to compute equations of state (EOS) for many classes of materials over a wide range of densities and temperatures. The first step in the development of a general EOS model is to determine the EOS for a one-component system, consisting of a single solid or fluid phase and a single chemical species. The results of several such calculations can then be combined to construct EOS for multiphase and multicomponent systems. For one-component solids and fluids, PANDA offers a variety of options for modeling various contributions to the EOS: the zero Kelvin isotherm, lattice vibrations, fluid degrees of freedom, thermal electronic excitation and ionization, and molecular vibrational and rotational degrees of freedom. Two options are available for computing EOS for multicomponent systems from separate EOS for the individual species and phases. The phase transition model is used for a system of immiscible phases, each having the same chemical composition. In the mixture model, the components can be either miscible or immiscible and can have different chemical compositions; mixtures can be either inert or reactive. PANDA provides over 50 commands that are used to define the EOS models, to make calculations and compare the models to experimental data, and to generate and maintain tabular EOS libraries for use in hydrocodes and other applications. Versions of the code are available for the Cray (UNICOS and CTSS), SUN (UNIX), and VAX (VMS) machines, and a small version is available for personal computers (DOS). This report describes the EOS models, use of the commands, and several sample problems.



Giant Panda (*Ailuropoda melanoleuca*)



# Contents

<b>1. Introduction</b>	10
1.1 Background	10
1.2 General Approach	11
1.3 Overview of Theoretical Models	12
1.4 Obtaining the Code	14
1.5 Code Execution	15
1.6 Conventions	19
1.7 Personal Computer Version	22
<b>2. One-Component Solids and Fluids</b>	24
2.1 General	24
2.2 The SET BAS Command	24
2.3 MOD SOL - The Solid Model	26
2.4 MOD LIQ - The Fluid Model	28
2.5 SOL TAB and LIQ TAB - Tabular EOS Input	29
2.6 Two-Temperature EOS	30
<b>3. The Zero-Kelvin Isotherm</b>	32
3.1 General	32
3.2 ICLD=1: Cold Curve from Shock Hugoniot	32
3.3 ICLD=2: Analytic Lennard-Jones (LJ) Formula	33
3.4 ICLD=3: Analytic EXP-N Formula	34
3.5 ICLD=4: Tabular Cold Curve	35
3.6 ICLD=5: Universal Metal EOS	36
3.7 The TFD Match	36
3.8 The LJ Match	37
3.9 The EXP6 Command	38
3.10 The TFD CURVE Command	39

<b>4. Solid Lattice Vibration Models</b>	40
4.1 General	40
4.2 The Debye Model	41
4.3 Solid-Gas Interpolation Formula	42
4.4 The Einstein Model	43
4.5 Options for the Gruneisen Function	43
4.6 The Virial Match	45
<b>5. Perturbation Theory of Fluids</b>	47
5.1 General	47
5.2 The Equations	48
5.3 Low Temperature Extrapolation	51
5.4 Radial Distribution and Structure Factor	51
5.5 Viscosity and Diffusivity	52
<b>6. Internal Vibrational and Rotational Terms</b>	54
6.1 General	54
6.2 Rotational Terms	54
6.3 Vibrational Terms	56
6.4 The BROTH Command	58
<b>7. Dimerization Corrections</b>	59
7.1 General	59
7.2 EOS For Dimer Molecules	59
7.3 Chemical Equilibrium Calculation	61
<b>8. Thermal Electronic Contributions</b>	62
8.1 General	62
8.2 Interpolation on Entropy Tables	63
8.3 Calculation from Specified Levels	65
<b>9. Ionization Equilibrium Theory</b>	66
9.1 General	66
9.2 Basic Theory	66
9.3 Continuum Lowering	68
9.4 The IONEQ Command	70
9.5 Calculation of Energy Levels	72

<b>10. Mixture-Chemical Equilibrium Model</b>	75
10.1 General	75
10.2 Theory	76
10.3 Input: the MOD MIX Command	77
10.4 Tabular EOS for Components	80
10.5 Analytic EOS for Components	81
10.6 The CONC PLOT Command	82
<b>11. The Phase Transition Model</b>	84
11.1 General	84
11.2 Input: the MOD TRN Command	84
11.3 Search for Phase Boundaries	86
11.4 The PHASE DIAG Command	87
<b>12. Options for Testing a Model</b>	88
12.1 General	88
12.2 The EOS Command	88
12.3 Isotherms and Isochores	89
12.4 Isobars	90
12.5 Isentropes	91
12.6 Hugoniots	92
12.7 Chapman-Jouguet State	94
12.8 Vaporization Curve	94
12.9 Spinodal Points	95
12.10 Critical Point	95
12.11 Melting Curve	97
<b>13. EOS Tables and Libraries</b>	98
13.1 Structure of Sesame Files	98
13.2 Constructing Sesame Tables	98
13.3 The 201 Table	100
13.4 Mesh for a 301 Table	101
13.5 The 301 Table: Maxwell Constructions	102
13.6 The 303 and 304 Tables	104
13.7 The 401 Table	105

<b>14. Maintaining a Sesame Data Base</b>	107
14.1 Structure of Binary and ASCII Files	107
14.2 Listing a Sesame Library File	108
14.3 The UPDATE, DELETE, and EXTRACT Commands	108
14.4 Converting Between ASCII and Binary Files	109
<b>15. Miscellaneous Options</b>	111
15.1 User-Defined Models	111
15.2 Making a File of Experimental Hugoniot Data	111
15.3 Defining a Material Strength Model	112
15.4 Monte Carlo Calculations	114
<b>16. Test Problems</b>	118
16.1 Test Problem 1: Aluminum EOS	118
16.2 Test Problem 2: Multiphase EOS for Calcium Carbonate	119
16.3 Test Problem 3: Chemical Equilibrium in Nitrogen Gas	120
16.4 Test Problem 4: Detonation Properties of an Explosive	122
<b>17. Acknowledgements</b>	124
<b>Appendix A. Separation of Degrees of Freedom</b>	125
A.1 Decoupling of Two Subsystems	125
A.2 Separating Electronic and Nuclear Motions	127
A.3 The Two-Temperature EOS	128
A.4 Separating Vibrational-Rotational and Translational Motions	129
<b>Appendix B. Calculation of Cold Curves From Hugoniot Data</b>	130
B.1 Analytic Formula for $\gamma$ and $\Theta$	130
B.2 Cold Curve Formula for $\gamma$ and $\Theta$	131
B.3 Interpolation and Extrapolation	131
<b>Appendix C. Corrections to the Einstein and Debye Models</b>	132
C.1 The Einstein Model	132
C.2 The Debye Model	133
<b>Appendix D. Monomer-Dimer Equilibrium</b>	135
<b>Appendix E. Output File for Test Problem 1</b>	137

Appendix F. Output File for Test Problem 2 . . . . .	143
Appendix G. Output File for Test Problem 3 . . . . .	155
Appendix H. Output File for Test Problem 4 . . . . .	159
References . . . . .	163

## Tables

1.1 Control Commands . . . . .	16
1.2 Commands Used to Define an EOS Model . . . . .	17
1.3 Commands for Testing an EOS Model . . . . .	18
1.4 Commands for Constructing EOS Tables and Libraries . . . . .	19
1.5 Special Input Symbols . . . . .	20
1.6 Symbols and Units . . . . .	21
8.1 Sample of Electronic Entropy Data File . . . . .	64
10.1 Keywords Used With MOD MIX Command . . . . .	79
12.1 Sample of PANDA Plot File . . . . .	89
13.1 Format of Sesame Data Records . . . . .	99

## Figures

13.1 Typical isotherms in the vapor-liquid coexistence region . . . . .	103
16.1 EOS calculations for aluminum. . . . .	119
16.2 Calculated phase diagram for calcium carbonate. . . . .	120
16.3 Calculated Hugoniot for shocked nitrogen gas. . . . .	121
16.4 Calculated molecular concentrations for shocked nitrogen gas. . . . .	121
16.5 Detonation velocity vs. loading density for PETN explosive. . . . .	123
16.6 Molar concentrations of detonation products for PETN. . . . .	123

# 1. Introduction

## 1.1 Background

The equation of state (EOS) of a substance describes the dependence of its thermodynamic properties, such as pressure and energy, upon density and temperature. The EOS and other constitutive properties of matter are important for many problems in both basic and applied research, including astrophysics, geophysics, reactor safety, inertial confinement fusion, the effects of explosions, and hypervelocity impact phenomena. Most of these investigations involve the dynamic loading of materials and require computer simulations using hydrodynamic codes. Stimulated by this broad interest, many techniques have been developed for measuring and calculating the EOS and related properties. Recent work in this field is surveyed in references [1]-[7].

In order to construct an EOS model that is valid over a wide range of densities and temperatures, it is necessary to consider many different physical and chemical phenomena [7]. In the low temperature solid regime, the EOS is determined primarily by the ground state electronic energy and by lattice vibrations; changes in thermodynamic properties due to polymorphic phase transitions may also be important. Melting and vaporization occur with higher temperatures and/or expansion; these transitions change the nature of the molecular thermal motions, markedly affecting the EOS. At still higher temperatures, thermal excitation and ionization of the electrons become most important; a model for the electronic structure of hot dense matter is required in this regime. For plastics, polymers, and other chemical compounds, dissociation and other reactions can also have profound effects on the EOS.

Many new theories for treating the above phenomena have been developed in recent years. Most of these models are much too complicated to be incorporated into analytic EOS packages for use in hydrocodes. However, the Sesame EOS library [8]-[14] does offer the capability to make use of such theories; it provides EOS data having a general, tabular format that is suitable for use in wave propagation codes [11]-[14]. Sesame tables can be used to represent EOS surfaces of arbitrary complexity. Therefore, extensive theoretical calculations can be made and saved, and it is possible to use sophisticated models that cannot be built into any analytic EOS option.

The PANDA code [15] was developed for constructing sophisticated equations of state to describe the behavior of complicated materials. It offers a basic set of theoretical modules that can be used to describe the various terms in the model. The user decides which of these options are to be included in the calculation, enters the necessary pa-

rameters, and performs various computations to test the EOS and compare results with experiment. After a model has been refined and deemed to be satisfactory, an EOS table is created and made available for hydrocodes and other applications using the machinery provided by the Sesame library.

The first version of PANDA [15] was designed for constructing EOS for either a one-component solid or fluid. It did not provide options for computing thermal electronic contributions to the EOS, a multiphase EOS, or an EOS for a mixture. Previously, these tasks were carried out using several other codes and small programs that were under development and were not documented. These and other capabilities have been added to the new version of PANDA. An interface has been added to install EOS models defined by users. The code has been converted to FORTRAN 77 and revised to meet higher standards for quality assurance [16]. A number of improvements and conveniences have also been added to the input and output interfaces; as a result, some minor revisions must be made to old input files before they can be processed by PANDA II.

## 1.2 General Approach

The goal of this work is to formulate a scheme that can be used for a “global” EOS, one that is realistic over a very wide range of densities and temperatures, yet includes as much of the physics and chemistry of matter as possible. The first problem in constructing such a model is to find a suitable division of the calculation into separate and tractable parts. This task is not a simple one, and it cannot be accomplished without introducing approximations.

Many EOS theories make assumptions that are accurate within a certain density-temperature region but give unacceptable results outside that domain. One solution to this difficulty is to construct an EOS in “pieces”. Several models are used, each in a different region of density and temperature, and the results are fitted together by interpolation and smoothing procedures. Although this methodology can give satisfactory results, it is very laborious. Several different computer codes may be needed, and considerable care and judgement must be exercised when fitting the models together in regions where they give significantly different predictions. Thermodynamic consistency is often lost in regions of interpolation.

Therefore, the PANDA code relies on a different approach, one in which fundamental parts of the EOS *model* are identified, treated separately, and assembled into one table, all within one code. These “pieces” consist of the individual solid and fluid phases, the different chemical species, and the contributions from various degrees of freedom to the thermodynamic properties. The theories that are used to treat each part of the problem have been developed to be thermodynamically consistent and to give reasonable results at all densities and temperature. This procedure for constructing an EOS consists of the following steps.

1. Begin with a one-component system, consisting of a single phase of a single chemical species. Separate the EOS into contributions from different degrees of freedom.
2. Assemble data for the ground electronic state ( $0^\circ K$  isotherm, or “cold curve”) and thermal electronic excitations from quantum mechanical calculations and experimental measurements.
3. Combine cold curve, contributions from nuclear degrees of freedom, and thermal electronic terms into a total EOS table for a one-component solid or fluid. (In this report, the term “fluid” refers to the liquid, vapor, and supercritical regions.)
4. To account for the effects of chemical reactions, construct an EOS for a mixture, using separate EOS tables for each chemical species. Make a chemical equilibrium calculation to determine the composition as a function of density and temperature.
5. If more than one phase is present, compute the phase boundaries and the multiphase EOS from separate EOS tables for each phase.

## 1.3 Overview of Theoretical Models

The above objectives are achieved by constructing an EOS model from a set of basic theoretical modules that are available in PANDA. The code offers the following options.

- $0^\circ K$  isotherm
- solid lattice vibrations
- fluid molecular thermal motion
- internal vibration and rotation
- dimerization corrections (fluids only)
- electronic excitation and ionization
- tabular input
- mixture-chemical equilibrium model
- phase transition model
- user-defined model



The first seven options are used to construct EOS for one-component solids and fluids. The general procedures for those problems are discussed in Ch. 2, while details pertaining to the individual options are given in Chs. 3-8. The mixture and phase transition models are discussed in Chs. 10 and 11, respectively. Section 15.1 describes how users can add a new model to the code.

The  $0^\circ K$  isotherm (Ch. 3) can be constructed from experimental static and shock wave measurements, band theoretical calculations, and a variety of other theoretical models [7]. PANDA provides several options for analyzing, fitting, and extrapolating the data selected by a user. The cold curve can be input to the code as a table, if desired.

For solids, the lattice vibration terms (Ch. 4) can be calculated using a Debye or Einstein model. The user may select one of several options for the Debye (Einstein) temperature and the Grüneisen function. The internal vibrational degrees of freedom (Ch. 6) can also be used for solids having more complicated phonon spectra. PANDA provides formulas for extrapolating the solid EOS to the ideal gas limit at high temperatures and low densities, for use in simple models where a user wishes to bypass the full theoretical treatment.

EOS for fluids (Ch. 5) are computed using the CRIS model [17]. Hard-sphere perturbation theory is used to calculate the contributions from thermal motion of the molecular centers of mass, and the solid cold curve is used to specify the necessary information about the intermolecular forces. Therefore, this model does *not* require the definition of a pair potential or a Grüneisen parameter. All input can be defaulted after the cold curve has been defined.

Contributions from internal vibrational and rotational degrees of freedom (Ch. 6) are calculated using the harmonic oscillator-rigid rotator approximation [18]. The user must supply vibrational frequencies and rotational constants, quantities normally obtained from spectroscopic data [18] [19]. Anharmonicity corrections can be included by specifying the density and temperature dependence of the vibrational frequencies; these features are useful in modeling the optical branches of a lattice vibrational spectrum.

The dimerization option (Ch. 7) is available to correct the EOS of a monatomic fluid for the formation of molecules in the vapor phase, a feature that is useful for certain metals. The mixture-chemical equilibrium model should be used for problems where higher densities or more complicated chemical reactions are involved.

The contributions from thermal electronic excitation can be calculated using one of three methods that are described in Chs. 8 and 9. The code offers two simple analytical models for calculating the thermal electronic term. In order to use more sophisticated quantum-mechanical models, which usually require large amounts of labor and computing time, PANDA also allows for this term to be computed separately and tabulated for future use. The tabular interpolation scheme and the two simple models are discussed in Ch. 8. An ionization equilibrium model that can be used to generate tables of the electronic

term is discussed in Ch. 9.

In addition to the options discussed above, all or part of the EOS can be read in to PANDA as a table in the standard Sesame format. This tabular option, discussed in Sec. 2.5, provides a link between other codes and the computing machinery provided by PANDA. It can also be used to study EOS tables that have been created in previous PANDA calculations and to generate files for plotting.

The mixture and phase transition models are used for multicomponent systems, *i.e.*, materials consisting of more than one chemical species and/or phase. In both of these models, the EOS is computed from separate EOS for the individual species and phases. The phase transition model (Ch. 11) pertains to a system of immiscible phases, each having the same chemical composition. In the mixture model (Ch. 10), the components of the mixture can be either miscible or immiscible and can have different chemical compositions. Mixtures can be either inert (composition independent of density and temperature) or reactive (composition varying as a function of density and temperature); in the latter case, the mixture composition is computed using the principles of chemical equilibrium.

## 1.4 Obtaining the Code

PANDA II is presently being used at Sandia National Laboratories, Albuquerque, NM (SNLA) on the Cray YMP (UNICOS) and the Department 1540 SUN LAN (UNIX). It can also be used on VAX (VMS) and Cray (CTSS) systems. Small versions of the code can be created for use on personal computers, as described in Sec. 1.7.

Code execution is the same for the Cray, VAX, and SUN versions, for which the FORTRAN source files are essentially identical. The VAX and SUN versions give good numerical results for most problems but are slow for certain options - an inconvenience when using the code in an interactive mode. On occasion, the VAX or SUN versions may encounter numerical problems, making it necessary to use the higher precision Cray machine. PANDA calculations often consist of several parts; it is often convenient to carry out the more lengthy computations on the Cray and to use the VAX or SUN for simpler tasks.

The files needed for Cray/UNICOS computing are available using the following node names:

/u0/gkerley/panda/panda.f - FORTRAN source file,

/u0/gkerley/panda/panda.x - executable binary file.

On the SUN, the corresponding files are:

/u3/gkerley/panda/panda.f - FORTRAN source file,

/u3/gkerley/panda/panda.x - executable binary file.

In addition to the code itself, various data files and libraries are required for specific problems. Discussions of these files, and where they can be obtained, are given in the chapters that pertain to their use.

## 1.5 Code Execution

PANDA uses interactive input and output. When executing the code from a terminal (TTY), the user chooses from more than 50 commands that are listed in Tables 1.1-1.4. The code sends messages and prompts to the TTY and creates an output file containing an echo of all code messages and user input. The user can also direct PANDA to take input from a file instead of the TTY. Standard utilities can be employed to submit jobs in batch mode.

When the code begins execution, it prints a header, followed by this prompt:

ENTER OUTPUT FILE NAME, PROBLEM IDENT, AND DATE

The user responds by specifying the name to be given to the output file listing, a problem identification of up to 10 characters, and a date of up to 8 characters. The problem ID and date will appear on the output listing and also on all plot files generated by the code. Any of these three entries can be defaulted. The default output file name is "panout". No output file will be generated if the file name "none" is specified.

Throughout the remainder of the problem, the code will prompt the user with

OPTION?

The user responds to this question by entering one of the commands listed in Tables 1.1-1.4. Depending on the nature of the command, the code may then prompt the user for additional information, as described in the various sections of this manual.

The commands listed in Table 1.1 are used to control certain features of the job execution. The first seven of these commands can be entered at *any* time the code is waiting to receive input from the user, including the response to the first prompt, discussed above. When PANDA receives one of these instructions, it carries out the indicated task and then returns to its previous wait status. The other four commands, and the commands in Tables 1.2-1.4, may only be entered in response to the OPTION? prompt.

**Table 1.1.** Control Commands

Command	Definition	Section
@FNAME	take input from file “fname” instead of TTY	1.5
EOF	(on input file) return input to TTY	1.5
TTY ON	turn on code messages to the terminal (default)	1.5
TTY OFF	turn off code messages to the terminal	1.5
OUTPUT ON	turn on messages to the output listing (default)	1.5
OUTPUT OFF	turn off messages to the output listing	1.5
END or QUIT	terminate calculation	1.5
PLOT FNAME	send data to a plot file called “fname”	1.5, 12.1
NO PLOT	turn off option to generate plot file (default)	1.5
RESET	start model input from scratch	1.5
PC VERSION	generate source files for use on personal computers	1.7

The command @FNAME instructs the code to begin taking commands from an ASCII input file called “fname” instead of the TTY; input reverts to the TTY when either the symbol EOF or an end file mark is encountered on the input file. (On the VAX, the complete name of the input file must be “fname.dat”, but the .dat suffix should not be used in PANDA commands.)

The commands TTY OFF and OUTPUT OFF suppress code messages to the terminal and the output file, respectively. TTY ON and OUTPUT ON restore the normal output state. Either END or QUIT will terminate the session.

The command PLOT FNAME directs the code to create an ASCII plot file called “fname” (“fname.dat” on the VAX). The NO PLOT command closes the file and turns this feature off. Plots of the data on these files can be made the GRAPH utility [20] or similar program; additional discussion of plotting capabilities is given in Sec. 12.1.

The command RESET is used to restore all parameters to the default values that are obtained at the beginning of a session. Previous definitions of models are destroyed, and input starts afresh. However, the input, output, and plot files remain in the same condition and all previous output is saved.

The command PC VERSION is discussed in Sec. 1.7.

**Table 1.2.** Commands Used to Define an EOS Model

Command	Definition	Section
BROT	compute rotational constant for molecule	6.4
COLD CURVE	enter parameters for 0°K isotherm	3.1
CRIS	enter parameters for CRIS fluid model	5.1
DIMER	enter parameters for fluid dimer model	7.1
ELEC	enter thermal electronic parameters	8.1
EXP6	compute cold curve parameters from pair potential	3.4
IONEQ	make ionization equilibrium calculation	9.4
LIQ TAB	get EOS table for fluid model	2.5
LJ MATCH	redefine parameters for LJ match	3.8
MOD MODTYP	define one of the following models:	
MODTYP=SOL	one-component solid	2.3
MODTYP=LIQ	one-component fluid	2.4
MODTYP=MIX	multicomponent mixture	10.3
MODTYP=TRN	multiphase system	11.2
MODTYP=USE	user-defined model	15.1
SET BAS	enter basic data for solid or fluid	2.2
SET STR	enter material strength parameters	15.3
SOL NUC	enter parameters for lattice vibrations	4.1
SOL TAB	get EOS table for solid model	2.5
TFD CURVE	compute TFD cold curve for a mixture	3.7
VIB ROT	enter vibration/rotation parameters	6.1

Table 1.2 gives a list of the commands that are used to define an EOS model, as discussed in Sec. 1.3. Details about the use of these instructions are given in the chapters that are indicated.

**Table 1.3.** Commands for Testing an EOS Model

Command	Definition	Section
CJ MODTYP	compute CJ state for model MODTYP	12.7
CONC PLOT	output concentrations for mixture model	10.6
CRIT MODTYP	compute critical point for model MODTYP	12.10
EOS MODTYP	compute EOS points for model MODTYP	12.2
HUGE MODTYP	energy-based Hugoniot for model MODTYP	12.6
HUG MODTYP	temperature-based Hugoniot for model MODTYP	12.6
ISOB MODTYP	compute isobar for model MODTYP	12.4
ISOC MODTYP	compute isochores for model MODTYP	12.3
ISOT MODTYP	compute isotherms for model MODTYP	12.3
ISEN MODTYP	compute isentrope for model MODTYP	12.5
LEVELS DATA	compute energy levels for specified states	9.3
LEVELS FILE	generate file of atomic energy levels	9.3
MELT	compute melt boundary between solid and fluid	12.11
MONTE CARLO	compute EOS for mixture using Monte Carlo method	15.4
PART FUNC	compute partition functions for atoms and ions	9.3
PHASE DIAG	output phase diagram for multiphase EOS	11.4
RDF LIQ	compute liquid radial distribution function	5.4
SHOCK DATA	obtain experimental Hugoniot data from data base	15.2
SFAC LIQ	compute liquid structure factor	5.4
SPN MODTYP	compute spinodal points for model MODTYP	12.9
VAP MODTYP	compute vaporization curve for model MODTYP	12.8
XPT LIQ	compute liquid transport coefficients	5.5

Table 1.3 lists the commands that make various calculations to test a model and compare it with experimental data. Details about the use of these instructions are given in the chapters that are indicated.



**Table 1.4.** Commands for Constructing EOS Tables and Libraries

Command	Definition	Section
ASC2BIN	make an EOS library from an ASCII file	14.4
BIN2ASC	make an ASCII file from an EOS library	14.4
DELETE	delete data from an EOS library	14.3
EXTRACT	extract data from an EOS library	14.3
LIST FNAME	list and check data on EOS library “fname”	14.2
MESH MODTYP	make 301 table mesh using model MODTYP	13.4
READ MESH	read 301 table mesh from an ASCII file	13.4
SAVE MESH	write 301 table mesh to an ASCII file	13.4
SLIB MODTYP	make an EOS table for model MODTYP	13.2
TRANS ASC	convert ASCII file from old to new format	14.4
UPDATE	add data from a binary file to an EOS library	14.3

The instructions listed in Table 1.4 are used to create EOS tables in the standard Sesame format, send them to external files, and perform various tasks that arise in the management of an EOS library. These commands are discussed in Chs. 13 and 14.

Several examples of PANDA calculations are given in Ch. 16.

## 1.6 Conventions

**Input Strings.** Input lines to PANDA are strings of blank-delimited alphanumeric words that may include commands, numerical data, character data, and special symbols. Each input string is first read as character data, separated into individual words, and checked for the special instructions listed in Table 1.1. Numerical variables are encoded after being checked for format errors. Quotation marks are not used for character variables. The code will accept either upper case or lower case input. (For internal use, all input data except file names are converted to upper case; file names are taken to be lower case, for convenience of use under CTSS.) Identical procedures are used for reading input from the TTY and ASCII files.

Table 1.5 lists special symbols that can be used in constructing input strings. These symbols should not be used in file names or for any purpose other than the one indicated.

Commas, equal signs, parentheses, and brackets can be used as delimiters in addition to blanks. Their sole purpose is to make an input string more readable. When

**Table 1.5.** Special Input Symbols

Symbols	Purpose
, = ( ) [ ]	delimiters
\$ !	comments
&	continuation
- *	defaults

interpreting an input string, PANDA treats these symbols the same as blanks; therefore, double commas cannot be used to define a blank field.

Anything on an input line that follows either a dollar sign or an exclamation point is interpreted as a comment. It is echoed to the output file but otherwise ignored. If either of these symbols is the first non-blank character on the line, the code echoes the line to the output line and continues reading. Blank lines are not skipped; they are interpreted as an input string of all zeros.

An ampersand (&) as the *last* non-blank character on the line is used to denote continuation of the input string to the next line. An input string can be continued to as many lines as desired. An ampersand that is followed by other words is *not* treated as a special symbol.

Many input variables can be defaulted. The default is normally obtained by entering a dash or an asterisk in the field corresponding to that variable. In addition, fields can be left blank if they are on the end of the input string. For numerical variables, blanks, dashes, and asterisks are interpreted as zeros. The code provides defaults for certain character variables as noted throughout this report.

**Energy Zero.** For the one-component solid and fluid models, the zero of energy is determined by the solid cold curve; the energy on the cold curve is chosen to be zero at zero pressure and solid density. (In PANDA, the solid cold curve does not include contributions from zero-point motion, which are part of the lattice vibrational term.) The user can change the energy zero, as discussed in Ch. 2. The energy zeros for the mixture and phase transition models are determined by the EOS of the individual components. Once again, the user can change the energy zero, as discussed in Chs. 10 and 11.

**Symbols and Units.** Table 1.6 gives a list of the principal symbols used in this report and their units. The same units are used for input, output, and internal calculations.

**Thermodynamic Consistency.** All EOS models in PANDA obey the basic equa-



**Table 1.6.** Symbols and Units

Symbol	Name	Units
$\rho$	density	$\text{g/cm}^3 = \text{Mg/m}^3$
$T$	temperature	$^{\circ}\text{K}$
$P$	pressure	GPa
$E$	internal energy	MJ/kg
$A$	Helmholtz free energy	MJ/kg
$G$	Gibbs free energy	MJ/kg
$S$	entropy	MJ/kg-K
$D_0$	dissociation energy	eV ( $8.61735 \times 10^{-5} \text{ }^{\circ}\text{K}$ )
$\omega$	vibrational frequency	$\text{cm}^{-1}$ ( $0.695038 \text{ }^{\circ}\text{K}$ )
$B_{rot}$	rotational constant	$\text{cm}^{-1}$
$\epsilon_i$	orbital energy	Hartree (27.2114 eV)
$r_i$	orbital radius	$a_0$ ( $0.529177 \times 10^{-13} \text{ km}$ )
$N_0$	Avogadro's number	$6.02214 \times 10^{23} \text{ mole}^{-1}$
$k$	Boltzmann's constant	$1.38066 \times 10^{-29} \text{ MJ/}^{\circ}\text{K}$
$R$	gas constant ( $N_0 k$ )	$8.31451 \times 10^{-3} \text{ MJ/kg-mole/}^{\circ}\text{K}$
$\beta$	$1/kT$	
$c$	speed of light	$2.99792 \times 10^5 \text{ km/s}$
$h$	Planck's constant	$6.62608 \times 10^{-40} \text{ MJ-s}$

tions of thermodynamic consistency, such as

$$\rho^2(\partial E/\partial \rho)_T = P - T(\partial P/\partial T)_\rho. \quad (1.1)$$

This relation is satisfied at all densities and temperatures because the pressure  $P$ , internal energy  $E$ , and entropy  $S$  are always determined from a Helmholtz free energy function  $A(\rho, T)$  using the standard thermodynamic formulas,

$$P(\rho, T) = \rho^2(\partial A/\partial \rho)_T, \quad (1.2)$$

$$E(\rho, T) = A - T(\partial A/\partial T)_\rho, \quad (1.3)$$

and

$$S(\rho, T) = (E - A)/T. \quad (1.4)$$

Equation 1.1 can be derived by differentiating Eq. 1.3 with respect to density, followed by substitution from Eq. 1.2. The only cases where exceptions to this condition may arise are in constructing the solid tension region at low densities and temperatures (Sec. 13.5) and the two-temperature EOS in the mixed-phase region (Sec. 13.6).

**Input and Output Files.** PANDA II uses both formatted (ASCII) and unformatted (binary) files for input and output. Standard FORTRAN 77 procedures are used in opening, closing, reading, and writing these files. However, differences between the Cray, VAX, SUN, and PC operating systems cause minor variations in file handling.

The user is prompted to enter the name for each file that is to be opened. (There is only one exception to this rule; if the code must create a scratch file, it is given the name “scrapan”. Users should avoid this name.) Default file names are available in certain cases, as specified in this manual. For ease of use on CTSS, *PANDA treats all file names as lower case.*

*In PANDA, file names specified by the user may consist of up to eight characters and should not include any prefixes or suffixes that are allowed under the operating system.* Paths and suffixes are available under UNIX and DOS but should not be used with PANDA. On the VAX (VMS), the system will assign the filetype suffix .dat to files that are created by the code; input files must also have this .dat suffix, although it is not used in PANDA commands. Such file attributes are not available under CTSS.

Each file that is created by PANDA is assumed to be “NEW” in the OPEN statement. If a file with that name already exists, the VAX (VMS) will create a new file with a higher version number. Under CTSS, UNIX, and DOS, the OPEN statement will return an error. PANDA intercepts this error and issues the message

```
*** FILE fname ALREADY EXISTS. OVERWRITE IT? (YES/NO)
```

If the user enters “yes” (or just “y”), the file will be reopened, and a message will be printed, notifying the user that the previous information on that file has been destroyed. If the user does not choose to overwrite the file, there are two possibilities. An unformatted file will not be reopened, and an error message will be printed. An ASCII file will be reopened; PANDA will skip to the end of the file before writing additional data and will print a message to that effect.

## 1.7 Personal Computer Version

PANDA can be installed on personal computers using the MS-DOS operating system [21]. The code has been compiled and linked using the Microsoft FORTRAN package [22], version 4.01. However, it is subject to certain limitations that have to do with code size and array size. In order to create the executable file, it is necessary to split the source code into smaller segments and to compile it using the /AH parameter (HUGE memory model). We also prefer to use the /Od parameter which suppresses code optimization. Finally, it has been found necessary to reduce the size of the code by removing 31 subroutines that are used in the mixture-chemical equilibrium model, the ionization equilibrium and

energy levels models, and the Monte Carlo package. (See routine APCV for a list of the routines that are eliminated.)

The instruction PC VERSION is used to process the PANDA source code and create the files needed for the smaller version of the code. This command has the form

PC VERSION *infile outfile delopt*

where *infile* and *outfile* are the names of the full source file and the PC source files, respectively. If the file names are not given on the command line, a prompt is issued. PANDA creates several output files that are named by appending letters to the root name specified by the user. For example, if the output file name is given as "pcpan", the code creates source files named "pcpana", "pcpanb", "pcpanc", *etc.* (Note that the DOS operating system does not assign the suffix .FOR to these files.) The executable code is created with the standard compiling and linking procedures [22]. The last input parameter, *delopt*, is optional. If the word "del" is entered, the 31 subroutines mentioned above will be deleted; otherwise, they will be kept in the PC source files.

*Note:* Some additional editing may be required before compiling and loading the code. Also, because the PC VERSION command does not remove calls to the deleted routines, unsatisfied externals will be encountered when loading the code. This problem does not result in a fatal error when using the Microsoft FORTRAN package.

## 2. One-Component Solids and Fluids

### 2.1 General

The equation of state for a one-component solid or fluid is constructed by combining contributions from the cold curve and thermal electronic and nuclear degrees of freedom, as outlined in Sec. 1.3. The instructions MOD SOL and MOD LIQ are used to specify which of these terms are to be included in the solid and fluid models, respectively. Other commands listed in Table 1.2, such as SET BAS and COLD CURVE, are used to enter the parameters that are needed for calculating each of these terms. Still other commands, such as EXP6 and BROTH, are available for computing parameters in the model from other information.

The PANDA code sets internal flags to indicate which data have been input by the user. When a MOD command is given, the code checks these flags to determine if the data needed for the specified model have been defined. If they have not, PANDA automatically carries out the instructions that are required. For example, the command SET BAS (Sec. 2.2) is used to enter certain basic data that are used in both the solid and fluid models. If the user gives the MOD SOL or MOD LIQ instruction, and these basic data have not been defined, the code will automatically prompt the user as if the SET BAS command had also been given. Subsequently, the SET BAS command must be given if the user wants to change the parameters that were input previously.

The MOD SOL, MOD LIQ, SET BAS, SOL TAB, and LIQ TAB commands are discussed in this chapter, while the other commands are discussed in separate chapters (see Table 1.2).

### 2.2 The SET BAS Command

The instruction SET BAS is used to enter the chemical formula and several material parameters that are used for the one-component solid and fluid models. As noted above, this instruction is executed automatically when the MOD SOL or MOD LIQ command is given and these data were not input previously. This command is not used in the phase transition and mixture models.

The code first prompts the user input the chemical formula for the material, to be modeled as a solid or fluid of a single molecular species.

## SOLID-LIQUID MODEL - ENTER MOLECULAR FORMULA

The formula is specified using the standard chemical symbols for the atomic elements. For example, calcium carbonate,  $\text{CaCO}_3$ , could be entered as

CA[1]C[1]O[3]

(Here brackets have been used as delimiters; as explained in Sec. 1.6, blanks and other symbols can be used with equivalent results.) The formula can include up to 25 elements. If the material is a monatomic element, only the element symbol need be given. The user may also forego entering the formula and enter a name, such as  $\text{CH}_4$ , which will be treated as a single element. PANDA computes the formula number (total number of electrons in the molecule), the formula weight, and also an average atomic number,  $Z_{av}$ , that is used in the TFD match for the cold curve (see Sec. 3.7). If the code encounters an unknown name or atomic symbol, the user is prompted to enter the formula number and weight.

The chemical formula can be defined in several ways, depending on how the nuclear degrees of freedom are to be treated in the model. In the above example, a molecule of  $\text{CaCO}_3$  would have 15 degrees of freedom - three of translational motion and 12 of internal vibrational and rotational motion. The formula could also be given as  $\text{CA}[\cdot 2]\text{C}[\cdot 2]\text{O}[\cdot 6]$ , which has the same stoichiometry; in that case, the material would be treated as an average atom having three translational degrees of freedom.

Next, the code issues the following prompt.

ENTER ECOH,RHOREF,TREF,GAMREF,DEBREF,CB,PSSN

	ECOH	- $E_{coh}$ = solid cohesive energy
	RHOREF	- $\rho_{ref}$ = reference density
	TREF	- $T_{ref}$ = reference temperature
where	GAMREF	- $\gamma_{ref}$ = Grüneisen parameter
	DEBREF	- $\Theta_{ref}$ = Debye or Einstein temperature
	CB	- $C_B$ = bulk sound speed
	PSSN	- $\sigma$ = Poisson's ratio

Use of the above parameters varies slightly, and often some of them can be defaulted, depending upon the EOS models specified by the user.

The cohesive energy  $E_{coh}$  is the experimental heat of vaporization of the solid at  $0^\circ\text{K}$ . (The code adds a correction for zero-point energy of lattice vibrations, when needed.) This quantity is used when the cold curve is computed from the Hugoniot, when the cold

curve is entered as a table, and in the low temperature extrapolation formula for the CRIS model.

The optional parameters  $\rho_{ref}$  and  $T_{ref}$  define a reference state for the solid (usually ambient temperature and pressure). When the cold curve is computed from shock data, this state is used to specify the initial conditions. These quantities are also used in the solid lattice vibration model (Ch. 4), in computing the internal vibrational frequencies (Ch. 6), and in making guesses and setting bounds on variables used in searches.

$\gamma_{ref}$  and  $\Theta_{ref}$  are the Grüneisen parameter and the Debye or Einstein temperature at the reference density and temperature. These quantities are used in the solid lattice vibration model (Ch. 4). The sound speed  $C_B$  and Poisson's ratio  $\sigma$  are optional and are used to compute a default value for  $\Theta_{ref}$ . If the user specifies  $\Theta_{ref} = 0$  but  $C_B \neq 0$ , the code uses the formula

$$\Theta_{ref} = 444.12 \sqrt{\frac{1-2\sigma}{1+\sigma}} C_B \left(\frac{\rho_{ref}}{W\lambda}\right)^{1/3}, \quad (2.1)$$

where

$$\lambda = 2 + \left(\frac{0.5 - \sigma}{1 - \sigma}\right)^{3/2}, \quad (2.2)$$

and  $W$  is the formula weight. This expression can be derived from the usual relation between  $\Theta$  and the longitudinal and transverse sound speeds [23]. Poisson's ratio can be defaulted; if the user specifies  $\sigma \leq 0$  or  $\sigma \geq 1/2$ , the code sets  $\sigma = 1/3$ .

## 2.3 MOD SOL - The Solid Model

The solid EOS is constructed using eight parameters that are defined with the MOD SOL command. The Helmholtz free energy  $A_s$ , internal energy  $E_s$ , pressure  $P_s$ , and entropy  $S_s$  are given by the following expressions.

$$A_s(\rho, T) = E_c + A_l + A_e + A_{vr} + A_{ts} + \Delta E_s - TS_{vac} - TS_{ws}, \quad (2.3)$$

$$E_s(\rho, T) = E_c + E_l + E_e + E_{vr} + E_{ts} + \Delta E_s, \quad (2.4)$$

$$P_s(\rho, T) = P_c + P_l + P_e + P_{vr} + P_{ts}, \quad (2.5)$$

and

$$S_s(\rho, T) = S_l + S_e + S_{vr} + S_{ts} + S_{vac} + S_{ws}. \quad (2.6)$$

$E_c, P_c$  are the energy and pressure on the cold curve (Ch. 3)

$A_l, E_l, P_l, S_l$  are the lattice vibrational terms (Ch. 4)

$A_e, E_e, P_e, S_e$  are the thermal electronic terms (Ch. 8)

$A_{vr}, E_{vr}, P_{vr}, S_{vr}$  are the vibration-rotation terms (Ch. 6)

$A_{ts}, E_{ts}, P_{ts}, S_{ts}$  are the tabular terms (Sec. 2.5)

$\Delta E_s$  is the shift in energy zero

$S_{vac}$  is the entropy from vacancy formation

$S_{ws}$  is the statistical weight contribution to the entropy

where



The MOD SOL command has the form

MOD SOL *options*

where *options* is a string of keywords and numerical values. If no options are specified on the input line, the user is prompted with a list of the eight keywords, as follows.

ENTER (NAMELIST) SOLID OPTIONS - CRV,NUC,TEL,  
VRT,TAB,ESFT,VAC,WSL

where	CRV=1 or CRV=0                      - turn cold curve on or off NUC=1 or NUC=0                      - turn lattice vibrational terms on or off TEL=1 or TEL=0                      - turn thermal electronic terms on or off VRT=1 or VRT=0                      - turn vibration-rotation terms on or off TAB=1, TAB=2, or TAB=0           - turn solid EOS table on or off ESFT= $\Delta E_s$ - specify energy shift VAC= $f_v$ - specify vacancy fraction parameter WSL= $w_{sol}$ - specify solid statistical weight
-------	---

The parameter  $w_{sol}$  has a default value of 1.0; each of the the other seven parameters has a default value of zero. The keywords CRV, NUC, TEL, VRT, and TAB are used to include certain terms in the solid EOS model or to remove terms that were previously specified. As discussed in Sec. 2.1, additional commands are used to enter the data needed for actually calculating these terms. Under the MOD SOL command, the code checks to see if those data have been entered and executes any instructions that are required. The parameter  $\Delta E_s$  is chosen to fix the zero of energy at the desired value. (*Note:* After the parameters for an option have been entered, they remain in place even after that option has been removed from the solid model using the MOD SOL command.)

The options TAB=1 and TAB=2 both include an EOS table in the solid model; the case TAB=2 is used in constructing a two-temperature EOS (Sec. 2.6). This feature allows part of the EOS to be computed from a table created in a previous calculation, using either PANDA or a different code. It is also useful for making calculations and plots with EOS tables from a Sesame data base.

PANDA offers an option for correcting the solid EOS for effects due to lattice imperfections. It is assumed that a certain fraction of the lattice sites,  $0 \leq f_v < 1$ , are vacant. The presence of these vacancies lowers the density of the solid from its ideal value and reduces the effective binding of the molecules. To account for these effects, the energy and pressure on the cold curve are modified according to the relations

$$E_c(\rho) \rightarrow (1 - f_v)E_c[(1 + f_v)\rho], \quad (2.7)$$

and

$$P_c(\rho) \rightarrow (1 - f_v)P_c[(1 + f_v)\rho]/(1 + f_v). \quad (2.8)$$

In addition, a contribution to the entropy is computed by assuming that the vacant sites are randomly distributed; the result is

$$S_{vac} = -R[f_v \ln f_v / (1 - f_v) + \ln(1 - f_v)]/W, \quad (2.9)$$

where  $R$  is the gas constant and  $W$  is the formula weight. In certain problems, the presence of vacancies can have a significant effect on calculated phase boundaries.

The entropy contribution from the statistical weight is given by

$$S_{ws} = R \ln w_{sol}/W. \quad (2.10)$$

A value of  $w_{sol} > 1.0$  may be required in cases where there is more than one configuration for the ground state. This situation can arise when the molecules are rotationally disordered or when the electronic ground state has more than one spin configuration.

## 2.4 MOD LIQ - The Fluid Model

The fluid EOS is constructed using seven parameters that are defined with the MOD LIQ command. The Helmholtz free energy  $A_f$ , internal energy  $E_f$ , pressure  $P_f$ , and entropy  $S_f$  are given by the following expressions.

$$A_f(\rho, T) = A_{cr} + A_e + A_{vr} + A_{tf} + A_{dm} + \Delta E_f - TS_{wl}, \quad (2.11)$$

$$E_f(\rho, T) = E_{cr} + E_e + E_{vr} + E_{tf} + E_{dm} + \Delta E_f, \quad (2.12)$$

$$P_f(\rho, T) = P_{cr} + P_e + P_{vr} + P_{tf} + P_{dm}, \quad (2.13)$$

and

$$S_f(\rho, T) = S_{cr} + S_e + S_{vr} + S_{tf} + S_{dm} + S_{wl}. \quad (2.14)$$

$A_{cr}, E_{cr}, P_{cr}, S_{cr}$  are the CRIS model terms (Ch. 5)

$A_e, E_e, P_e, S_e$  are the thermal electronic terms (Ch. 8)

$A_{vr}, E_{vr}, P_{vr}, S_{vr}$  are the vibration-rotation terms (Ch. 6)

where  $A_{tf}, E_{tf}, P_{tf}, S_{tf}$  are the tabular terms (Sec. 2.5)

$A_{dm}, E_{dm}, P_{dm}, S_{dm}$  are the dimerization corrections (Ch. 7)

$\Delta E_f$  is the shift in energy zero

$S_{wl}$  is the statistical weight contribution to the entropy

The CRIS model predicts the contribution to the EOS from translational motion of the molecules, using the solid cold curve to specify the intermolecular forces. Hence there is a close relationship between the solid and fluid models, although the two phases can have significantly different properties. The thermal electronic and vibration-rotation terms are the same for both solid and fluid, but different tabular terms can be entered for the two cases.

Use of the MOD LIQ command is similar to that for MOD SOL.



## MOD LIQ *options*

where *options* is a string of keywords and numerical values. If no options are specified on the input line, the user is prompted with a list of the seven keywords, as follows.

ENTER (NAMELIST) FLUID OPTIONS - CRS,TEL,VRT,  
TAB,DIM,ESFT,WLQ

	CRS=1 or CRS=0	- turn CRIS model on or off
	TEL=1 or TEL=0	- turn thermal electronic terms on or off
	VRT=1 or VRT=0	- turn vibration-rotation terms on or off
where	TAB=1, TAB=2, or TAB=0	- turn fluid EOS table on or off
	DIM=1 or DIM=0	- turn dimer corrections on or off
	ESFT= $\Delta E_f$	- specify energy shift
	WLQ= $w_{liq}$	- specify liquid statistical weight

The parameter  $w_{liq}$  has a default value of 1.0; each of the other six parameters has a default value of zero. The keywords CRS, TEL, VRT, TAB, and DIM are used to include certain terms in the fluid EOS model or to remove terms that were previously specified. As discussed in Sec. 2.1, additional commands are used to enter the data needed for actually calculating these terms. Under the MOD LIQ command, the code checks to see if those data have been entered and executes any instructions that are required. If the CRIS model is specified but no solid cold curve has been defined, the code will prompt the user for that information as well. (The parameters that are entered for an option remain in place even after that option has been removed from the models using either the MOD SOL or the MOD LIQ command.) The options TAB=1 and TAB=2 both include an EOS table in the fluid model; the case TAB=2 is used in constructing a two-temperature EOS (Sec. 2.6). The parameter  $\Delta E_f$  is chosen to fix the zero of energy at the desired value. (Because the solid and fluid models in PANDA have the same zero of energy, the same energy shift should normally be used in the two cases. However, the user may vary the two parameters separately, in order to adjust the melting point.)

The entropy contribution from the statistical weight is given by

$$S_{wl} = R \ln w_{liq}/W. \quad (2.15)$$

Interpretation and use of this term is the same as for the solid, Eq. 2.10.

## 2.5 SOL TAB and LIQ TAB - Tabular EOS Input

As noted above, the MOD SOL and MOD LIQ commands can be used to compute all or part of the solid or fluid EOS from tables having the standard Sesame format. (See Ch. 13 for a discussion of Sesame EOS tables and files.) The commands SOL TAB and

LIQ TAB instruct PANDA to open a binary library file and to load EOS tables for the solid and fluid model, respectively. These instructions are automatically executed when a MOD SOL or MOD LIQ command is given and the tables were not loaded previously. PANDA uses only the 301 tables and loads separate tables for the two models. A rational function algorithm [24] is used to interpolate on the EOS tables.

The user is prompted as follows.

ENTER MATERIAL NUMBER AND FILE NAME FOR EOS TABLE

The user responds by entering the material number (real) for the EOS and the file name of the data library to be searched for the table. An error message is printed if the library file or EOS table cannot be found, or if there is insufficient storage space to load the table.

*Warning:* EOS tables for the one-component solid-liquid model, the mixture model, and the phase transition model all share the same storage array and directory. Therefore, these three options can conflict with one another; if tables are loaded for one option, any tables that had been loaded for a different option will be destroyed, and a warning message will be given. This situation seldom arises with normal code usage and can be avoided by making separate PANDA runs for the three different models. If a conflict does occur, the user must keep track of which tables are actually present and restore the tables that are needed for the option being used.

## 2.6 Two-Temperature EOS

In some hydrodynamic models, the EOS is split into two parts, an *ion* EOS and an *electron* EOS. This approach, called the two-temperature approximation [25], is used to study problems in which the ions and the electrons are not in local thermodynamic equilibrium. In PANDA, separate tables for the ions and the electrons can be generated along with the total EOS table, using the SLIB SOL and SLIB LIQ commands (Ch. 13).

The two-temperature EOS is an *ad hoc* concept. At low temperatures and high densities, where the ions and electrons are strongly coupled, definition of the ion and electron terms in the EOS is partly arbitrary. However, Zwanzig [26] has shown how to treat the electronic and nuclear degrees of freedom separately in the calculation of statistical mechanical averages. The two subsystems are coupled *mechanically*, because the electronic free energy depends upon the nuclear coordinates. However, the electrons and the nuclei can be decoupled in the calculation of *thermal* averages. Although these arguments apply rigorously only in the case of thermal equilibrium, the result suggests an operational definition for the nonequilibrium case. More detailed discussion of this problem is given in Appendix A.

In PANDA, the following prescriptions are used for the two-temperature EOS.

- The ion EOS is defined as a system in which the nuclear degrees of freedom are thermally excited but the electrons remain in the ground state. It is calculated by subtracting the electron EOS from the total.
- The electron EOS includes only those contributions to the EOS from thermal excitation and ionization. Hence the electron contribution to the pressure, energy, and Helmholtz energy go to zero at  $T = 0$ ; the electron contribution to the entropy can be finite at  $T = 0$ .
- The thermal electronic terms, denoted by  $A_e$ ,  $E_e$ ,  $P_e$ , and  $S_e$  in Eqns. 2.3 - 2.14, are always included in the electron EOS.
- If a tabular term is included in the EOS, the MOD SOL and MOD LIQ commands must specify whether it belongs to the ion or electron EOS. For the ion EOS, set TAB=1; for the electron EOS, set TAB=2.

Note that the solid cold curve is included in the ion EOS rather than in the electron EOS. The principal reason for this decision is that the cold curve is not an additive term in the fluid EOS model; it is strongly coupled to the thermal motion of the molecules. Moreover, the fluid EOS does not extrapolate to the solid cold curve at  $T = 0$  because the molecular arrangement is disordered and therefore different from that of the solid. Similar changes in structure occur when phase changes and chemical reactions take place.

In principle, the above concept could be extended to the mixture and phase transition models. However, the present version of PANDA does not offer a two-temperature EOS treatment for those two options.

## 3. The Zero-Kelvin Isotherm

### 3.1 General

PANDA offers five options for constructing the  $0^\circ K$  isotherm for the solid (cold curve) from experimental or theoretical data obtained by the user. In addition, it provides features for extrapolating to high densities (the TFD match) and to low densities (the LJ match).

The instruction COLD CURVE is used to enter the data. If the code needs cold curve data, this command will be executed automatically under several other commands, including MOD SOL, SOL NUC, MOD LIQ, AND CRIS. The user is prompted as follows.

COLD CURVE - ENTER ICLD,RTFD,RLJ,FACLJ

	ICLD	- one of the following options:
	ICLD=1,	compute from Hugoniot
	ICLD=2,	analytic LJ formula
	ICLD=3,	analytic EXP-N formula
where	ICLD=4,	tabular cold curve
	ICLD=5,	universal metal EOS
	RTFD	- $\rho_{TFD}$ = density for TFD match
	RLJ	- $\rho_{LJ}$ = density for LJ match
	FACLJ	- $f_{LJ}$ = exponent for LJ match

### 3.2 ICLD=1: Cold Curve from Shock Hugoniot

In many applications, a good estimate of the  $0^\circ K$  curve can be made from shock-wave data by a direct calculation assuming the Mie-Grüneisen EOS [27] [28]. In this case (ICLD=1), the user must specify the Hugoniot and define a model for the solid lattice vibration terms. The experimental curve of shock velocity  $U_s$  vs. particle velocity  $U_p$  is represented by a polynomial,

$$U_s = C_0 + S_1 U_p + S_2 U_p^2, \quad (3.1)$$

where  $C_0$  is the bulk sound speed. When the user specifies cold curve option ICLD=1, the code checks to see if the lattice vibration model has been defined and requests these data, if necessary (see Ch. 4). Next, PANDA issues the following prompt.

## ENTER 3-PARAMETER FIT TO US-UP CURVE

The user responds by entering the three coefficients  $C_0$ ,  $S_1$ , and  $S_2$  in Eq. 3.1. The cold curve is computed and saved as a table, along with interpolation coefficients. Extrapolation procedures are used below the normal solid density and above the density at which the Hugoniot curve has an infinite asymptote. Details of the calculation are given in Appendix B.

*Note:* The procedure described above has several important limitations. It is possible to specify a Hugoniot and a Grüneisen function that are inconsistent, in that they define a physically unreasonable cold curve. In some cases (but not all), the code will identify such problems and print out an error message. The Mie-Grüneisen approximation may break down if thermal electronic or vibration-rotation terms are important or if melting occurs. The method should not be applied to porous materials or substances that undergo phase transitions when shocked, unless the Hugoniot data are first analyzed and recentered to an appropriate initial state.

### 3.3 ICLD=2: Analytic Lennard-Jones (LJ) Formula

If ICLD=2, the cold curve is calculated from the simple analytic formulas

$$E_c(\rho) = a_1\rho^{a_2} - a_3\rho^{a_4} + E_B, \quad (3.2)$$

and

$$P_c(\rho) = \rho(a_1a_2\rho^{a_2} - a_3a_4\rho^{a_4}). \quad (3.3)$$

PANDA prompts the user as follows.

ENTER LJ CONSTANTS, A1,A2,A3,A4

The user enters the four constants in Eqs. 3.2 and 3.3. The code computes  $E_B$  to adjust the zero of energy as required by the convention. Setting  $P_c(\rho) = 0$ ,  $E_c(\rho) = 0$  gives

$$\rho_0 = (a_3a_4/a_1a_2)^{1/(a_2-a_4)}, \quad (3.4)$$

and

$$E_B = a_3\rho_0^{a_4} - a_1\rho_0^{a_2}. \quad (3.5)$$

This form of the cold curve is interesting because it can be derived from simple pair potentials that have been studied with Monte Carlo and molecular dynamics techniques [29]. However, the repulsive part of the potential is known to be unrealistic. Hence this option will not be useful at high densities unless it is used along with the TFD match option.

### 3.4 ICLD=3: Analytic EXP-N Formula

If ICLD=3, the cold curve is calculated from the analytic formulas

$$E_c(\rho) = a_1 \exp(-a_2/\rho^{1/3}) - a_3\rho^{a_4} + E_B, \quad (3.6)$$

and

$$P_c(\rho) = \frac{1}{3}a_1a_2\rho^{2/3} \exp(-a_2/\rho^{1/3}) - a_3a_4\rho^{a_4+1}. \quad (3.7)$$

As  $\rho \rightarrow 0$ ,  $E_c \rightarrow E_B$ ; hence  $E_B$  is the binding energy of the solid (called EBZPE in the code). Using the conditions  $P_c(\rho_0) = 0$ ,  $E_c(\rho_0) = 0$ , constants  $a_1$  and  $a_3$  can be written as follows.

$$a_1 = \frac{3a_3a_4}{a_2} \rho_0^{a_4+1/3} \exp(a_2/\rho_0^{1/3}). \quad (3.8)$$

$$a_3 = \frac{E_B}{\rho_0^{a_4}(1 - 3a_4\rho_0^{1/3}/a_2)}. \quad (3.9)$$

The constant  $a_2$  is related to the bulk modulus of the solid, as follows.

$$a_2 = \frac{1}{2}\rho_0^{1/3}(Q + \sqrt{Q^2 - 36\beta_0/\rho_0 E_B}), \quad (3.10)$$

where

$$\beta_0 = (\rho dP_c/d\rho)_{\rho_0} \quad (3.11)$$

and

$$Q = 1 + 3a_4 + 3\beta_0/a_4\rho_0 E_B. \quad (3.12)$$

Equations 3.8, 3.9, and 3.10 are used to eliminate the constants  $a_1$ ,  $a_2$ , and  $a_3$  so that more familiar and convenient quantities can be used for input. PANDA prompts the user as follows.

ENTER EXP-N CONSTANTS, EBZPE,RZRO,BZRO,A4

The user enters  $E_B$ ,  $\rho_0$ ,  $\beta_0$ , and  $a_4$ , as defined above.

The exponential terms in Eqs. 3.6 and 3.7 usually give a reasonable representation of the repulsive forces in solids, which are dominated by electron-electron overlap effects. Therefore, the EXP-N form is much more realistic at high densities than the LJ form. However, it breaks down in the very high density limit, where both  $E_c$  and  $P_c$  are negative. The TFD match option should be used to correct this problem, especially when the CRIS model is used.

Parameter  $a_4$  depends upon the range of the attractive forces in the solid and varies with material type. For example, rare gases and molecular solids are bound by van der Waals forces, for which  $a_4 = 2$ . In that case, the EXP-N form is closely related to the



Buckingham potential; the command EXP6 (Sec. 3.9) can be used to compute the cold curve parameters from the pair potential parameters. By contrast, ionic solids are bound by Coulomb forces that have a much longer range;  $a_4 = 1/3$  in that case. The EXP-N option also gives good results for metals, when  $a_4$  is treated as an adjustable parameter in fitting data.

### 3.5 ICLD=4: Tabular Cold Curve

If ICLD=4, the cold curve is entered as a table of pressure *vs.* density. Tabular values may be read from the TTY or from an ASCII file. PANDA prompts the user as follows.

ENTER NAME OF INPUT FILE

The user enters either “tty” (the default case) or the name of the ASCII file containing the cold curve table. If input is from the TTY, the following prompt is also given.

ENTER DENSITY AND PRESSURE, POINT BY POINT

In either case, the code reads in pairs of density and pressure, with each pair on a separate line. A density of zero signifies the end of input. A minimum of four points and a maximum of 75 points are allowed.

The code sorts the density-pressure points so that densities are monotonically increasing, and it calculates the energy, which must satisfy the relation

$$P_c(\rho) = \rho^2 dE_c(\rho)/d\rho. \quad (3.13)$$

The following interpolation formula is used.

$$E_c(\rho) = E_c(\rho_i) + \rho_i^{-1} [P_c(\rho_i)x + A_1(i)x^2 + A_2(i)x^3 + A_3(i)x^4], \quad (3.14)$$

and

$$P_c(\rho) = (\rho/\rho_i)^2 [P_c(\rho_i) + 2A_1(i)x + 3A_2(i)x^2 + 4A_3(i)x^3]. \quad (3.15)$$

where  $\rho_i \leq \rho < \rho_{i+1}$ ,  $x = \rho/\rho_i - 1$ , and the coefficients  $A_1(i)$ ,  $A_2(i)$ , and  $A_3(i)$  are chosen by fitting Eq. 3.15 to the pressure table. Equation 3.14, together with the convention for the zero of energy, determines the quantities  $E_c(\rho_i)$ . Note that the procedure just described does not give continuous derivatives of the pressure.

For low densities,  $\rho < \rho_1$ , the code extrapolates. The LJ match option (Sec. 3.8) should be used to guarantee that the cold curve has the correct behavior in this region. For high densities, the TFD match is done automatically.  $\rho_{TFD}$  is not permitted to exceed the highest density in the cold curve table. If the user specifies  $\rho_{TFD} = 0$ , the match defaults to the highest density.

### 3.6 ICLD=5: Universal Metal EOS

If ICLD=5, the cold curve is calculated from a three-parameter formula that is due to Rose, *et. al.* [30].

$$E_c(\rho) = E_B - E_B(1 + a + 0.05a^3) \exp(-a), \quad (3.16)$$

$$P_c(\rho) = -\sqrt{\frac{\beta_0 E_B}{\rho_0}} \left(\frac{\rho_0}{\rho}\right)^{1/3} \rho (a - 0.15a^2 + 0.05a^3) \exp(-a), \quad (3.17)$$

where

$$a = 3\sqrt{\frac{\beta_0}{\rho_0 E_B}} \left[\left(\frac{\rho_0}{\rho}\right)^{1/3} - 1\right]. \quad (3.18)$$

$E_B$ ,  $\rho_0$ , and  $\beta_0$  are the binding energy, density, and bulk modulus of the solid at zero pressure. PANDA prompts the user as follows.

ENTER FIT PARAMETERS - EBZPE,RZRO,BZRO

The user enters  $E_B$ ,  $\rho_0$ , and  $\beta_0$ .

Equations 3.16 and 3.17 were originally proposed for metals [30] but have been found to give very good results for the compression region of other classes of materials as well, in the absence of phase transitions [31]. In many cases, the pressure from Eq. 3.17 approaches the TFD curve at high compressions, so that a large value for  $\rho_{TFD}$  can be used. The success of this formula has been attributed to the universal behavior of repulsive forces, which are dominated by electron-electron overlap effects [31]. The formula is less “universal” in the tension region, where the behavior is dominated by attractive forces that vary with material type. However, this problem can be corrected by using the LJ match option in tension.

### 3.7 The TFD Match

PANDA offers an analytic formula for extrapolating the cold curve to arbitrarily high densities. To obtain this option, the user enters a finite value for  $\rho_{TFD}$ . (The extrapolation procedure is always used if ICLD=1 or ICLD=4.) The high-density formula is based upon the Thomas-Fermi-Dirac (TFD) statistical model of the atom [32] [33], which is believed to be accurate at pressures above about  $10^3$  GPa. The following expressions are used to interpolate from the cold curve at  $\rho = \rho_{TFD}$  to the TFD formula at high densities.

$$E_c(\rho) = [E_T(\rho) - E_T(\rho_{TFD})]y(\rho) + \Delta E_c, \quad (3.19)$$

$$P_c(\rho) = P_T(\rho)y(\rho) + \rho[E_T(\rho) - E_T(\rho_{TFD})]dy/d\rho, \quad (3.20)$$



and

$$y(\rho) = 1 + b_1/\rho + b_2/\rho^{4/3} + b_3/\rho^{5/3}, \quad (3.21)$$

where  $E_T$  and  $P_T$  are the TFD energy and pressure. The quantities  $\Delta E_c$ ,  $b_1$ ,  $b_2$ , and  $b_3$  are determined by requiring that the energy, pressure, and two pressure derivatives be continuous at  $\rho = \rho_{TFD}$ .

In PANDA, the TFD energies and pressures are represented by analytical formulas that agree with numerical calculations [34] to better than 2% for pressures above 100 GPA.

$$E_T(\rho) = \frac{1505.2125}{Wx^2} Z \exp[-F(x)], \quad (3.22)$$

$$P_T(\rho) = \frac{1003.475}{x^5} \left(1 + \frac{x}{2} \frac{dF}{dx}\right) \exp[-F(x)], \quad (3.23)$$

and

$$F(x) = C_1x + C_2x^2 + C_3x^2 \ln x, \quad (3.24)$$

where  $x = (W/Z\rho)^{1/3}$ .  $Z$  and  $W$  are the formula number and formula weight, respectively, computed with the SET BAS command (Sec. 2.2). The quantities  $C_1$ ,  $C_2$ , and  $C_3$  are given by

$$C_1 = 0.703473 + 1.130622Z_{av}^{2/3}, \quad (3.25)$$

$$C_2 = 0.3 - \frac{0.00245Z_{av}^{5/2}}{1 + 0.0028Z_{av}^2}, \quad (3.26)$$

and

$$C_3 = 0.6 + 0.0386Z_{av}^{4/3}. \quad (3.27)$$

PANDA computes the average atomic number  $Z_{av}$  when the SET BAS command is executed (Sec. 2.2). By definition,  $Z_{av} = Z$  for monatomic elements. In the general case, the TFD pressure for the system is computed from the additive volume approximation (Sec. 3.10);  $Z_{av}$  is chosen to match the calculated density at  $10^3$  GPa.

### 3.8 The LJ Match

A low density extrapolation formula suggested by Bennett [35] can be obtained by entering nonzero values for the parameters  $\rho_{LJ}$  and  $f_{LJ}$ . These quantities can also be entered separately, using the command LJ MATCH. In that case, PANDA prompts the user as follows.

LJ MATCH - ENTER RLJ,FACLJ

For  $\rho \leq \rho_{LJ}$ , the following expressions are used.

$$E_c(\rho) = f_1\rho^{f_2} - f_3\rho^{f_{LJ}} + E_B, \quad (3.28)$$

and

$$P_c(\rho) = \rho(f_1 f_2 \rho^{f_2} - f_3 f_{LJ} \rho^{f_{LJ}}). \quad (3.29)$$

Although these formulas are similar to Eqs. 3.2 and 3.3, the LJ match is a completely separate option and can be used with any value of ICLD. The parameters  $f_1$ ,  $f_2$ , and  $f_3$  are determined by requiring that the energy, pressure, and first derivative of the pressure are continuous at  $\rho = \rho_{LJ}$ .  $E_B$  is the solid binding energy, which is available from previous computations.

The LJ match is useful for making adjustments to the cold curve in the tension region, where no experimental data are available. The critical point and liquid density on the coexistence boundary may be sensitive to these adjustments.

### 3.9 The EXP6 Command

In many materials, especially the rare gases and molecular solids [17] [54], the intermolecular forces can be described by a pair potential having the Buckingham (exp-6) form [55],

$$\phi(r) = \frac{\epsilon}{\alpha - 6} (6 \exp[\alpha(1 - r/r_m)] - \alpha(\frac{r_m}{r})^6). \quad (3.30)$$

The energy of the solid is obtained by summing over all shells of neighbors in the lattice. It can be written in the form of Eq. 3.6,

$$E_c(\rho) = \frac{N_0}{2} \sum_l n_l \phi(r_l) = a_1 \exp(-a_2/\rho^{1/3}) - a_3 \rho^{a_4}, \quad (3.31)$$

where  $n_l$  is the number of neighbors and  $r_l$  is the radius of the  $l$ -th shell. For a close-packed lattice, the constants in Eq. 3.31 are found to be

$$a_1 = 36 N_0 \epsilon \exp(\alpha) / (\alpha - 6), \quad (3.32)$$

$$a_2 = \alpha (\sqrt{2} W / N_0 r_m^3)^{1/3}, \quad (3.33)$$

$$a_3 = 7.22696 N_0 \epsilon \frac{\alpha}{\alpha - 6} (\frac{N_0 r_m^3}{\sqrt{2} W})^2, \quad (3.34)$$

and

$$a_4 = 2, \quad (3.35)$$

where  $W$  is the molecular weight. These results are obtained by using the values of  $n_l$  and  $r_l$  that are given in Ref. [55], except that only the nearest neighbor shell is considered in the sum over the short-range exponential term.

The EXP6 option is used to calculate the cold curve parameters from the above formulas. The command line consists of the keyword, following by numerical values for the four parameters.

EXP6  $\alpha \in r_m W$

where  $\epsilon$  has units of  $^{\circ}K$  and  $r_m$  has units of  $\text{\AA}$ . If the user does not enter the four input parameters on the command line, a prompt is given. The code computes and prints out the constants  $a_1$ ,  $a_2$ , and  $a_3$ , and the density  $\rho_0$ , energy  $E_0$ , and bulk modulus  $\beta_0$  at zero pressure. These parameters can be used as input to the COLD CURVE command for option ICLD=3 (Sec. 3.4).

### 3.10 The TFD CURVE Command

The option TFD CURVE generates a curve of pressure *vs.* density using Thomas-Fermi-Dirac theory for the elements [32], combined with the additive volume approximation for mixtures. These data are useful for plotting and comparing to the cold curve model in the high density limit. The command line consists of the keyword and three numerical parameters.

TFD CURVE  $P_{min} P_{max} n_p$

PANDA computes the TFD isotherm at  $n_p$  values of the pressure, in exponentially spaced intervals from  $P_{min} \leq P \leq P_{max}$ . If the user does not enter any parameters on the input line, a prompt is given. A value for  $P_{min}$  is required; default values for the other two parameters are  $P_{max} = 1000P_{min}$  and  $n_p = 10$ .

According to the additive volume approximation, the molar volume  $V$  for a mixture of elements at pressure  $P$  is given by

$$V(P) = \sum_i \chi_i V_i(P), \quad (3.36)$$

where  $\chi_i$  is the number of moles and  $V_i$  is the molar volume of element  $i$  in one mole of the mixture. Here  $V_i(P)$  is computed by inverting Eq. 3.23 to make pressure the independent variable. The elemental composition of the system is taken from the chemical formula, entered using the SET BAS command (Sec. 2.2). This instruction is executed automatically, if the formula has not been provided previously.

PANDA calculates the density, volume, and average atomic number as functions of pressure, and also the pressure that is obtained by fitting Eq. 3.23 to the mixture, as discussed in Sec. 3.7. If a plot file has been opened, these results will also be written to that file, and the user will be prompted to enter a label for the data.

## 4. Solid Lattice Vibration Models

### 4.1 General

In PANDA, the lattice vibrational model describes contributions to the EOS from the three “translational” degrees of freedom of the molecule, while the contributions from “internal” degrees of freedom are computed using the models discussed in Ch. 6. However, molecules in solids do not move independently; their motions are best described using collective coordinates, *i.e.* phonons [36]. General expressions for the thermodynamic properties involve sums over all frequencies, with the phonon spectrum as a weighting function. For solids having complicated phonon spectra, the distinction between translational and internal degrees of freedom may be somewhat arbitrary. Nevertheless, it should be possible to use these concepts to construct a model that gives a reasonable description of the thermodynamic properties. In such cases, certain branches of the spectrum can be treated as dispersed in frequency while others can be adequately characterized by a single frequency. The lattice vibrational model should be used for the contributions from the dispersed branches. The other branches can be described using the models in Ch. 6. The chemical formula entered with the SET BAS command (Sec. 2.2) should be chosen so that the phonon spectrum has the correct number of branches of each type.

PANDA offers five models for computing the contributions from lattice vibrations to the EOS. There are also five options for the Grüneisen function and Debye temperature that can be used with each of these models. In addition, the code provides a gaslike extrapolation formula, the virial match, which can be used for low densities.

The instruction SOL NUC is used to enter the data. This instruction will be issued automatically, if the code needs the data, under several other commands, including MOD SOL and COLD CURVE. The user is prompted as follows.

```
LATTICE VIBRATION MODEL - ENTER INPT,IGRN,RV,TG,GAML
```

	INPT	- option for the lattice vibration model:
	INPT=1,	Debye model
	INPT=-1,	Debye model with cutoff
	INPT=2,	solid-gas interpolation formula
	INPT=3,	Einstein model
	INPT=-3,	Einstein model with cutoff
where	IGRN	- option for the Grüneisen function:
	IGRN=0,	constant Grüneisen function
	IGRN=1,	cold curve formula
	IGRN=2,	Sesame formula
	IGRN=3,	ANEOS formula
	IGRN=4,	generalized analytic formula
	RV	- $\rho_v$ = density for virial match
	TG	- $\tau_g$ = parameter in Grüneisen formula
	GAML	- $\gamma_\infty$ = high-density limit for Grüneisen function

The above parameters completely define the lattice vibration model. The user will receive no additional prompts unless cold curve data are needed (for the case IGRN=1).

## 4.2 The Debye Model

PANDA provides two versions of the Debye model. In the standard model (INPT=1), the Helmholtz free energy, internal energy, pressure, and entropy are given by the following standard expressions [37]-[39].

$$A_l(\rho, T) = \frac{R}{W} \left[ \frac{9}{8} \Theta + 3T \ln(1 - e^{-\Theta/T}) - TD(\Theta/T) \right], \quad (4.1)$$

$$E_l(\rho, T) = \frac{R}{W} \left[ \frac{9}{8} \Theta + 3TD(\Theta/T) \right], \quad (4.2)$$

$$P_l(\rho, T) = \frac{R}{W} \rho \gamma(\rho) \left[ \frac{9}{8} \Theta + 3TD(\Theta/T) \right], \quad (4.3)$$

and

$$S_l(\rho, T) = \frac{R}{W} [4TD(\Theta/T) - 3 \ln(1 - e^{-\Theta/T})], \quad (4.4)$$

where

$$D(x) = \frac{3}{x^3} \int_0^x \frac{y^3}{e^y - 1} dy. \quad (4.5)$$

$\gamma$  and  $\Theta$  are the Grüneisen function and Debye temperature (Sec. 4.5),  $W$  is the molecular weight, and  $R$  is the gas constant. Note that these formulas include the contributions from zero-point motion. Therefore, the cold curve in PANDA should *not* include these terms.

In the modified Debye model (INPT=-1) the sum over the lattice vibrational levels is cut off when the amplitudes of vibration become comparable with intermolecular distances. The harmonic approximation breaks down for these high vibrational states, where the lattice becomes mechanically unstable. The standard Debye model, which includes these levels, gives an unreasonable prediction of the free energy at very high temperatures, and erroneous results occur in the calculation of melting phenomena. The cutoff formulas overcome these problems.

Formulas for the cutoff model are discussed in Appendix C. Corrections to the standard model are normally very small over the entire range where the solid is thermodynamically stable (relative to the fluid phase). When the temperature is raised above the melting curve, the corrections become important, and the solid becomes mechanically unstable. At still higher temperatures, PANDA uses the ideal gas formula.

*Note:* The very high temperature region of the solid is fictitious and artificial. For best results, the fluid model should be used in this region. PANDA can be used to generate separate EOS tables for the fluid and solid phases, and the phase transition model (Sec. 11) can be used to construct the multiphase EOS. For a crude treatment of melting, the solid-gas interpolation formula (INPT=2, Sec. 4.3) may give better results than the cutoff model.

## 4.3 Solid-Gas Interpolation Formula

For INPT=2, PANDA provides a formula that smoothly interpolates between the Debye model, at low temperatures or high densities, and the ideal gas law, at high temperatures and low densities. This model should not be confused with the virial match, which is described in Sec. 4.6.

The Helmholtz free energy is given by the following formula.

$$A_l(\rho, T) = \frac{R}{W} \left( \frac{9}{8} \Theta + \frac{3}{2} T \ln \left[ \frac{f_0 + f_1(x)}{f_0 + f_1(x) + f_2(x)} \right] \right), \quad (4.6)$$

where  $x = \Theta/T$ ,

$$f_0 = 111.56(\rho/W)^{2/3}/WT, \quad (4.7)$$

$$f_1 = 0.513417x^2 + 0.010855x^3 + 0.052934x^4, \quad (4.8)$$

and

$$f_2 = 1.0 + 0.687497x. \quad (4.9)$$

If one sets  $f_0 = 0$  in Eq. 4.6, the result so obtained is in good numerical agreement with the Debye formula, Eq. 4.1. When the  $f_0$  term is included, Eq. 4.6 goes to the ideal gas limit [38] as  $T \rightarrow \infty$  or as  $\Theta \rightarrow 0$  (low densities).

The internal energy, pressure, and entropy are found from the thermodynamic relations.

$$E_l = A_l - T\left(\frac{\partial A_l}{\partial T}\right)_\rho = \frac{R}{W}\left[\frac{9}{8}\Theta + 3T\frac{f_0/2 + f_3(x)}{[f_0 + f_1(x)][f_0 + f_1(x) + f_2(x)]}\right], \quad (4.10)$$

$$P_l = \rho^2\left(\frac{\partial A_l}{\partial \rho}\right)_T = \frac{R\rho}{W}\left[\frac{9}{8}\gamma\Theta + T\frac{3\gamma[f_0/2 + f_3(x)] + (1 - 3\gamma/2)f_0f_2(x)}{[f_0 + f_1(x)][f_0 + f_1(x) + f_2(x)]}\right], \quad (4.11)$$

and

$$S_l = (E_l - A_l)/T, \quad (4.12)$$

where

$$f_3(x) = 0.513417x^2 + 0.192769x^3 + 0.113331x^4 + 0.054588x^5. \quad (4.13)$$

This model can be used either with or without the virial match (Sec. 4.6). However, the latter is preferred if IGRN=1.

## 4.4 The Einstein Model

PANDA provides two versions of the Einstein model [39]. In the standard model (INPT=3), the thermodynamic functions are given by

$$A_l = \frac{R}{W}\left[\frac{3}{2}\Theta + 3T\ln(1 - e^{-\Theta/T})\right], \quad (4.14)$$

$$E_l = \frac{R}{W}\left[\frac{3}{2}\Theta + \frac{3\Theta}{e^{\Theta/T} - 1}\right], \quad (4.15)$$

and

$$P_l = \frac{R}{W}\rho\gamma\left[\frac{3}{2}\Theta + \frac{3\Theta}{e^{\Theta/T} - 1}\right], \quad (4.16)$$

(The Einstein temperature  $\Theta$  is identical with the Debye temperature, discussed in Sec. 4.5.)

In the modified Einstein model (INPT=-3), the sum over the lattice vibrational levels is cut off for large amplitude vibrations. The qualitative features of the model are the same as those for the Debye model with a cutoff. Details are given in Appendix C.

## 4.5 Options for the Grüneisen Function

PANDA offers five options for the Grüneisen function  $\gamma$  and the Debye or Einstein temperature  $\Theta$  in each of the above models. These two parameters are related by

$$\gamma = d \ln \Theta / d \ln \rho. \quad (4.17)$$



For INPT=0, the Grüneisen function is a constant,  $\gamma = \gamma_{ref}$ , where  $\gamma_{ref}$  is the value specified with the SET BAS command (Sec. 2.2). From Eq. 4.17, the Debye temperature is found to be

$$\Theta = \Theta_{ref}(\rho/\rho_{ref})^{\gamma_{ref}}, \quad (4.18)$$

where  $\Theta_{ref}$  is also entered with the SET BAS command.

For IGRN=1, PANDA uses an expression that relates the Grüneisen function to the pressure and its derivatives on the cold curve.

$$\gamma = -\frac{1}{6} + \frac{1}{2} \frac{\beta'_c - 2\tau_g \beta_c/3}{\beta_c - 2\tau_g P_c/3}, \quad (4.19)$$

where

$$\beta_c = \rho dP_c/d\rho, \quad (4.20)$$

and

$$\beta'_c = \rho d\beta_c/d\rho. \quad (4.21)$$

Here  $\tau_g$  is the parameter entered with the SOL NUC command as discussed above. Equation 4.19 represents three well-known relations:

- $\tau_g = 0$  is the Slater formula [23].
- $\tau_g = 1$  is the Dugdale-MacDonald formula [40].
- $\tau_g = 2$  is the free volume formula [41].

In PANDA,  $\tau_g$  can have noninteger values in addition to the above. If the user has entered a nonzero value of  $\gamma_{ref}$  with the SET BAS command, the code solves for  $\tau_g$  from Eq. 4.19 and ignores the value of  $\tau_g$  specified by the user. In this case, however, the code does not allow a value of  $\tau_g > 2.5$ , which gives poor results at high densities; it sets  $\tau_g$  and resets  $\gamma_{ref}$ . If the user specifies  $\gamma_{ref} = 0$  on input, PANDA takes the specified value of  $\tau_g$  in Eq. 4.19; any value for  $\tau_g$  can be entered in that case. The Debye temperature for IGRN=1 is given by

$$\Theta = C_\Theta(\beta_c - 2\tau_g P_c/3)^{1/2}/\rho^{1/6}, \quad (4.22)$$

where the constant  $C_\Theta$  is determined from parameters  $\gamma_{ref}$  and  $\Theta_{ref}$ .

*Note:* Equation 4.19 fails when  $\beta_c \leq 2\tau_g P_c/3$ , which typically occurs in the tension region, outside the normal solid density range. At these low densities, the code avoids numerical problems by setting  $\gamma = 2/3$  and  $\Theta = 0$ , but the model should not be used in this region. This difficulty can be eliminated with the virial match.

PANDA also offers three simple analytic options for  $\gamma$  and  $\Theta$ . Setting IGRN=2 specifies the so-called Sesame formula,

$$\gamma = \gamma_{ref}/\eta + \gamma_\infty(1 - 1/\eta), \quad (4.23)$$

and

$$\Theta = \Theta_{ref} \eta^{\gamma_{\infty}} \exp(\gamma_{ref} - \gamma). \quad (4.24)$$

where  $\eta = \rho/\rho_{ref}$  and  $\gamma_{\infty}$  is the high density limit of the Grüneisen function, entered using the SOL NUC command, as discussed above. The default value is  $\gamma_{\infty} = 1/2$ .

Setting IGRN=3 specifies the following formula, a generalization of the one that is used in the ANEOS model of Thompson and Lauson [38],

$$\gamma = \gamma_{ref}/\eta + \gamma_{\infty}(1 - 1/\eta)^2, \quad (4.25)$$

and

$$\Theta = \Theta_{ref} \eta^{\gamma_{\infty}} \exp[\gamma_{ref} - \gamma + \frac{1}{2}\gamma_{\infty}(\eta^{-2} - 1)]. \quad (4.26)$$

Setting IGRN=4 gives a more general formula,

$$\gamma = (\gamma_{ref} - \gamma_{\infty})/\eta^{\tau_g} + \gamma_{\infty}, \quad (4.27)$$

and

$$\Theta = \Theta_{ref} \eta^{\gamma_{\infty}} \exp[(\gamma_{ref} - \gamma)/\tau_g], \quad (4.28)$$

where the code requires that  $\tau_g \geq 1$ . Note that the parameter  $\tau_g$  has a different meaning here than for ICLD=1. If  $\tau_g = 1$ , Eq. 4.27 is identical to the case IGRN=2.

## 4.6 The Virial Match

For densities  $\rho < \rho_v$ , PANDA provides a smooth interpolation formula between the solid model and the low-density ideal gas law. This option uses the idea of Barnes and Fickett [42], as extended by Bennett [35]. The user obtains this option by entering a nonzero value for  $\rho_v$  when specifying the lattice vibration model with the SOL NUC command.

Formulas for the thermodynamic functions are as follows.

$$A_l(\rho, T) = A_l(\rho_v, T) + \frac{RT}{W} \ln(\rho/\rho_v) + C_1(T)\mu + C_2(T)\mu^2 + C_3(T)\mu^3, \quad (4.29)$$

$$E_l(\rho, T) = E_l(\rho_v, T) + D_1(T)\mu + D_2(T)\mu^2 + D_3(T)\mu^3, \quad (4.30)$$

and

$$P_l(\rho, T) = \frac{RT\rho}{W} + \frac{\rho^2}{\rho_v} [C_1(T) + 2C_2(T)\mu + 3C_3(T)\mu^2], \quad (4.31)$$

where  $\mu = \rho/\rho_v - 1$ . The entropy is given by Eq. 4.12. Continuity of the pressure at  $\rho = \rho_v$  requires

$$C_1(T) = P_l(\rho_v, T)/\rho_v - RT/W. \quad (4.32)$$

At low densities, the free energy must approach the ideal gas limit.

$$A_l \rightarrow \frac{RT}{W} [7.07228 - \ln(W/\rho) - \frac{3}{2} \ln(WT)] \text{ as } \rho \rightarrow 0. \quad (4.33)$$

PANDA also requires that the first derivative of the pressure be continuous at  $\rho = \rho_v$ . These three conditions determine  $C_1$ ,  $C_2$ , and  $C_3$ . At low densities, the internal energy must approach the ideal gas limit,

$$E_l \rightarrow \frac{3}{2} \frac{RT}{W} \text{ as } \rho \rightarrow 0. \quad (4.34)$$

In addition, the first and second derivatives of the energy must be continuous at  $\rho = \rho_v$ . Hence there are three relations for  $D_1$ ,  $D_2$ , and  $D_3$ . Thermodynamic consistency requires that

$$D_k(T) = C_k(T) - T dC_k/dT, \quad (4.35)$$

where  $k = 1, 2, 3$ . The above requirements on continuity of the derivatives automatically insure that these conditions are satisfied.

The virial match can be used with any of the lattice vibration models, but it gives best results with INPT=-2, the solid-gas formula. In this case, it gives a smoother interpolation to the low-density ideal gas limit than the model does without a match. At high temperatures, the virial match does not give good results when used with the Debye and Einstein options, because the free energy in these models agrees very poorly with that for an ideal gas. Both Eqs. 4.1 and 4.14 give

$$A_l \rightarrow 3 \frac{RT}{W} \ln(\Theta/T) \text{ as } T \rightarrow \infty. \quad (4.36)$$

Matching Eq. 4.29 onto this result is found to give unphysical loops in the pressure at high temperatures. The cutoff models, INPT=-1 and INPT=-3, also give poor results with the virial match because the pressure and internal energy do not have continuous derivatives everywhere (see Appendix C).

## 5. Perturbation Theory of Fluids

### 5.1 General

The CRIS model [17] [43] [44] describes the translational degrees of freedom for a fluid of interacting molecules. It includes not only the contribution from thermal nuclear motion, but also the contribution from the intermolecular interactions that govern the thermal motions. These interactions are computed from the cold curve for the solid; however, the cold curve and the contributions from thermal motion are not additive, as they are in the case of the solid. The theory is valid over the entire fluid range: the liquid, vapor, and supercritical regions. At low temperatures, isotherms calculated using the model display van der Waals loops, indicating a vapor-liquid coexistence region and a critical point. When the CRIS model is used together with a model for the solid phase, the melting curve can be calculated. Finally, the fluid model also provides estimates of the structure factor and radial distribution function, the bulk and shear viscosities, and the diffusivity.

The thermodynamic properties are computed from an expansion about a hard-sphere reference system, in which the hard-sphere diameter is chosen by a variational principle. The model uses the  $0^\circ K$  isotherm of the solid to define an expression for the energy of a molecule in the field of its neighbors. In PANDA, the cold curve is constructed as described in Ch. 3. This quantity contains all the information about intermolecular forces needed for the model; the user does not have to specify a pair potential.

Parameters needed for the model are entered using the command CRIS. This instruction will be issued automatically, if the code needs the data, under the command MOD LIQ. When the user specifies the CRIS model, the code checks for a cold curve and prompts the user if data have not been entered. Next, the code prompts the user to enter ten parameters, all of which can be defaulted.

CRIS MODEL - ENTER BEXP,EFAC,QFAC,TMIN,NGS,  
NZI,EPS,DR,DT,XG

	BEXP	- $B_x$ , used in high density formula (see below)
	EFAC	- $\Delta E_x$ = energy shift (default is 0)
	QFAC	- $Q_x$ = quantum correction factor (default is 0)
	TMIN	- $T_{min}$ = low temperature floor (see below)
where	NGS	- number of primary quadrature points (default is 1000)
	NZI	- number of secondary quadrature intervals (default is 1)
	EPS	- error criterion (default is $10^{-5}$ )
	DR	- step for density derivatives (default is 0.01)
	DT	- step for temperature derivatives (default is 0.01)
	XG	- initial guess in search for packing fraction (default is 0.4)

Use of the first four parameters,  $B_x$ ,  $\Delta E_x$ ,  $Q_x$ , and  $T_{min}$ , is discussed in Sec. 5.2 and 5.3. The other six parameters apply to numerical procedures and are usually defaulted. The CRIS model requires computation of several integrals of a single variable, which can be done by either Gauss or adaptive quadrature. For  $NGS \geq 60$ , the adaptive scheme [45] is used; the integrand is evaluated a maximum of NGS times or until the error check is satisfied. For  $1 \leq NGS \leq 59$ , the range of integration is divided into subintervals and a 10-point Gauss quadrature formula is used.  $NGS = 10$  gives enough accuracy for most routine calculations, and it saves computing time. There is one integral of two variables in the model. The outer integration is done as just described, whereas the inner integration is always done using the 10-point Gauss formula on NZI subintervals.  $NZI = 1$  is usually sufficient, but higher values are needed occasionally. The user may want to make spot checks.

The code prints out the values of the parameters that are being used in the model.

## 5.2 The Equations

Equations for the CRIS model are discussed in detail in Refs. [17] and [44]. The formulas in PANDA have been generalized somewhat, to include quantum corrections and to permit the user to make empirical adjustments that improve agreement with experiment.

In the CRIS model, each fluid molecule is assumed to be located in a spherical cage formed by its neighbors. The radius of the cage  $R$  and the coordination number  $\bar{\nu}$  vary from molecule to molecule. There is a solid density  $\rho_s$  that corresponds to each value of the radius  $R$ ; it is given by

$$\rho_s = W\sqrt{2}/N_0R^3. \quad (5.1)$$

The coordination number varies with  $R$  in such a way that the volume per molecule is constant throughout the fluid and equal to the macroscopic value. If the macroscopic density is  $\rho$ , the coordination number is

$$\bar{\nu} = 12\rho/\rho_s. \quad (5.2)$$

The energy  $\phi$  of a fluid molecule in a cage of radius  $R$  is equal to the energy of a molecule in the solid at density  $\rho_s$ , times a correction for the coordination number. A fluid molecule has a fraction  $\bar{\nu}/12$  of the bonds that it would have in the solid lattice. To a first approximation,

$$N_0\phi \simeq E_c(\rho_s)\rho/\rho_s. \quad (5.3)$$

However, Eq. 5.3 is exact only if the bonds are additive in energy. This approximation breaks down at very high densities, where the electrons are completely delocalized and  $E_c \propto \rho_s^{2/3}$ . In PANDA, Eq. 5.3 is revised as follows.

$$N_0\phi = [(1-f)\rho/\rho_s + f(\rho/\rho_s)^{2/3}][E_c(\rho_s) - \Delta E_x]. \quad (5.4)$$

Here  $f$  is the fraction of electrons that are delocalized. It is assumed to have the following form.

$$f = \exp(-B_x/\rho_s^{1/3}), \quad (5.5)$$

where  $B_x$  is entered by the user. If the user sets  $B_x = 0$ , the code calculates a default value from the formula

$$B_x = (0.23 + 0.6544Z_{av}^{2/3})(W/Z)^{1/3}, \quad (5.6)$$

where  $Z$ ,  $W$ , and  $Z_{av}$  are the formula number, formula weight, and average atomic number, respectively, computed using the SET BAS command (Sec. 2.2). The above expression was obtained by making a rough estimate of the number of free electrons from the TFD theory. Calculated properties are not very sensitive to this parameter. The reason for using Eq. 5.4 is that at high densities, all the electrons become delocalized and the leading term in the energy is independent of the positions of the nuclei. As  $\rho \rightarrow \infty$  and  $\rho_s \rightarrow \infty$ , Eq. 5.4 gives

$$N_0\phi \rightarrow E_c(\rho_s)(\rho/\rho_s)^{2/3} \rightarrow E_c(\rho). \quad (5.7)$$

Hence Eq. 5.4 provides an extrapolation to the correct limit.

The parameter  $\Delta E_x$  in Eq. 5.4 has been introduced for empirical reasons. It can be used to adjust the free energy of the liquid so that the calculated melting point agrees with experiment. Liquid metals usually require  $\Delta E_x$  to be  $\sim 3$ -5% of the solid binding energy to match the melting point. Such a small factor has very little effect upon any of the other calculated properties. The need for such an empirical factor shows that Eq. 5.4 is not completely satisfactory for metals; corrections for delocalization of the electrons should be taken into account. However, these corrections are fairly small, because the CRIS model gives very good results for liquid metals.

The Helmholtz free energy of the fluid is given by

$$A_{cr}(\rho, T) = A_0(\rho, T) + A_{hs} + Q_x A_{qm} + N_0 \langle \phi \rangle_0 + \Delta A_1 + \Delta A_2, \quad (5.8)$$

where  $A_0$  is the free energy for an ideal gas.

$$A_0 = \frac{RT}{W} [7.07228 - \ln(W/\rho) - \frac{3}{2} \ln(WT)]. \quad (5.9)$$

$A_{hs}$  is the excess free energy for a classical hard-sphere fluid,  $N_0\langle\phi\rangle_0$  is the first order perturbation term, and  $\Delta A_1$  and  $\Delta A_2$  are higher order terms [44]. The additional term,  $A_{qm}$ , is a quantum correction to the hard-sphere free energy. (To obtain this correction, set  $Q_x = 1$  on input.) The formula of Singh and Sinha [46] is used.

$$A_{qm} = \frac{RT}{W} (C_1\eta + C_2\eta^2), \quad (5.10)$$

where

$$C_1 = 4.24264(\lambda/\sigma_0) + 1.27324(\lambda/\sigma_0)^2, \quad (5.11)$$

and

$$C_2 = 3.21645(\lambda/\sigma_0)^2. \quad (5.12)$$

Here  $\lambda$  is the thermal wavelength,

$$\lambda = (h^2/2\pi WkT)^{1/2}. \quad (5.13)$$

The packing fraction is  $\eta = N_0\pi\sigma_0^3W/6\rho$ , and  $\sigma_0$  is the effective hard-sphere diameter. These quantities are determined from the variational principle [44],

$$\frac{\partial}{\partial\eta} (A_{hs} + Q_x A_{qm} + N_0\langle\phi\rangle_0)_{\rho,T} = 0. \quad (5.14)$$

The corresponding energy, pressure, and entropy formulas are [44]

$$E_{cr}(\rho, T) = \frac{3}{2} \frac{RT}{W} + Q_x E_{qm} + N_0\langle\phi\rangle_0 + \Delta E_1 + \Delta E_2, \quad (5.15)$$

$$P_{cr}(\rho, T) = \frac{RT\rho}{W} + P_{hs} + Q_x P_{qm} + N_0\rho^2 \left( \frac{\partial\langle\phi\rangle_0}{\partial\rho} \right)_{\eta,T} + \Delta P_1 + \Delta P_2, \quad (5.16)$$

and

$$S_{cr}(\rho, T) = [E_{cr}(\rho, T) - A_{cr}(\rho, T)]/T, \quad (5.17)$$

where

$$E_{qm} = \frac{RT}{W} (C_3\eta + C_2\eta^2), \quad (5.18)$$

$$P_{qm} = 2\rho E_{qm}/3, \quad (5.19)$$

and

$$C_3 = 2.12132(\lambda/\sigma_0) + 1.27324(\lambda/\sigma_0)^2. \quad (5.20)$$

The above treatment of quantum effects on the EOS gives reasonable results when applied to  $H_2$  and  $D_2$  [17]. Rosenfeld [47] [48] has developed another model for computing quantum corrections to the CRIS model, but his approach is not included in the code at present.



### 5.3 Low Temperature Extrapolation

The CRIS model gives good results over the entire fluid range and most of the super-cooled region as well. However, there is a region near normal solid density and very low temperatures where the model has numerical problems and gives unsatisfactory results. Although this region has no physical significance, PANDA provides a thermodynamically consistent extrapolation formula that eliminates pathologies and enables the user to generate a rectangular table for the fluid, including a  $T = 0$  curve. For temperatures  $T < T_{min}$ , it sets

$$A(\rho, T) = \frac{T}{T_{min}}[A(\rho, T_{min}) - E(\rho, T_{min})] + E(\rho, T_{min}), \quad (5.21)$$

$$E(\rho, T) = E(\rho, T_{min}), \quad (5.22)$$

$$P(\rho, T) = P(\rho, T_{min}) + (T - T_{min})\left(\frac{\partial P}{\partial T}\right)_{T_{min}}, \quad (5.23)$$

and

$$S(\rho, T) = [E(\rho, T_{min}) - A(\rho, T_{min})]/T_{min} = S(\rho, T_{min}), \quad (5.24)$$

where  $A$ ,  $E$ ,  $P$ , and  $S$  are the *excess* thermodynamic quantities (deviations from the ideal gas values). The extrapolation temperature  $T_{min}$  is specified by the user. If the user sets  $T_{min} = 0$ , the code uses the default value

$$T_{min} = 2.5W E_{coh}, \quad (5.25)$$

where  $E_{coh}$  is the cohesive energy that was entered using the SET BAS command (Sec. 2.2). Equation 5.25 should put the extrapolation region below the melting point for all materials.

### 5.4 Radial Distribution and Structure Factor

The CRIS model can be used to calculate the first peak in  $g(R)$ , the radial distribution function of the fluid [17] [44]. The structure factor is defined by

$$S(Q) = 1 + \frac{N_0\rho}{W} \int [g(R) - 1] \exp(i\vec{Q} \cdot \vec{R}) d\vec{R}. \quad (5.26)$$

It is convenient to write  $S(Q)$  as the sum of two terms.

$$S(Q) = S_0(Q) + \Delta S(Q), \quad (5.27)$$

$$\Delta S(Q) = \frac{N_0\rho}{W} \int [g(R) - g_0(R)] \exp(i\vec{Q} \cdot \vec{R}) d\vec{R}. \quad (5.28)$$

The hard-sphere structure factor  $S_0(Q)$  is given by the equations of Verlet and Weis [49], using the hard-sphere diameter predicted by Eq. 5.14. The terms  $g(R)$  and  $g_0(R)$

differ primarily in the nearest neighbor peak, where  $g_0(R)$  has a sharp cutoff for  $R < \sigma_0$ . Hence the most important contribution to  $\Delta S(Q)$  can be calculated from the fluid model predictions for  $g(R)$  and  $g_0(R)$ . There is, however, one problem with this procedure. Because the expressions for  $g(R)$  and  $g_0(R)$  have a cutoff [44] for large  $R$ , Eq. 5.28 gives erroneous oscillations for small wavelengths. However, the results are satisfactory for the first peak in  $S(Q)$  and for larger wavelengths. In general, the corrections  $\Delta S(Q)$  are small.

The command RDF LIQ is used to generate a table of the radial distribution for a liquid at a given density and temperature. The following prompt is given.

ENTER RHO, TEMP, R1, R2, NPTS

where	RHO	- density
	TEMP	- temperature
	R1,R2	- lower and upper limits on radius ( $\text{\AA}$ )
	NPTS	- number of points on interval

Points on the interval are equally spaced. PANDA prints out a table of the radius,  $g(R)$ , and  $g_0(R)$ . These same data are sent to the plot file if one has been defined.

The command SFAC LIQ is used to generate a table of the structure factor for the liquid at a given density and temperature. The following prompt is given.

ENTER RHO, TEMP, Q1, Q2, NPTS

where	RHO	- density
	TEMP	- temperature
	Q1,Q2	- lower and upper limits on wavelength ( $1/\text{\AA}$ )
	NPTS	- number of points on interval

Points on the interval are equally spaced. PANDA prints out a table of the wavelength,  $S(Q)$ , and  $S_0(Q)$ . These same data are sent to the plot file if one has been defined.

Before using the commands RDF LIQ and SFAC LIQ, the CRIS model parameters must be set up using either the MOD LIQ command or the SET BAS and CRIS commands.

## 5.5 Viscosity and Diffusivity

Dymond and Alder [50] proposed a hard-sphere model for calculating transport coefficients in simple liquids. They asserted that repulsive forces play the dominant role

in transport phenomena. To a rough approximation, the molecules are in free flight between collisions when they are in attractive regions of the potential. If perturbation theory is used to expand the transport coefficients about a hard-sphere reference system, first order terms in the expansion should be less important than they are for the EOS [50], thereby making a correlation between the equilibrium and transport properties.

In PANDA, the viscosity and diffusivity are calculated from the hard-sphere formulas, using the hard-sphere diameter computed from the CRIS model. This approximation was found to give reasonable results when applied to iron [17]. Dymond's fit [51] to the molecular dynamics results [52] is used for the shear viscosity  $v_s$ .

$$v_s = v_0 \frac{6.1525\eta}{1 - 1.869\eta}, \quad (5.29)$$

where  $v_0 = 1.237 \times 10^{-5} \sqrt{WT}(\rho/W\eta)^{2/3}$  poise. Numerical results for the bulk viscosity  $v_b$  are not as accurate as those for  $v_s$ . Hence PANDA uses the Enskog formula [52],

$$v_b = 16.2975v_0\eta^2 g_0(\sigma_0), \quad (5.30)$$

where  $g_0(\sigma_0)$  is the hard-sphere radial distribution function at contact. Molecular dynamics results for hard spheres [52] and soft spheres [53] indicate that  $v_b$  is less than the Enskog value at high densities. The diffusivity  $d$  is also computed from Dymond's fit [51],

$$d = 1.525v_0(1 - 1.869\eta)/\rho \text{ (cm}^2/\text{s)}. \quad (5.31)$$

The command XPT LIQ is used to compute the transport properties as functions of density and temperature. The user is prompted as follows.

ENTER DENSITY (G/CC) AND TEMPERATURE (K)

The user responds by entering the density and temperature at each point to be computed. PANDA prints out the density, temperature, bulk viscosity, shear viscosity, diffusivity, and hard-sphere packing fraction. If a plot file has been opened, these variables will be sent to that file, along with the hard-sphere diameter. The code continues to read density-temperature points until the user specifies a zero density. Before using the XPT LIQ command, the CRIS model parameters must be set up using either the MOD LIQ command or the SET BAS and CRIS commands.

## 6. Internal Vibrational and Rotational Terms

### 6.1 General

The contributions from vibrational and rotational degrees of freedom to the EOS of a one-component system should be included when modeling molecular solids and fluids or solids having complicated lattice vibrational spectra. The total number of degrees of freedom is determined by the chemical formula, entered with the SET BAS command (Ch. 2). For a molecular solid or fluid, the chemical formula specifies the total number of atoms in the molecule. If there are  $N$  atoms, the molecule has 3 translational degrees of freedom and  $3N - 3$  internal degrees of freedom, to be distributed among the rotational and vibrational modes. For other types of solids, the chemical formula defines the acoustic branch of the lattice vibrational spectrum, which is to be computed using the Debye or Einstein model (Ch. 4). The remaining  $3N - 3$  degrees of freedom represent optical branches of the spectrum, some of which are best modeled as vibrations and others as rotations.

In PANDA, the contributions from the rotational degrees of freedom to the EOS of a one-component solid or fluid are calculated from the rigid-rotator approximation [18]. The contributions from the vibrational degrees of freedom are derived from harmonic oscillator expression [18], but anharmonicity effects can be included by allowing for density and temperature dependence of the vibrational frequencies. Data for the model are entered using the command VIB ROT. If the code needs data for this option, this instruction will be issued automatically under the commands MOD SOL and MOD LIQ.

### 6.2 Rotational Terms

After giving the VIB ROT command, the rotational data are entered first. The user is prompted as follows.

ROTATIONAL TERM - ENTER IRT,BRT,SRT,WRT

	IRT	- one of the following
	IRT=0,	no rotation or terminate input
	IRT=1,	linear molecule
where	IRT=2,	non-linear molecule
	BRT	- $B_{rot}$ = rotational constant in $\text{cm}^{-1}$
	SRT	- $\sigma_{rot}$ = molecular symmetry number
	WRT	- $w_{rot}$ = weight assigned to rotational term

The above parameters must be entered for each rotational term that is to be defined (up to a maximum of 10 terms). PANDA repeats the above prompt until IRT=0 is specified. In most cases,  $B_{rot}$  and  $\sigma_{rot}$  can be obtained from spectroscopic data compilations. The command BROT can be used to compute a rotational constant from the geometry of the rotating group (Sec. 6.4). By definition, each rotator in the molecule has a weight of unity; the value given for  $w_{rot}$  should be consistent with the chemical formula given with the SET BAS command (Sec. 2.2).  $\sigma_{rot}$  and  $w_{rot}$  both have a default value of unity.

Rotational contributions to the EOS depend only on temperature. The Helmholtz free energy for a rotational mode is given by

$$A_{rot}(T) = -w_{rot}RT \ln Q_{rot}/W, \quad (6.1)$$

where  $R$  is the gas constant,  $Q_{rot}$  is the rotational partition function, and  $W$  is the formula weight. In PANDA, the formulas for  $Q_{rot}$  are taken from high-temperature expansions [18] with minor modifications to insure reasonable behavior at low temperatures.

A *linear rotator* (IRT=1) has two degrees of freedom. The partition function is given by

$$Q_{rot} = (x^3 + x^2 + 1)^{1/3} / \sigma_{rot}, \quad (6.2)$$

where

$$x = 0.695038T/B_{rot}. \quad (6.3)$$

Equation 6.2 agrees with the high-temperature expansion [18] for large  $x$ . At low temperatures it is well behaved and is approximately correct, although not exact. The internal energy for a linear rotator is

$$E_{rot}(T) = w_{rot} \frac{RT}{W} \frac{x^3 + (2/3)x^2}{1 + x^2 + x^3}. \quad (6.4)$$

A *nonlinear rotator* has three degrees of freedom, each of which can have a different rotational constant. For this case (IRT=2),  $B_{rot}$  is defined to be the geometric mean of the three constants,

$$B_{rot} = (B_1 B_2 B_3)^{1/3}. \quad (6.5)$$

At high temperatures, the partition function for any nonlinear molecule reduces to the case of the spherical top ( $B_1 = B_2 = B_3 = B_{rot}$ ), provided  $B_{rot}$  is defined as above [18]. In PANDA, the formulas partition function and internal energy are given by

$$Q_{rot} = (\pi x^3 + \pi x^2/2 + 1)^{1/2} / \sigma_{rot}, \quad (6.6)$$

and

$$E_{rot}(T) = w_{rot} \frac{RT}{W} \frac{(3/2)x^3 + x^2/2}{x^3 + x^2/2 + 1/\pi}. \quad (6.7)$$

Equation 6.6 agrees with the high temperature result for  $x \gg 1$  and is well behaved, although not exact, at low temperatures.

The rotational contribution to the entropy is

$$S_{rot}(T) = [E_{rot}(T) - A_{rot}(T)]/T. \quad (6.8)$$

There is no contribution to the pressure in this approximation.

The above expressions, which describe freely rotating molecules, are good approximations at sufficiently high temperatures. At low temperatures, it may be necessary to include corrections for hindered rotation and other effects of condensation. To a first approximation, these corrections can be included in the solid cold curve (see Ref. [54]). Alternately, the motion can be treated as a torsional vibration, or “libration”.

## 6.3 Vibrational Terms

Continuing discussion of the VIB ROT command, data for the vibrational terms are entered after the data for the rotational terms have been input as described above. The user is prompted as follows.

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

	WVB	- $\omega_0$ = vibrational frequency in $\text{cm}^{-1}$
	GVB	- $g_\omega$ = degeneracy of vibrational mode
where	FVB	- $n_\omega$ = cutoff in number of levels
	GAM	- $\gamma_0$ = Grüneisen parameter for mode
	PVB	- $p_\omega$ = density dependence parameter
	TVB	- $t_\omega$ = temperature dependence parameter

The above parameters must be entered for each vibrational term that is to be defined (up to a maximum of 15 terms). PANDA repeats the above prompt until a zero frequency is encountered. The vibrational frequencies and degeneracies are normally obtained from compilations of spectroscopic data. Default values for the other parameters are  $n_\omega = 100$ ,  $\gamma_0 = 0$ ,  $p_\omega = 0$ , and  $t_\omega = \infty$ .

The Helmholtz free energy for a vibrational mode is given by

$$A_{vib}(\rho, T) = -g_\omega RT \ln Q_{vib}/W, \quad (6.9)$$

where  $Q_{vib}$  is the vibrational partition function. In PANDA, the standard harmonic oscillator formulas [18] are modified to exclude the contribution from excited vibrational levels with energies far in excess of the molecular dissociation energy. If this cutoff is not used, the harmonic oscillator approximation gives an unreasonable prediction for the entropy and energy at very high temperatures, causing problems in the calculation of dissociation. When the cutoff is used, these very high temperature problems are eliminated without affecting the EOS at low temperatures where the molecules are stable. The modified expression for the vibrational partition function is

$$Q_{vib} = \sum_{n < n_\omega} \exp(-n\beta h c \omega) = \frac{1 - \exp(-n_\omega \beta h c \omega)}{1 - \exp(-\beta h c \omega)}. \quad (6.10)$$

Although it is important to include the cutoff, the results are not very sensitive to the value of  $n_\omega$ ; a reasonable estimate can be made by dividing the bond energy by  $\omega_0$ . Note that Eq. 6.10 does not include a contribution from zero-point motion; that term is ignored in PANDA because it affects only the energy zero of the EOS.

The density and temperature dependence of the vibrational frequency are given by

$$\omega = \omega_0(\rho/\rho_{ref})^{1/2} \exp[(\gamma_0 - \gamma_\omega)/p_\omega] f_v(T/t_\omega), \quad p_\omega \neq 0, \quad (6.11)$$

or

$$\omega = \omega_0(\rho/\rho_{ref})^{\gamma_0} f_v(T/t_\omega), \quad p_\omega = 0, \quad (6.12)$$

where  $\rho_{ref}$  is the reference density supplied with the SET BAS command (Sec. 2.2).  $\gamma_\omega$  is the Grüneisen parameter for the vibrational mode,

$$\gamma_\omega = (\gamma_0 - 1/2)(\rho_{ref}/\rho)^{p_\omega} + 1/2. \quad (6.13)$$

The function  $f_v$  can be used to describe the softening of a vibrational mode with increasing temperature, a phenomenon that arises because of anharmonicity. For example, Salje and Viswanathan [56] use the expression  $f_v(\tau) = \sqrt{1 - \tau}$ , for  $\tau < 1$ , to describe the frequency shifts in calcite. To avoid the problem of imaginary frequencies for  $\tau \geq 1$ , PANDA uses the following low temperature expansion of their formula.

$$f_v(\tau) = (1 + \tau/2 + 3\tau^2/8 + 5\tau^3/16 + 35\tau^4/128)^{-1}. \quad (6.14)$$

Using Eqs. 6.9 - 6.14, and the standard thermodynamic relations, the following expressions are obtained for the internal energy and pressure contributions for a vibrational mode.

$$E_{vib}(\rho, T) = g_\omega \frac{RT}{W} (1 - d \ln f_v / d \ln T) \beta h c \omega F_\omega, \quad (6.15)$$

and

$$P_{vib}(\rho, T) = g_\omega \frac{RT}{W} \rho \gamma_\omega \beta h c \omega F_\omega, \quad (6.16)$$



where

$$F_{\omega} = \frac{1}{\exp(\beta h c \omega) - 1} - \frac{n_{\omega}}{\exp(n_{\omega} \beta h c \omega) - 1} \quad (6.17)$$

The entropy is computed from

$$S_{vib}(\rho, T) = [E_{vib}(\rho, T) - A_{vib}(\rho, T)]/T. \quad (6.18)$$

## 6.4 The BROT Command

The command BROT is used to compute the rotational constant for a molecule from its structure. When this instruction has been entered, the user is prompted as follows.

ENTER SYMBOL AND COORDINATES FOR EACH ATOM

The user responds by entering the atomic symbol, followed by the Cartesian coordinates (in Å), for each atom in the molecule. A separate line is used for each atom, and input is terminated by a blank line. The atomic coordinates can be given with respect to any convenient axis system. PANDA computes and prints out the geometric average of the three principal rotational constants [18],

$$B_{rot} = \frac{h}{8\pi^2 c (I_x I_y I_z)^{1/3}} = \frac{2.79928 \times 10^{-39}}{(I_x I_y I_z)^{1/3}}, \quad (6.19)$$

where  $I_x$ ,  $I_y$ , and  $I_z$  are the three principal moments of inertia, having units of g-cm<sup>2</sup>.

## 7. Dimerization Corrections

### 7.1 General

The dimerization corrections to the PANDA fluid model, Sec. 2.4, are used for materials that are monatomic in the condensed phase but can form diatomic molecules in the vapor phase. A simple approximation is used to calculate the thermodynamic functions for a mixture of the dimer and monomer molecules, and the free energy is minimized to determine the equilibrium composition. The dimer molecules are treated as hard spheres, rigid rotators, and harmonic oscillators. The mixture-chemical equilibrium model, which is much more general and powerful, should be used when these approximations are not acceptable.

The command DIMER is used to enter data for the model. This instruction will be executed automatically, under the command MOD LIQ, if the code needs data. The user is prompted as follows.

DIMER - ENTER RZRO,DZRO,WVIB,BROT,SYM,QE,FACN

	RZRO	- $\rho_0$ = hard sphere density for dimer
	DZRO	- $D_0$ = dissociation energy of dimer (eV)
	WVIB	- $\omega_v$ = vibrational frequency of dimer ( $\text{cm}^{-1}$ )
	BROT	- $B_{rot}$ = rotational constant for dimer ( $\text{cm}^{-1}$ )
where	SYM	- symmetry factor
	SYM = 1,	for heteronuclear molecules
	SYM = 2,	for homonuclear molecules
	QE	- $Q_e$ = electron factor for monomer
	FACN	- $F_v$ = cutoff factor for vibrational states

With the exception of  $Q_e$ , all of the above parameters are used to calculate the EOS of a fluid of dimer molecules, as described in Sec. 7.2. The factor  $Q_e$  (normally unity) is used in the chemical equilibrium calculation, described in Sec. 7.3 and Appendix D.

### 7.2 EOS For Dimer Molecules

The free energy, internal energy, pressure, and entropy for a fluid of dimer molecules are given by

$$A_D(\rho, T) = A_0(\rho, T) + A_{hs}(\rho, T) + A_{vr}(T) + \Delta E_D, \quad (7.1)$$

$$E_D(\rho, T) = \frac{3}{2} \frac{RT}{W_D} + E_{vr}(T) + \Delta E_D, \quad (7.2)$$

$$P_D(\rho, T) = \frac{RT\rho}{W_D} + P_{hs}(\rho, T), \quad (7.3)$$

and

$$S_D(\rho, T) = [E_D(\rho, T) - A_D(\rho, T)]/T, \quad (7.4)$$

where  $W_D$  is the molecular weight of a dimer molecule, taken as twice the formula weight  $W$  computed under the SET BAS command (Sec. 2.2).  $A_0$  is the free energy of an ideal gas, as given in Eq. 5.9.  $A_{hs}$  and  $P_{hs}$  are the excess free energy and pressure for a hard-sphere fluid [44]. The packing fraction is defined by

$$\eta = \pi\sigma_0^3\rho/6W_D = 0.645\rho/\rho_0. \quad (7.5)$$

The user specifies a value for the hard sphere density, given by

$$\rho_0 = 4.916W_D/\sigma_0^3, \quad (7.6)$$

where  $\sigma_0$  is the hard-sphere diameter in Å. In this simple model,  $A_D$  and  $P_D$  are infinite at  $\rho = \rho_0$ , and no dimer molecules can form for  $\rho \geq \rho_0$ . However, this fact should cause no difficulties because the model is intended for problems where the molecules are stable only at low densities. In such cases, the EOS is fairly insensitive to  $\rho_0$ . As a rough approximation,  $\sigma_0$  can be taken to be twice the internuclear distance of the molecule.

The vibrational and rotational terms,  $A_{vr}$  and  $E_{vr}$ , are calculated as described in Ch. 6 for a linear rotator with one vibrational degree of freedom. (The vibrational frequency is independent of density and temperature.) The symmetry factor should be SYM=2 in normal use of the model, because dimer molecules are homonuclear. The cutoff in the sum over the vibrational levels is given by

$$n_\omega = 8067F_v D_0/\omega_v. \quad (7.7)$$

With  $F_v = 1$ , Eq. 7.7 excludes all vibrational levels with energies exceeding the dissociation energy. The parameter  $F_v$  can be varied to study the sensitivity of the EOS to the vibrational model.

The constant term  $\Delta E_D$  is needed so that the energy zero for the dimer EOS is the same as that for the monomer; it is the energy required to go from the monomer solid to the ideal dimer vapor at 0°K. Hence

$$\Delta E_D = E_B - RD_0/W_D, \quad (7.8)$$

where  $E_B$  is the binding energy of the solid, which is obtained from the cold curve. (The gas constant is  $R = 96.48445$  for  $D_0$  in eV.)

### 7.3 Chemical Equilibrium Calculation

Dimer corrections to the EOS are computed from a chemical equilibrium model, which is derived in Appendix D. The Helmholtz free energy for a mixture of monomer and dimer components is given by

$$A(\rho, T) = f A_M(\rho, T) + (1 - f)[A_D(\rho, T) + \frac{RT}{W} \ln Q_e] + \frac{RT}{W} [f \ln f + \frac{1}{2}(1 - f) \ln(1 - f)]. \quad (7.9)$$

The monomer fraction  $f$  is given by

$$f = \frac{1}{2}(\sqrt{x^2 + 4x} - x), \quad (7.10)$$

where

$$x = \exp [2W(A_D - A_M)/RT + 2 \ln Q_e - 1]. \quad (7.11)$$

The internal energy, pressure, and entropy are given by

$$E(\rho, T) = f E_M(\rho, T) + (1 - f) E_D(\rho, T), \quad (7.12)$$

$$P(\rho, T) = f P_M(\rho, T) + (1 - f) P_D(\rho, T), \quad (7.13)$$

and

$$S(\rho, T) = f S_M(\rho, T) + (1 - f)[S_D(\rho, T) - \frac{R}{W} \ln Q_e] - \frac{R}{W} [f \ln f + \frac{1}{2}(1 - f) \ln(1 - f)]. \quad (7.14)$$

The thermodynamic quantities for the monomer component,  $A_M$ ,  $E_M$ ,  $P_M$ , and  $S_M$ , are constructed from the contributions specified by the user with the MOD LIQ command (the five keywords CRS, TEL, TAB, ESFT, and WLQ), as described in Sec. 2.4. The EOS for a monatomic fluid must include a translational term (the CRIS model) and it may include a thermal electronic term. The vibration-rotation term should not be specified, because these degrees of freedom are present only in the dimer component. The general purpose tabular term can be used in addition to, or in place of, the translational and electronic contributions in defining the monomer model.

The parameter  $Q_e$  is the electron spin degeneracy for the ground state of the atom. In principle, the effects of spin degeneracy should be included in the thermal electronic contributions to the EOS. This contribution can also be included using the statistical weight parameter  $w_{liq}$  (see Sec. 2.4). Therefore, the user should set  $Q_e = 1$  when the electronic weight has already been included in the model for the monomer component. If this term is not included in the monomer EOS, the value of  $Q_e$  for an isolated atom should be entered so that the model predicts the correct amount of dissociation.

## 8. Thermal Electronic Contributions

### 8.1 General

PANDA provides three options for including contributions from thermal electronic excitation and ionization in the EOS of a one-component solid or fluid (Ch. 2). There are many theoretical models for calculating this term [3]-[7]; some of them are so complex and require so much numerical computation that it would be impractical to include them as options in PANDA. Therefore, the code provides a method for computing the thermal electronic terms by interpolating on a table of the electronic entropy as a function of density and temperature. This entropy table can be constructed using the ionization equilibrium model discussed in Ch. 9 or from data generated by other computer programs, such as the INFERNO code [57] [58]. PANDA also offers options for calculating the thermal electronic term from TFD theory or by specifying energy levels explicitly.

The thermal electronic model is defined using the command ELEC. This instruction will be issued automatically, if the code needs the data, under the commands MOD SOL and MOD LIQ. The user is prompted as follows.

ELECTRONIC TERM - ENTER ENTROPY FILE NAME OR OPTION

The user may respond to this option in one of three ways.

- Enter “TFD” to compute the thermal electronic contributions to the EOS using the temperature-dependent Thomas-Fermi-Dirac theory of the atom [33]; PANDA uses a simple approximation to this model that is computationally fast [59].
- In order to use the tabular entropy option, enter the name of the file containing the data (Sec. 8.2).
- Enter “LEV” to compute the thermal electronic term from specified energy levels (Sec. 8.3).

Note that the two option names, “tfd” and “lev”, cannot be used as names for the entropy data file.

## 8.2 Interpolation on Entropy Tables

If the user specifies the name of a data file, PANDA computes the thermal electronic contributions to the Helmholtz free energy  $A_e$ , internal energy  $E_e$ , and pressure  $P_e$  from the following thermodynamic relations.

$$A_e(\rho, T) = - \int_0^T S_e(\rho, T^*) dT^*, \quad (8.1)$$

$$E_e(\rho, T) = A_e(\rho, T) + TS_e(\rho, T), \quad (8.2)$$

and

$$P_e(\rho, T) = \rho^2 [\partial A_e(\rho, T) / \partial \rho]_T, \quad (8.3)$$

where  $S_e(\rho, T)$  is the electronic entropy.

The entropy data are tabulated at discrete densities covering the range of interest. A minimum of four densities is required. When constructing the density mesh,  $\ln \rho$  should be spaced at approximately equal intervals, with additional points in regions where the derivative of the entropy varies most rapidly. For each density in the mesh, several lines of input are required to tabulate the entropy as a function of temperature on the isochore.

- The first line gives the density for the isochore and NT, the number of temperatures that are tabulated.
- The following lines give NT pairs of temperature-entropy points, T(I),S(I), I=1,NT. There are no designated fields, so that more than one pair of T,S points can be given on a single line.

The entropy file consists of several decks as described above, one for each isochore. Note that each isochore can have a different temperature mesh if desired. PANDA sorts the input data, so that densities and temperatures can be given in any order.

A portion of an electronic entropy data file for aluminum is depicted in Table 8.1. The data on this file were generated using the INFERNO code, as described in Ref. [58].

The following numerical procedure is used to define a continuous EOS surface from the discrete entropy data points. First, a rational function method [24] interpolates for the entropy as a function of temperature along each isochore. Using Eqs. 8.1 and 8.2, the entropy is integrated (analytically) to give the free energy and internal energy. In this way,  $S_e$ ,  $A_e$ , and  $E_e$  are specified as continuous and consistent functions of temperature at discrete densities.

To interpolate on density, the functions  $F$  and  $G$  are defined by

$$A_e(\rho, T) = T(\alpha - \exp[F(x, T)]) \quad (8.4)$$

Table 8.1. Sample of Electronic Entropy Data File

-----			
.64044127e+00	28		
0.	.62879125e-03	.23092955e+04	.69579789e-03
.32144465e+04	.71149175e-03	.44677325e+04	.72918883e-03
.61968030e+04	.75292616e-03	.85989345e+04	.80272827e-03
.11929426e+05	.92797646e-03	.16559622e+05	.11672581e-02
.22988515e+05	.15001124e-02	.31889166e+05	.18922361e-02
.44259563e+05	.23266906e-02	.61422619e+05	.27942770e-02
.85223448e+05	.32861402e-02	.11826146e+06	.38740920e-02
.16411084e+06	.48632975e-02	.22771510e+06	.64125419e-02
.31599054e+06	.84087455e-02	.43846443e+06	.10789187e-01
.60842394e+06	.13521574e-01	.84426219e+06	.16471897e-01
.11715091e+07	.19342109e-01	.16256048e+07	.21860790e-01
.85412384e+00	28		
0.	.11836121e-03	.23092955e+04	.49087980e-03
.32144465e+04	.55578832e-03	.44677325e+04	.61471744e-03
.61968030e+04	.67180221e-03	.85989345e+04	.74564473e-03
.11929426e+05	.87716083e-03	.16559622e+05	.11008011e-02
.22988515e+05	.14066120e-02	.31889166e+05	.17673767e-02
.44259563e+05	.21662898e-02	.61422619e+05	.25983316e-02
.85223448e+05	.30631685e-02	.11826146e+06	.36281374e-02
.16411084e+06	.45642911e-02	.22771510e+06	.60283956e-02
.31599054e+06	.79306658e-02	.43846443e+06	.10186734e-01
.60842394e+06	.12762359e-01	.84426219e+06	.15558303e-01
.11715091e+07	.18344717e-01	.16256048e+07	.20832340e-01
.11394855e+01	28		
0.	0.	.23092955e+04	.27998983e-03
.32144465e+04	.36070573e-03	.44677325e+04	.44955936e-03
.61968030e+04	.54383383e-03	.85989345e+04	.65182003e-03
.11929426e+05	.79915029e-03	.16559622e+05	.10137782e-02
.22988515e+05	.12975776e-02	.31889166e+05	.16330583e-02
.44259563e+05	.20039983e-02	.61422619e+05	.24048576e-02
.85223448e+05	.28418753e-02	.11826146e+06	.33816479e-02
.16411084e+06	.42666781e-02	.22771510e+06	.56517956e-02
.31599054e+06	.74570419e-02	.43846443e+06	.96053355e-02
.60842394e+06	.12034669e-01	.84426219e+06	.14686315e-01
.11715091e+07	.17355546e-01	.16256048e+07	.19810746e-01
-----			

and

$$E_e(\rho, T) = [\alpha T - A_e(\rho, T)]G(x, T), \quad (8.5)$$

where  $x = \ln \rho$ . An arbitrary constant,  $\alpha = 10^{-20}$  has been introduced so that  $F$  and  $G$  are well behaved functions as  $T \rightarrow 0$ . From Eq. 8.3, the pressure is given by

$$P_e(\rho, T) = -\rho T \exp [F(x, T)](\partial F / \partial x)_T. \quad (8.6)$$

Thermodynamic consistency also requires that

$$E_e = A_e - T(\partial A_e / \partial T)_\rho \quad (8.7)$$

and

$$G(x, T) = T(\partial F / \partial T)_x. \quad (8.8)$$

The functions  $F$  and  $G$  are defined as piecewise cubic polynomials in  $x$ , with continuous derivatives. In the interval  $x_i \leq x < x_{i+1}$ , coefficients of the polynomial are determined



from the values of the function and its first derivative at  $x_i$  and  $x_{i+1}$ . The derivative at  $x_i$  is defined by fitting a quadratic polynomial through the points  $x_{i-1}$ ,  $x_i$ , and  $x_{i+1}$ , which insures that  $P_e$  is a continuous function. (However,  $\partial P_e / \partial \rho$  is not continuous.) Furthermore, it can be shown that Eq. 8.8 is satisfied. The proof of this result follows from the fact that  $F$  and  $G$  are polynomials of the same order in  $x$ ; the coefficients of the two polynomials have the correct temperature dependence because Eq. 8.7 is satisfied at the tabulated values of  $x$ .

The numerical procedure has been tested by using the TFD option to generate an entropy table, then comparing the exact results with those obtained from the tabular option. The pressures and energies computed from the entropy tables agree quite well with the exact values when a reasonable choice of the density-temperature mesh is made.

### 8.3 Calculation from Specified Levels

If the user specifies option "LEV", the thermal electronic contributions to the EOS are computed from energy levels and degeneracies that are entered as follows. The following prompt is issued.

ELECTRONIC TERM - ENTER WEL AND GEL

where      WEL   -  $\omega_k$  = electronic energy in  $\text{cm}^{-1}$   
               GEL   -  $g_k$  = degeneracy of electronic level

The above parameters must be given for each electronic level that is to be defined, including the ground state, up to a maximum of 20 terms. PANDA repeats the above prompt until a zero degeneracy is encountered.

In this approximation, the thermal electronic terms depend only on temperature and there is no contribution to the pressure. The Helmholtz free energy is given by

$$A_e(T) = -RT \ln Q_e / W. \quad (8.9)$$

Here  $R$  is the gas constant,  $W$  is the formula weight, and  $Q_e$  is the electronic partition function,

$$Q_e = \sum_k g_k \exp(-\beta h c \omega_k) \quad (8.10)$$

where the sum is taken over all energy levels. The internal energy and entropy are given by

$$E_e(T) = \frac{RT}{W} \sum_k g_k \beta h c \omega_k \exp(-\beta h c \omega_k) \quad (8.11)$$

and

$$S_e(T) = [E_e(T) - A_e(T)] / T. \quad (8.12)$$

## 9. Ionization Equilibrium Theory

### 9.1 General

PANDA provides an ionization equilibrium (IEQ) model for creating a table of the electronic entropy for a single atomic element. This table can be used as input in defining the contributions from thermal electronic excitation and ionization to the EOS of a solid or fluid consisting of a single atomic species, as described in Ch. 8. The IEQ model is based upon a fast and simple approximation for computing the ionization potentials and energy levels of atomic ions from a tabulation of orbital data [60], together with approximations for treating the free electrons and the effects of continuum lowering. The model can also be used to compute energy levels and partition functions for atomic ions, as described below.

Sections 9.2 and 9.3 give a brief description of the IEQ model, sufficient to define the main concepts and terms needed for its use. The present version of the model should be regarded as preliminary; the theory is still in a developmental state, and there will be changes and additions to it in the future. A more complete and detailed discussion will be given elsewhere.

Use of the instruction IONEQ, which is used to create the electronic entropy table, is given in Sec. 9.4. Section 9.5 discusses use of the LEVELS DATA, LEVELS FILE, and PART FUNC commands, which are used to compute information about the ionization potentials and energy levels calculated by the model.

The energy level and ionization equilibrium models discussed in this chapter make use of an atomic orbital data file that contains data for all elements up through  $Z = 103$  [60]. This file is available under node names /u0/gkerley/libs/orbdat (Cray) and /u3/gkerley/libs/orbdat (SUN); these files can be accessed when running PANDA by creating symbolic links with either the ASSIGN command (UNICOS) or the LN -S command (SUN). A copy of the orbital data file is also available on IFS under node name /e00024305/libs/orbdat.

### 9.2 Basic Theory

Consider a system having a volume  $V$  at temperature  $T$ , containing  $N_0$  atoms and ions of an element with atomic number  $Z$  and atomic weight  $W$ . A *particular* electronic

configuration of this system is specified by giving the populations of the electronic orbitals, each orbital describing the state of a single electron. The energy of a particular configuration is computed according to the principles of quantum mechanics. To calculate the thermodynamic properties of the system, it is necessary to take a thermal average over *all* electronic configurations of the system, according to the principles of statistical mechanics.

In order to enumerate and compute the properties of the different electronic configurations, it is useful to distinguish between two types of electronic orbitals. A *bound electron* is one that does not have sufficient energy to escape the potential well of an ion; these states are best represented by atomic-like orbitals that are localized about the various nuclei in the system. A *free electron* is one that does have sufficient energy to escape from an ion and move throughout the entire volume  $V$ ; these states are best represented by delocalized orbitals that are plane waves except in the regions of the ion cores. The thermodynamic properties are obtained from the partition function for the system, which is a sum over all possible configurations of electrons among these orbitals. Standard forms of the IEQ equations can be obtained either by balancing the ionization and recombination rates or by minimizing the free energy as a function of the ionization state.

The PANDA model uses an average atom approximation to the IEQ equations [61]. Like other average atom models, the properties of the system are computed by considering the electronic structure of a single atom. However, this model is unique in that it explicitly sums over all electronic configurations of the atom instead of considering a single “average” configuration. In this way, it avoids certain errors in the electron statistics that are implicit in other models [61].

The electronic part of the Helmholtz free energy is given by

$$A_e = -\frac{RT}{W} \ln q_e, \quad (9.1)$$

where  $q_e$ , the electronic partition function for an “average ion”, is a sum over all  $Z + 1$  states of ionization.

$$q_e = \sum_{z=0}^Z q_z \exp(-\beta[u_z + za_f^0(z)]). \quad (9.2)$$

Here  $a_f^0$  is the free energy (per electron) for an electron gas in which there are  $z$  free electrons per ion; this term is computed from an analytic fit to the thermodynamic properties of a homogeneous electron gas, which includes the effects of Fermi-Dirac statistics. (See the appendix of Ref. [62].)  $q_z$  is the partition function for an ion of charge  $z$ .

$$q_z = \sum_n g_z(n) \exp[-\beta\epsilon_z(n)], \quad (9.3)$$

where  $g_z(n)$  and  $\epsilon_z(n)$  are the statistical weights and energy levels of the ion, and the sum is taken over all configurations of the electrons.  $u_z$  is the ground state energy for an

atomic ion of charge  $z$ , relative to the neutral atom. Equation 9.2 ignores fluctuations in the total charge within an ion sphere. Corrections for this approximation were derived in Ref. [61]; however, those terms are not included in the present version of PANDA.

To compute the partition functions  $q_z$ , the ion energy levels and their degeneracies are first calculated for the isolated ion, then corrected for continuum lowering effects as described in Sec. 9.3. The methods that are used for the isolated ion are based upon ideas presented in Refs. [63]-[65]. The atomic wavefunction for a particular electronic state of an ion is taken to be an antisymmetrized product of one-electron orbital wavefunctions  $\psi_A$ . Let  $n_A$  be the number of electrons in orbital A for a particular configuration of an ion having charge  $z$ . The total number of bound electrons is

$$\sum_A n_A = Z - z. \quad (9.4)$$

The energy of a configuration for an isolated ion is given by [60]

$$\epsilon_z^0(n) = \sum_A n_A(t_A + v_A) + (1/2) \sum_A \sum_B n_A(n_B - \delta_{AB})w_{AB}, \quad (9.5)$$

where  $t_A$ ,  $v_A$ , and  $w_{AB}$  are the kinetic energy, electron-nuclear potential energy, and electron-electron potential energy integrals, respectively. The statistical weight is

$$g_z^0(n) = \prod_A \frac{g_A!}{n_A!(g_A - n_A)!}, \quad (9.6)$$

where  $g_A$  is the maximum occupation number for orbital A. In PANDA, the ionization potentials, energy levels, and degeneracies are calculated from Eq. 9.5, by generating the various states of occupation  $n_A$ . The integrals  $t_A$ ,  $v_A$ , and  $w_{AB}$  are computed from approximate formulas, using the orbital energies and radii for the ground state configuration of the neutral atom [60]. The details of the energy levels calculation will be described elsewhere.

### 9.3 Continuum Lowering

At very low densities, the Coulomb interactions between the ions and the free electrons can be neglected. However, these interactions become significant at higher densities, lowering the energy of the free electron continuum relative to the bound electron energy levels. This phenomenon, which is called *continuum lowering*, causes the effective ionization energy for the bound electrons to decrease with increasing density. In fact, each bound electron orbital has some density at which the ionization energy falls to zero; at higher densities, that level ceases to exist as a bound state and becomes a part of the free electron continuum. That phenomenon is called *pressure ionization*.

Continuum lowering can have profound effects on the electronic structure and the equation of state of a material. Metallization, a dramatic example, occurs when the

occupied orbitals highest in energy (the valence electrons) become pressure ionized. For typical metallic elements, this transition between insulating and metallic behavior occurs at roughly half the ambient solid density. For materials that are insulating at ambient conditions, metallization occurs under pressure.

Continuum lowering corrections to the energy levels and statistical weights can be derived by placing each ion inside an average cell, called an *ion sphere*. The ion sphere radius  $R_I$  is fixed by the average volume per ion, as follows.

$$R_I = \left(\frac{3V}{4\pi N_0}\right)^{1/3} = \left(\frac{3}{4\pi N_0} \frac{W}{\rho}\right)^{1/3}. \quad (9.7)$$

The energy level corrections are computed from the Coulomb interactions between the free electrons and the atomic nucleus as screened by the bound electrons. For the sake of brevity, only the results are given in this report. There are two terms. The ground state energy for an ion of charge  $z$  becomes

$$u_z = u_z^0 + \Delta u_z, \quad (9.8)$$

where  $u_z^0$  is the value for an isolated ion, and

$$\begin{aligned} \Delta u_z &= -\frac{9z^2e^2}{10R_I} - \frac{ze^2}{2R_I^3} \langle \sum r^2 \rangle_{0z} \\ &= -\frac{19.6}{V^{1/3}} \left( \frac{9z^2}{10} + \frac{z}{2R_I^2} \langle \sum r^2 \rangle_{0z} \right) \text{ eV/atom.} \end{aligned} \quad (9.9)$$

Here  $\langle \sum r^2 \rangle_{0z}$  is a sum of the squares of the radii for all occupied orbitals in the ground state configuration of the ion.

The energy levels for excited states are corrected by

$$\epsilon_z(n) = \epsilon_z^0(n) + \Delta \epsilon_z(n), \quad (9.10)$$

where

$$\begin{aligned} \Delta \epsilon_z(n) &= -\frac{ze^2}{2R_I^3} (\langle \sum r^2 \rangle_{nz} - \langle \sum r^2 \rangle_{0z}) \\ &= -\frac{9.8z}{V^{1/3}} \frac{1}{R_I^2} (\langle \sum r^2 \rangle_{nz} - \langle \sum r^2 \rangle_{0z}) \text{ eV/atom.} \end{aligned} \quad (9.11)$$

Here  $\langle \sum r^2 \rangle_{nz}$  is summed over all occupied orbitals in the excited state configuration of the ion.

Continuum lowering also has an effect on the statistical weights of the ion,  $g_z(n)$ . It is well known that an isolated atom or ion has an infinite number of bound energy levels, so that the partition function is formally infinite, even at low temperatures. However, it

can be argued that an electron state is fictitious if it has an orbital radii that is larger than the ion sphere radius. A complementary argument is that a bound orbital is fictitious if its effective ionization energy is less than zero. Hence the problem is usually resolved by introducing some density-dependent cutoff in the sum over the bound energy levels. At low densities, where only the high energy excited states are affected, the results are insensitive to details of the cutoff model. At higher densities, where metallization occurs, the cutoff model becomes extremely important.

The PANDA IEQ model uses a bound level cutoff that is derived from and consistent with the continuum lowering term, Eq. 9.9. For the ground state configuration of an ion with charge  $z$ , the effective ionization potential is found to be

$$I_{0z} = u_{z+1} - u_z = I_{0z}^0 + \Delta I_z, \quad (9.12)$$

where

$$\begin{aligned} \Delta I_z &= \Delta u_{z+1} - \Delta u_z \\ &= -\frac{19.6}{V^{1/3}} \{0.9(2z+1) + \frac{0.5}{R_I^2} [(z+1) \langle \sum r^2 \rangle_{0,z+1} - z \langle \sum r^2 \rangle_{0z}] \} \text{ eV/atom} \end{aligned} \quad (9.13)$$

is the shift in the bottom of the free electron continuum, relative to the ion ground state.  $I_{0z}$  is the energy required to remove the most weakly bound electron from the ion and put it into the continuum. The ionization energy for an excited state is defined in an analogous manner,

$$I_{nz} = I_{nz}^0 + \Delta I_z, \quad (9.14)$$

where  $I_{nz}^0$  is the ionization energy for the excited state of the isolated ion.  $I_{nz}$  is a monotonically decreasing function of density. An energy level  $\epsilon_z(n)$  is excluded from the partition function ( $g_z(n) = 0$  in Eq. 9.3) for those densities where  $I_{nz} \leq 0$ .

An important feature of this model is that the cutoff is determined from the ionization energy, *not* the total energy  $\epsilon_z(n)$  of a bound level. As a result, the model allows the existence of “autoionizing” states, *i.e.* bound states having greater energies than are needed for ionization of one electron. These states can arise when there are two or more electron-hole excitations. Calculations using the model show that these autoionizing states can make very large contributions to the EOS, even exceeding those from the other states for high- $Z$  elements at high temperatures.

## 9.4 The IONEQ Command

The IONEQ command is used to generate a table of the electronic entropy for a single atomic element, using the IEQ model that is described above. This instruction has the following form.



IONEQ *symbol orbfile sfile*

where *symbol* is the standard chemical symbol for the atomic element, *orbfile* is the name of the input orbital data file, discussed above, and *sfile* is the name of the output entropy data file. If the atomic symbol is not entered on the command line, a prompt will be issued. The default name for the orbital data file is “orbdatt”. The default name for the entropy data file is “ieqfle”. The entropy data will have the format that is described in Sec. 8.2 and shown in Table 8.1.

PANDA first reads in and prints out the orbital data for the specified element. Then the user is prompted as follows.

ENTER MX, EFAC, F1, F2, KS

	MX	- maximum number of electron-hole excitations
	EFAC	- factor used in energy cutoff of levels (default is 1.0)
where	F1	- coefficient of $\Delta u_z$ , Eq. 9.9 (default is 1.0)
	F2	- coefficient of $\Delta \epsilon_z(n)$ , Eq. 9.11 (default is 1.0)
	KS	- number of smoothing passes

These parameters are used in the following way.

- When generating the excited configurations for each ion, PANDA promotes electrons from the occupied orbitals into the empty or partially occupied orbitals. The parameter MX designates the maximum number of such electron-hole pairs that are to be included in the tabulation, up to a limit of MX=4. A value of MX=2 or higher is usually needed to generate all of the important contributions to the entropy, except for the low-*Z* elements. MX=4 can result in extremely long computation times for high-*Z* elements.
- The energy levels for an ion will also be cut off at a maximum energy given by  $EMX = EFAC \cdot EION$ , where *EION* is the ionization potential for the ion. Note that  $EFAC > 1.0$  is required to generate autoionized states. Some experimentation with this parameter may be needed to insure that all important contributions to the entropy are being included.
- The parameters F1 and F2 can be used to modify the magnitude of the continuum lowering terms, Eqs. 9.9 and 9.11, if desired.
- PANDA computes a table of the entropy  $S(i, j)$  at discrete values of the density  $\rho_i$  and temperature  $T_j$ , as discussed below. The density dependence of the entropy will often exhibit discontinuities or other spurious features that result from



approximations made in treating pressure ionization. The following operation can be applied to smooth out this structure.

$$S(i, j) \rightarrow S(i, j) \left[ \frac{S(i-1, j)S(i+1, j)}{S(i, j)^2} \right]^{1/4}. \quad (9.15)$$

The code will repeat this smoothing operation KS times.

After entering the model parameters, the user must specify a rectangular density and temperature grid for tabulating the entropy. The procedure is similar to that for constructing a Sesame 301 table, as described in Sec. 13.4. PANDA first prompts the user for the densities.

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE

The user responds by entering the lower and upper limits of the density interval, the number of points on the interval, and the type of mesh. There are two mesh options, MTYPE=1 (linear) and MTYPE=2 (exponential). The code prompts the user for a second section of mesh, a third section, and so on, until MTYPE=0 is specified or the number of points exceeds 64. The densities are sorted and duplicated values are eliminated. Next, PANDA prompts the user for the temperatures.

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE

Up to 64 values of the temperature can be entered in the same fashion as the density.

As the code generates the entropy table, it prints out the charge  $z$  and ionization potential for each ionization state as it is being computed, along with the metallization density and statistical weight for the ion ground state configuration.

Calculations using the IEQ model are most efficient on the Cray, where the code vectorizes. Therefore, it is recommended that this option be used on that machine for all but the simplest cases.

## 9.5 Calculation of Energy Levels

PANDA provides three commands for examining the energy levels that are used in the IEQ model. The instruction LEVELS DATA is used to generate the energy levels for specific configurations. The form of this command is

LEVELS DATA *symbol orbfile*

where *symbol* is the standard chemical symbol for the atomic element, and *orbfile* is the name of the orbital data file discussed above. If the atomic symbol is not entered on the command line, a prompt will be issued. The default file name is "orbdatt". PANDA obtains and prints out the orbital data for the specified element. Then the user is prompted as follows.

## ENTER ORBITALS AND POPULATIONS FOR EXCITED STATE

The user specifies an energy level by giving the orbital symbols and occupation numbers for those orbitals *differing* from the ground state configuration. For example, the ground state configuration for a neutral magnesium atom is

1s+[2] 2s+[2] 2p-[2] 2p+[4] 3s+[2] 3p-[0] 3p+[0] .....

The ground state configuration for an  $Mg^{+3}$  ion would be indicated by

2p+[3] 3s+[0]

The following input line would designate an excited state of  $Mg^{+1}$ .

2p+[3] 3s+[1] 3p+[1]

Up to 25 orbitals may be given when specifying the configuration. For each electronic state, the code prints out the energy (relative to the ground state of the neutral atom), the statistical weight from Eq. 9.6, and the orbital energies and radii for the occupied orbitals. PANDA continues to prompt the user until no orbitals are entered.

The instruction LEVELS FILE is used to generate a file of ionization potentials, energy levels, and statistical weights for all ionization states of an element. Before using this option, the user must open a plot file as described in Sec. 1.5. Next, the input line has the form

LEVELS FILE *symbol orbfile*

where *symbol* is the standard chemical symbol for the atomic element, and *orbfile* is the name of the orbital data file discussed above. If the atomic symbol is not entered on the command line, a prompt will be issued. The default file name is "orbdatt". PANDA obtains and prints out the orbital data for the specified element. Then the user is prompted as follows.

ENTER MX, EFAC, NB, AND RMIN

	MX	- maximum number of electron-hole excitations
where	EFAC	- factor used in energy cutoff of levels (default is 1.0)
	NB	- maximum number of energy bins (default is 200)
	RMIN	- $\rho_{min}$ = minimum density for cutoff of levels (default is $10^{-4}$ )

When generating the excited configurations of an ion, PANDA promotes electrons from the occupied orbitals into the empty or partially occupied orbitals. The parameter MX designates the maximum number of such electron-hole pairs that are to be included in the tabulation, up to a limit of MX=4. The energy levels for an ion will also be cut off at a maximum energy given by  $EMX = EFAC \cdot EION$ , where EION is the ionization potential for the ion. The level data are grouped into NB energy bins with energies ranging from 0 to EMX. (Bins having zero statistical weight are eliminated from the tabulation.) Finally, a level is also cut off if the maximum radius of the occupied orbital exceeds the ion sphere radius, Eq. 9.7, at the density  $\rho_{min}$ .

The energy level data are sent to the plot file. PANDA prints out a block of data for each ionization state. The first line of data in each block gives the ion symbol, the ionization potential, the number of occupied energy bins, and the values for MX and RMIN. This line is followed by a tabulation of the energies and statistical weights.

The instruction PART FUNC is used to generate a file of partition functions for all ionization states of an element, using the data file obtained with the LEVELS FILE command. Before using this option, the user must open a plot file as described in Sec. 1.5. Next, the input line has the form

PART FUNC *orbfile*

where *orbfile* is the name of the input file of energy level data. If no file name is entered on the input line, a prompt is issued. PANDA sends one block of data for each ionization state to the plot file. The partition functions are computed from Eq. 9.3, using a temperature grid that is equally spaced from 0 to  $kT = I_{0z}$ , where  $I_{0z}$  is the ionization potential for the ionization state (without the continuum lowering term). The first line of data in each block gives the same information as on the input file. This line is followed by the temperatures, partition functions, and values of  $T/I_{0z}$ .

## 10. Mixture-Chemical Equilibrium Model

### 10.1 General

Chapters 2 - 9 describe how PANDA is used to construct an EOS for a single-component solid or fluid, *i.e.*, a system containing only one molecular species. The PANDA mixture model is used to compute an EOS for a mixture of two or more species, using a modified form of ideal mixing [66]. The model may be used for either inert or reactive mixtures. In an inert mixture, the different species do not undergo any reactions; the chemical composition is independent of density and temperature and is fixed by the user input. In a reactive mixture, chemical reactions cause the composition of the system to change with density and temperature [67] [68]. In this case, PANDA computes the composition from the principle of chemical equilibrium; the user specifies only an “initial” composition that is consistent with the overall elemental composition of the system.

The first step in using the mixture option is to determine which components are to be allowed in the model. *PANDA will not include any chemical species except those explicitly defined by the user.* Therefore, the user should consider those molecules that could be formed as a result of decomposition and other reactions as well as those that are present at ambient pressure and temperature.

The second step in using the model is to construct a separate EOS for the mixture components, treating each species as a single-component fluid or solid. Two options are available. An EOS table can be generated, using the options discussed in Chs. 2 - 9, and read in as input as described in Sec. 10.4. A simple analytic EOS, described in Sec. 10.5, is also available; this option is adequate for many problems and is also useful for sensitivity studies.

The final step in use of the mixture option is to define the system and load the EOS tables using the MOD MIX command, as discussed in Sec. 10.3. Once the mixture parameters have been defined, the PANDA commands for testing the model (Ch. 12) and for generating EOS data tables (Ch. 13) can be employed. In addition, the CONC PLOT command, described in Sec. 10.6, can be used to study how the mixture composition varies as a function of density and temperature.

## 10.2 Theory

Only a brief and somewhat preliminary description of the model, sufficient to define the main concepts and terms needed for its use, will be provided here. More detailed discussions will be given elsewhere. Furthermore, the model is still in a state of development, and it is likely that there will be some changes and additions to the theory in the near future.

Consider a system having a volume  $V$  and temperature  $T$ , containing  $N$  moles of various molecular species. We want to relate the Helmholtz free energy for the mixture (expressed in units of energy per unit mass) to the free energies of the pure components. The following definitions are useful.

$n_i$	-	number of moles of component $i$ , $\sum_i n_i = N$
$W_i$	-	molecular weight for component $i$
$W = \sum_i n_i W_i$	-	total weight of system
$\rho_i$	-	density for component $i$
$\rho = W/V$	-	density of mixture
$V_i = W_i/\rho_i$	-	molar volume for component $i$
$A_i, E_i, P_i, S_i$	-	thermodynamic functions for component $i$
$p_i$	-	phase type for component $i$ , where $p_i = 0$ for an immiscible component $p_i = 1$ for a miscible component
$\Delta E_{mix}$	-	shift in zero internal energy

In PANDA, the free energy of the mixture is given by

$$A_{mix}(\rho, T) = W^{-1} \sum_i n_i [W_i A_i(V_i, T) + RT p_i \ln(n_i/N_p)] + \Delta E_{mix}, \quad (10.1)$$

where

$$N_p = \sum_i n_i p_i. \quad (10.2)$$

Note that setting the phase type  $p_i = 0$  eliminates the entropy of mixing term [66] for a component  $i$ . Hence Eq. 10.1 is written so that it can describe a mixture of one homogeneous phase, consisting of several miscible species, and additional phases consisting of those species that are immiscible.

The molar volumes are required to satisfy the following constraint.

$$V = \sum_i n_i V_i. \quad (10.3)$$

For an ideal solution, the  $V_i$  are determined by equilibrating the pressures  $P_i$  of the various species [66]. In PANDA, this approximation has been modified to allow for EOS

in which the pressure is not a monotonic function of volume; this condition can arise in the vapor-liquid coexistence region and other situations involving phase transitions. For each mixture component, a “pseudopressure” function  $\phi_i(V_i, T)$  is defined that is a monotonically decreasing function of volume. Then the molar volumes are determined from the relation

$$\phi_1(V_1, T) = \phi_2(V_2, T) = \dots = \Phi(\rho, T), \quad (10.4)$$

where  $\Phi$  is the pseudopressure for the mixture. For the analytic EOS option (Sec. 10.5), the pseudopressure is identical with the pressure, which is a monotonic function of volume. For a tabular EOS, the pseudopressure is defined by modifying the pressure in the nonmonotonic regions, as described in Sec. 10.4.

The molar composition of the mixture is determined by minimizing the Helmholtz free energy with respect to the  $n_i$ , at constant density and temperature, subject to the constraints that follow from the chemical formulas of the various species. Letting  $f(a, i)$  be the number of atoms of element  $a$  in a molecule of type  $i$ , it can be seen that  $f_a = \sum_i n_i f(a, i)$  for each element must be constant for all allowed chemical compositions of the mixture. The code determines the  $f_a$  from the molecular formulas and the initial concentration provided by the user and reduces the constraints to a linearly independent set of equations. The system is found to be inert if the number of independent constraints is equal to the number of chemical species; hence user input is identical for inert and reactive mixtures.

By using the standard thermodynamic relations, the expressions for the pressure and internal energy are found to be

$$P_{mix}(\rho, T) = \sum_i n_i \lambda_i P_i(V_i, T) / \sum_i n_i \lambda_i, \quad (10.5)$$

and

$$E_{mix}(\rho, T) = W^{-1} \sum_i n_i [W_i E_i(V_i, T) + \lambda_i (P_i - P) T (\partial \phi_i / \partial T)_{V_i}] + \Delta E_{mix}, \quad (10.6)$$

where

$$\lambda_i = -W_i (\partial V_i / \partial \phi_i)_T. \quad (10.7)$$

The entropy is given by

$$S_{mix}(\rho, T) = [E_{mix}(\rho, T) - A_{mix}(\rho, T)] / T. \quad (10.8)$$

## 10.3 Input: the MOD MIX Command

The instruction MOD MIX, which is used to define the mixture model, has the form

MOD MIX EZRO= $\Delta E_{mix}$



Here  $\Delta E_{mix}$  (real) is used to fix the energy zero of the EOS at some convenient point. (This parameter is optional; the default is  $\Delta E_{mix} = 0$ .) After entering this command, the user must respond to two prompts for each of the chemical components in the mixture. The first prompt is

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

The formula is entered using the standard chemical symbols for the atomic elements, just as in response to the SET BAS command (Sec. 2.2). The second prompt is

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

In this case, the user specifies certain data that are needed to define the EOS for the chemical component. These data are entered using keywords, followed by names or numerical values for the parameters. The general nature of the input lines can be seen in the following example, a portion of the PANDA output file for test problem 4 (Sec. 16.4). Here upper case letters are used for code messages, and lower case letters are used for user input.

```
OPTION?  
mod mix  
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED  
c[1]o[2]  
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES  
moles=5. name=co2 eshift=-8.9363 matid=201 file=hesps  
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED  
n[2]  
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES  
moles=2. name=n2 matid=202
```

The code continues to issue these prompts until the user terminates input by entering a blank line when prompted for the chemical formula. PANDA allows up to 30 chemical species to be entered (provided there is sufficient storage to load the necessary EOS tables).

The keywords that are used with the MOD MIX command are defined in Table 10.1. Note that certain keywords apply only to the tabular EOS option, that others apply only to the analytic EOS option, and that others are used for both options. Most of the parameters have default values if not entered explicitly. A file name for the EOS library must be given for the first tabular EOS that is entered; thereafter, the same name is used unless otherwise specified. In most cases, the formula weight FW and number FZ will



**Table 10.1.** Keywords Used With MOD MIX Command

Command	Definition	Data Type	Default
BROT <sup>a</sup>	rotational constant $B_{rot}$	real	none
CVOL <sup>a</sup>	molecular covolume $v_i$ in $\text{\AA}^3$	real	0.0
ESHIFT <sup>b</sup>	energy shift $\Delta E_i$	real	0.0
FILE <sup>c</sup>	file name for EOS table	character	previous name <sup>d</sup>
FW <sup>b</sup>	molecular weight $W_i$	real	computed
FZ <sup>b</sup>	formula number	real	computed
IROT <sup>a</sup>	type of rotational motion	real	0
MATID <sup>c</sup>	material number for EOS table	real	none
MOLES <sup>b</sup>	initial number of moles $n_i$	real	0.0
NAME <sup>b</sup>	species name ( $\leq 10$ characters)	character	“****”
NVIB <sup>a</sup>	number of vibrational frequencies (see Sec. 10.5 for additional input for NVIB)	real	0
PTYP <sup>b</sup>	miscibility parameter $p_i$	real	1.0
SYM <sup>a</sup>	molecular symmetry number $\sigma_{rot}$	real	1.0
STW <sup>b</sup>	statistical weight $w_i$	real	1.0

<sup>a</sup> Used for analytic EOS only. Omit for a tabular EOS.

<sup>b</sup> Used for either analytic or tabular EOS option.

<sup>c</sup> Used for tabular EOS only. Omit for an analytic EOS.

<sup>d</sup> A file name is required for the first EOS table specified.

be computed by the code and need not be entered. The species name is used for output only and is optional. The keyword ESHIFT specifies an amount that is to be added to the internal energy (both tabular and analytic EOS options): this parameter is normally used to adjust the energy zeros for all of the components to the same standard state. An ampersand (&) can be used for continuing the keyword list to the next line, as discussed in Sec. 1.6.

The concentration of the system is specified by giving the number of moles for each of the chemical species. In determining appropriate values for the MOLES parameter, it should be realized that the *total* number of moles is irrelevant; only the relative proportions of the different species are significant. For a reactive system, the mole numbers correspond to an artificial “initial” concentration  $n_i$  that is used to determine the chemical constraints and as a guess in the free energy minimization procedure. In that case, the only requirement on the mole numbers is that they be consistent with the overall elemental composition of the system; this condition can often be satisfied in a number of ways, all of which are equivalent and will give identical numerical results.

The keyword PTYP specifies the phase miscibility  $p_i$ . Numerical problems are usually encountered if one specifies a very small value for this parameter, as in the case of an immiscible phase. Therefore, the code resets  $p_i = 0.01$  when the user enters  $p_i = 0.0$ , in order to obtain satisfactory results.

## 10.4 Tabular EOS for Components

Before using the mixture model, EOS tables for the individual components are constructed and saved on one or more libraries having the Sesame format (see Chs. 13 and 14). The keywords MATID and FILE give the material number and file name for the EOS table that is to be used for a particular mixture component. PANDA requires only the 301 tables. A rational function algorithm [24] is used to interpolate on the data. An error message is printed if the library file or EOS table cannot be found, or if there is insufficient storage space to load the table. (The size of the storage array is specified by PARAMETER statements in the source code, with a variable named MAXTAB.)

*Warning:* EOS tables for the one-component solid-liquid model, the mixture model, and the phase transition model all share the same storage array and directory. Therefore, these three options can conflict with one another; if tables are loaded for one option, any tables that had been loaded for a different option will be destroyed, and a warning message will be given. This situation seldom arises with normal code usage and can be avoided by making separate PANDA runs for the three different models. If a conflict does occur, the user must keep track of which tables are actually present and restore the tables that are needed for the option being used.

Two other parameters can be entered that modify the tabular EOS. The keyword ESHIFT specifies an additive shift in the internal energy; this parameter is normally used to adjust the energy zero of the material to correspond to a certain definition of the standard state. The keyword STW can be used to add a statistical weight contribution to the entropy; this term is computed from Eq. 2.10.

Because EOS tables for complicated materials often have regions where the pressure is not a monotonic function of density, PANDA constructs a fourth table, the pseudo-pressure  $\phi_i$ , for determining the molar volumes  $V_i$  of the mixtures components (Eq. 10.4). The code scans each isotherm in the pressure  $P_i(\rho, T)$  for component  $i$ . In regions where the pressure is positive and monotonic, it sets  $\phi_i = P_i$ . If it finds a section on the isotherm where  $P_i \leq 0$  or  $(\partial P_i / \partial \rho)_T \leq 0$ , it replaces the pressure in that region by

$$\phi_i(\rho, T) = p_{0,i}(T) + p_{1,i}(T)\rho. \quad (10.9)$$

Equation 10.9 is similar to a “Maxwell construction” (see Sec. 13.5), except that  $\phi_i$  has a small positive derivative with respect to density along the isotherm, and no attempt is made to find the equilibrium pressure. PANDA locates the two densities that bound the

region (the spinodals). The parameters  $p_{0,i}$  and  $p_{1,i}$  are chosen so that  $\phi_i$  is a positive value, intermediate between the spinodal pressures, and that  $(\partial \ln \phi_i / \partial \ln \rho)_T \approx .01$  in the modified section of the isotherm.

## 10.5 Analytic EOS for Components

The analytic EOS option is an approximation that is intended for use in problems where a complicated model is not needed (such as at low densities and/or high temperatures) and for making sensitivity studies to examine the importance of certain chemical species in the mixture equilibrium. The parameters used to define the analytic EOS model are entered using seven keywords, ESHIFT, NVIB, IROT, BROT, SYM, STW, and CVOL (see Table 10.1). Test problem 3, in Sec. 16.3, illustrates the input for an analytic EOS. This model can be used for some of the species while EOS tables are used for others.

The expressions for the free energy, internal energy, pressure, and entropy for mixture component  $i$  are given by

$$A_i(\rho_i, T) = A_{tr}(\rho_i, T) + A_{vr}(T) - TS_{wi} + \Delta E_i, \quad (10.10)$$

$$E_i(\rho_i, T) = E_{tr}(\rho_i, T) + E_{vr}(T) + \Delta E_i, \quad (10.11)$$

$$P_i(\rho_i, T) = P_{tr}(\rho_i, T), \quad (10.12)$$

and

$$S_i(\rho_i, T) = [E_i(\rho_i, T) - A_i(\rho_i, T)]/T. \quad (10.13)$$

$A_{tr}$ ,  $E_{tr}$ , and  $P_{tr}$  are the contributions to the EOS from the molecular translational degrees of freedom. These terms are computed using the covolume  $v_i$  and the BKW approximation [69] to account for nonideal gas corrections (effects of finite molecular size).

$$A_{tr}(\rho_i, T) = A_0(\rho_i, T) + \frac{RT}{W_i b} [\exp(bX_i) - 1], \quad (10.14)$$

$$E_{tr}(\rho_i, T) = \frac{RT}{W_i} \left[ \frac{3}{2} + \frac{TX_i}{2(T + \theta)} \exp(bX_i) \right], \quad (10.15)$$

and

$$P_{tr}(\rho_i, T) = \frac{RT\rho_i}{W_i} [1 + X_i \exp(bX_i)], \quad (10.16)$$

where

$$X_i = 11.85v_i\rho_i/W_i\sqrt{T + \theta}. \quad (10.17)$$

Here the constants are given by  $b = 0.09$  and  $\theta = 400$ .  $A_0$  is the free energy of an ideal gas, given by Eq. 5.9.

The vibrational and rotational terms,  $A_{vr}$  and  $E_{vr}$ , are calculated using simplified versions of the equations given in Ch. 6. The three rotational keywords, IROT, BROT, and SYM are used to define a single rotational term, which can be either a linear or nonlinear rotator. (The rotational weight is unity.) The vibrational frequencies are independent of density and temperature. If NVIB  $\neq$  0, the keyword list must be followed by data for the vibrational levels. The following prompt is given.

ENTER WE, GE, AND NE FOR [NVIB] VIBRATIONAL LEVELS

The user responds by entering NVIB additional lines of input, each line giving the frequency, degeneracy, and cutoff number for a vibrational level. (See test problem 3, Sec. 16.3, for an example.)

The quantity  $S_{wi}$  is a constant contribution to the entropy from the statistical weight  $w_i$  and is given by Eq. 2.10. A value of  $w_i > 1.0$  is normally used to account for multiple electronic configurations.

## 10.6 The CONC PLOT Command

The instruction CONC PLOT is used to compute the molar concentrations of the mixture as functions of density and temperature and send these data to a file for plotting. The mole numbers are output as a table, along with a thermodynamic quantity that is selected by the user as the independent variable for plotting purposes. The following prompt is given.

ENTER SYMBOL FOR THERMODYNAMIC VARIABLE - R, T,  
P, E, OR S

The user responds by entering R for density, T for temperature, P for pressure, E for energy, or S for entropy.

Next, the user is prompted as follows.

ENTER DENSITY (G/CC) AND TEMPERATURE (K)

The user responds by entering the density and the temperature at each point to be computed. The code prints out the specified thermodynamic variable (first column), along with mole numbers for the first five chemical species in the mixture, at the chosen density and temperature. If a plot file has been opened, the same data will be sent to that file, except that mole numbers for the first 11 species will be included; the user will also be prompted to enter a label for the plot file. (If there are more than 11 species in the mixture, those of greatest interest should be entered first when using the MOD

MIX command.) The code continues to read density-temperature points until the user specifies a zero density.

# 11. The Phase Transition Model

## 11.1 General

The previous chapters describe how the one-component solid and liquid models and the mixture-chemical equilibrium model are used to construct an EOS for a single phase. The PANDA phase transition model is used to compute the phase diagram and to assemble an EOS table for a material that can exist in two or more phases. This method, developed by Kerley and Rood, was originally used in the TUTTI code [70] [71]; the routines from TUTTI have been revised and adapted for use in PANDA.

The phase transition model is based upon the following well-known principle of thermodynamic equilibrium: if a substance can exist in more than one phase, the stable phase at a given pressure and temperature is the one having the lowest Gibbs free energy. Hence the problem of constructing a multiphase EOS is essentially an exercise in bookkeeping. The procedure used in PANDA can handle phase diagrams of arbitrary complexity, including such features as triple points and reversal in slope of phase lines. At each temperature, the code searches for the stable phase as a function of pressure and locates the phase boundaries.

The first step in constructing a multiphase EOS is to develop a model and generate a Sesame EOS table (see Ch. 13) for each of the separate phases to be considered, using the other options available in PANDA. The MOD TRN command (Sec. 11.2) is used to load these tables and define the phase transition model. The procedure that is used to locate the phase boundaries is discussed in Sec. 11.3. The command PHASE DIAG (Sec. 11.4) is used to compute the phase diagram and send it to a file for plotting. As with the other options, the SLIB command (Ch. 13) is used to generate a Sesame EOS table.

## 11.2 Input: the MOD TRN Command

The instruction MOD TRN, which is used to define the phase transition model, has the form

MOD TRN *parameters*

where *parameters* is a list of up to six constants that are used in the search for the phase boundaries. If no parameters are entered on the command line, the user is prompted

with a list, as follows.

ENTER PHASE SEARCH PARAMETERS - RREF,RCRT,TCRT  
PCPS,NCPS,ERR

where

RREF	- ambient solid density
RCRT	- density at critical point
TCRT	- temperature at critical point
PCPS	- factor used in pressure search
NCPS	- number of points in pressure search
ERR	- maximum error in pressure search

Each of these parameters can be defaulted. Their use is discussed in Sec. 11.3.

Next the code loads EOS tables for the individual phases; these data are accessed by material number from one or more binary files. This option uses only the 301 tables, which give pressure, internal energy, and entropy as functions of density and temperature. A rational function algorithm [24] is used to interpolate on the EOS tables.

The user is prompted as follows.

ENTER MATERIAL NUMBER, FILE NAME, AND ENERGY SHIFT

An input line must be given for each phase that is to be considered (a minimum of two and a maximum of 30 phases). PANDA repeats the above prompt until a zero material number is encountered. The file name must always be given for the first phase; thereafter, the previous name becomes the default file name. The energy shift is an optional constant that is added to the energy of a phase; it can be used to adjust the energy zeros and so shift the phase boundaries.

There is no preferred order for specifying the different phases. However, each phase is assigned a consecutive number in the order that it is loaded. These numbers are used to label the phases in output generated by the PHASE DIAG command. An error message is written if a library file or EOS table cannot be located or if there is insufficient space to store the data.

*Warning:* EOS tables for the one-component solid-liquid model, the mixture model, and the phase transition model all share the same storage array and directory. Therefore, these three options can conflict with one another; if tables are loaded for one option, any tables that had been loaded for a different option will be destroyed, and a warning message will be given. This situation seldom arises with normal code usage and can be avoided by making separate PANDA runs for the three different models. If a conflict does occur, the user must keep track of which tables are actually present and restore the tables that are needed for the option being used.



### 11.3 Search for Phase Boundaries

PANDA maps out the phase diagram by searching for and tabulating the phase transition pressures while holding the temperature fixed. At each temperature, the code scans a coarse grid of NCPS points, from the lowest to the highest tabulated pressure. The pressures in the grid are spaced in roughly exponential intervals; PCPS is the width of the first pressure interval. Default values for these parameters are PCPS=0.25 and NCPS=100.

At each pressure in the grid, the stable phase is determined by comparing the Gibbs free energies. If the stable phase is different from the one at the last pressure, a transition has occurred somewhere within the interval. In that case, the code does a binary search to determine the transition pressure. Parameter ERR is the maximum allowed uncertainty in the transition pressure; the default value is  $\text{ERR}=10^{-5}$ .

PANDA also makes provision for tables that have a vapor-liquid region, in which the pressure is not a monotonic function of density. In setting up the grid for the pressure search at each temperature, the code determines either the liquid spinodal point or the lowest tabulated density for each phase. Then it starts with the highest spinodal pressure and works down until it finds a the phase that is stable at its own spinodal. This pressure becomes the lower limit in the search for transition pressures. Parameters RREF, RCRT, and TCRT are used as bounds in searching for the liquid spinodal. RREF is an upper density limit (default is  $\text{RREF}=10^5$ ), RCRT is a lower density limit (default is  $\text{RCRT}=0$ ), and TCRT is an upper temperature limit (default is  $\text{TCRT}=10^5$ ).

In constructing the multiphase EOS, the following three situations arise.

- In a single phase region above the liquid spinodal density, the thermodynamic functions are taken from those for the stable phase, *i.e.* the phase having the lowest Gibbs free energy.
- In a two-phase region, the pressure is constant and equal to the transition pressure; the Lever rule is used for the energy and entropy.

$$E(\rho, T) = (1 - f_2)E_1(\rho_1, T) + f_2E_2(\rho_2, T), \quad (11.1)$$

and

$$S(\rho, T) = (1 - f_2)S_1(\rho_1, T) + f_2S_2(\rho_2, T), \quad (11.2)$$

where

$$f_2 = \frac{1 - \rho_1/\rho}{1 - \rho_1/\rho_2}. \quad (11.3)$$

Here the subscripts 1 and 2 denote the low and high density phases, respectively.

- Below the liquid spinodal density, the thermodynamic functions are taken from the phase having the lowest Helmholtz free energy. This feature allows construction of a multiphase EOS table having van der Waals loops in the vapor-liquid coexistence region.

## 11.4 The PHASE DIAG Command

The instruction PHASE DIAG is used to compute the phase diagram and send it to a file for plotting. When this command is entered, the user is prompted to set up a temperature grid for calculating the phase boundaries.

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE

The user responds by entering the lower and upper limits, the number of points on the temperature interval, and the type of spacing. There are two mesh options, MTYPE=1 (equal spacing) and MTYPE=2 (exponential spacing). The code prompts the user for a second section of mesh, a third section, and so on until MTYPE=0 is specified or until the number of points exceeds 200. The temperatures are sorted and duplicated values are eliminated.

PANDA prints out a table of the temperature, the pressure, the numbers of the low and high density phases, and the densities of the phases for each phase transition that is located. If a plot file has been opened, these data will also be sent to that file, along with the internal energies and entropies of the phases. The user will be prompted to enter a label for the data on the plot file.

## 12. Options for Testing a Model

### 12.1 General

The PANDA code offers a variety of options for making calculations using an EOS model that has been defined by the user. With the exceptions that are noted, the commands in this chapter have the form

*COMMAND MODTYP parameters*

where *COMMAND* is one of the instructions listed in Table 1.3, and *MODTYP* is one of the keywords used for the five models (SOL, LIQ, MIX, TRN, or USE). All of the commands require certain parameters to be entered. In certain cases, the user has the option to enter these parameters on the input line; if the required parameters are not entered along with the command, the user is prompted.

Output from the calculations consists of up to six columns of data that are sent to the TTY and the output file. In addition, up to 12 columns of data can be sent to the plot file, depending upon the option. The command PLOT FNAME is used to open a file called "fname"; the default file name is "panplt". The plot file has a QA identification line [16] giving the code name, version, and date, and the problem name and date, followed by one or more blocks of data. Each section of data is preceded by a label and by column headings. If a plot file has been opened, the user is prompted to enter a label for each section. If the user enters the word "skip" when prompted for a label, that block of data is not sent to the plot file, but the file remains open for future use. For compatibility with the plotting utility GRAPH [20], the QA line, labels, and column headings are printed with a ! in column 1, to denote comments. Table 12.1 shows portions of the plot file that is produced in test problem 1 (Sec. 16.1). (For the sake of space, the file has been edited to eliminate some of the lines and columns.)

### 12.2 The EOS Command

The instruction EOS *MODTYP* is used to generate the thermodynamic functions and derivatives at specified densities and temperatures. No parameters are entered on the input line. The user is prompted as follows.

ENTER DENSITY (G/CC) AND TEMPERATURE (K)

Table 12.1. Sample of PANDA Plot File

```

-----
! PLOT FILE FROM PANDA, CTSS VERSION 2.01:  PROB - TESTPROB_1, DATE - 12/04/89
! Theoretical melting curve for aluminum
!   T(K)      PL(GPA)    RL(G/CC)    RS(G/CC)    EL(MJ/KG)    ES(MJ/KG)    ....
  9.5000e+02  2.2858e-01  2.4866e+00  2.5692e+00  1.1411e+00  9.7425e-01    ....
  1.0000e+03  9.5784e-01  2.5119e+00  2.5897e+00  1.1786e+00  1.0078e+00    ....
  1.2000e+03  4.7570e+00  2.6360e+00  2.6992e+00  1.3593e+00  1.1512e+00    ....
  1.4000e+03  1.0624e+01  2.8031e+00  2.8593e+00  1.6339e+00  1.3561e+00    ....
  .....
  1.0000e+04  2.1608e+04  3.3299e+01  3.3503e+01  4.7603e+02  4.7195e+02    ....
! Theoretical Hugoniot for solid aluminum
!   RHO(G/CC)   T(K)      P(GPA)    E(MJ/KG)    UP(KM/S)    US(KM/S)    ....
  2.7296e+00  3.0500e+02  8.5371e-01  3.1007e-01  5.8668e-02  5.3897e+00    ....
  2.7973e+00  3.2165e+02  2.9267e+00  3.2723e-01  1.9431e-01  5.5788e+00    ....
  2.9549e+00  3.7161e+02  8.4793e+00  4.4388e-01  5.2063e-01  6.0323e+00    ....
  3.1139e+00  4.5488e+02  1.5221e+01  6.8314e-01  8.6578e-01  6.5116e+00    ....
  .....
  3.9399e+00  2.3200e+03  7.5209e+01  4.6920e+00  2.9610e+00  9.4078e+00    ....
! Theoretical Hugoniot for liquid aluminum
!   RHO(G/CC)   T(K)      P(GPA)    E(MJ/KG)    UP(KM/S)    US(KM/S)    ....
  4.2024e+00  2.5850e+03  1.0545e+02  7.2907e+00  3.7369e+00  1.0452e+01    ....
  4.2122e+00  2.6368e+03  1.0660e+02  7.3957e+00  3.7649e+00  1.0487e+01    ....
  4.2410e+00  2.7934e+03  1.1000e+02  7.7108e+00  3.8477e+00  1.0589e+01    ....
  4.2875e+00  3.0573e+03  1.1561e+02  8.2360e+00  3.9819e+00  1.0753e+01    ....
  .....
  5.0452e+00  9.4384e+03  2.2874e+02  2.0000e+01  6.2756e+00  1.3500e+01    ....
-----

```

The user responds by entering the density and temperature at each point to be computed. The code prints out the density, temperature, pressure, internal energy, entropy, and bulk sound speed at each point. If a plot file has been opened, these variables will be sent to that file, along with the isothermal bulk modulus, constant-volume heat capacity, specific volume, and Helmholtz free energy. The density and temperature derivatives are computed by numerical differentiation. The code continues to read density-temperature points until the user specifies a zero density.

## 12.3 Isotherms and Isochores

The instructions ISOT and ISOC are used to compute and display the EOS variables along a set of isotherms (curves of constant temperature) and isochores (curves of constant

density), respectively. These commands have the form

ISOT *MODTYP parameters*

and

ISOC *MODTYP parameters*

where *parameters* is a list of eight quantities that specify the density and temperature mesh for the calculated results. All eight parameters are required. If they are not entered on the command line, the user is prompted with a list, as follows.

ENTER R1,R2,NR,MR,T1,T2,NT,MT

PANDA computes the EOS at NR points on the density interval from R1 to R2, and at NT points on the temperature interval from T1 to T2. There are two mesh options: MR=1 and MT=1 give equal spacing, and MR=2 and MT=2 give exponential spacing. The code prints out the density, temperature, pressure, internal energy, entropy and free energy at each density-temperature point. If a plot file has been opened, these data are also sent to that file, along with the specific volume.

The ISOT and ISOC commands differ only in the method for sweeping through the density-temperature mesh. For isotherms, temperature is the outer loop (slowly changing variable) and density is the inner loop (rapidly changing variable). For isochores, density is the outer loop and temperature is the inner loop. In either case, the code allows a maximum of 25 points in the outer loop and a maximum of 100 points in the inner loop. The code reverses direction of the inner loop each time it advances to the next point on the outer loop; this feature makes it possible to plot the entire file with a single GRAPH [20] command.

## 12.4 Isobars

The ISOB instruction is used to compute and display the EOS variables along an isobar (curve of constant pressure). This command has the form

ISOB *MODTYP parameters*

where *parameters* is a list of five quantities, all of which are required. If they are not entered on the command line, the user is prompted with a list, as follows.

ENTER P,T1,TN,NPTS,R1(GUESS)

where

P	- pressure on isobar
T1,TN	- lower and upper temperature limits
NPTS	- number of points on temperature interval
R1	- guess of density at temperature T1

PANDA computes and prints out the density, temperature, internal energy, entropy, enthalpy, and free energy at NPTS points, equally spaced on the temperature interval from T1 to TN. If a plot file has been opened, these data are also sent to that file, along with the specific volume and pressure. (In certain cases, the code will not be able to find a density corresponding to the specified pressure and temperature; then nothing will be printed out.)

## 12.5 Isentropes

The ISEN instruction is used to compute and display the EOS variables along an isentrope (curve of constant entropy). This command has the form

ISEN *MODTYP parameters*

where *parameters* is a list of six quantities, of which the first five are required. If they are not entered on the command line, the user is prompted with a list, as follows.

ENTER T1,R1,R2,NPTS,MTYPE,UP1

where

T1	- initial temperature on isentrope
R1,R2	- lower and upper density limits
NPTS	- number of points on density interval
MTYPE=1	- equal spacing of densities
MTYPE=2	- exponential spacing of densities
UP1	- initial particle velocity (optional)

PANDA computes and prints out the density, temperature, pressure, internal energy, entropy, and sound speed at the specified densities on the isentrope. If a plot file has been opened, these data are also sent to that file, along with particle velocity, specific volume, and free energy.

The bulk sound velocities  $C_B$  along the isentrope are estimated by numerical differentiation of the tabulated pressure-density curve, using

$$C_B(\rho) = \sqrt{(\partial P / \partial \rho)_s}. \quad (12.1)$$

Some EOS models can predict an imaginary sound speed in certain regions of density and temperature; in such cases, the code sets  $C_B = 0$  and prints out a warning message. *Note:* Because the sound speeds are calculated numerically, the accuracy of the results will depend upon the number and spacing of the densities on the isentrope; a sensitivity study should be made when quantitative results are required.

The particle velocities  $U_p$  along the isentrope are computed from the sound velocities, using the Riemann integral [27]

$$U_p(\rho) = U_p(\rho_1) \pm \int_{\rho_1}^{\rho} \frac{C_B(\varrho)}{\varrho} d\varrho, \quad (12.2)$$

where  $\rho_1$  and  $U_p(\rho_1)$  are the initial density and particle velocity (R1 and UP1) on the isentrope. Here the sign of the integral is chosen so that  $U_p$  always *increases* along the isentrope. This convention has been chosen to give the usual results for two typical problems - the shockless acceleration of a plate (compression), and the interaction of a shock wave with a free surface (expansion).

## 12.6 Hugoniot

The commands HUG and HUGE are used to compute and display the EOS along a Hugoniot curve. A Hugoniot is a locus of points along the EOS surface that satisfy the energy conservation law for propagation of a steady shock wave,

$$E_H(\rho, T) = E_0 + (1/2)[P_H(\rho, T) + P_0](1/\rho_0 - 1/\rho), \quad (12.3)$$

where  $\rho_0$ ,  $P_0$ , and  $E_0$  are the initial conditions. PANDA offers two forms of this command. With the HUG instruction, temperature is the independent variable; with the HUGE instruction, energy is the independent variable. These commands have the form

HUG *MODTYP parameters*

and

HUGE *MODTYP parameters*

where *parameters* is a list of eight quantities, of which the first six are required. If they are not entered on the command line, the user is prompted with a list, as follows.

ENTER RZRO,PZRO,EZRO,T1,T2,NPTS,UP0,IEP    (HUG command)

and



ENTER RZRO,PZRO,EZRO,E1,E2,NPTS,UP0,IEP (HUGE command)

	RZRO,PZRO,EZRO	- initial density, pressure, and energy
	T1,T2	- lower and upper temperature limits
where	E1,E2	- lower and upper energy limits
	NPTS	- number of points on interval
	UP0	- initial particle velocity
	IEP	- set IEP=1 to obtain material strength

PANDA computes and prints out the density, temperature, pressure, internal energy, particle velocity, and shock velocity at NPTS points on the specified interval. If a plot file has been opened, these data are also sent to that file, along with the entropy, specific volume, and free energy. For a temperature-based Hugoniot, the k-th point on the temperature interval is chosen by the following rule.

$$T(k) = T1 + (T2 - T1) \left( \frac{k - 1}{NPTS - 1} \right)^2 \quad (12.4)$$

For an energy-based Hugoniot, the k-th point on the energy interval is chosen by the following rule.

$$E(k) = E1 + (E2 - E1) \left( \frac{k - 1}{NPTS - 1} \right)^2 \quad (12.5)$$

The initial state need not be consistent with the EOS model and frequently is not. For example, to calculate the Hugoniot for a solid that melts when shocked, the HUG LIQ command should be used, but the initial conditions should be determined from the solid model. Similarly, the solid can be shocked from an initial state that corresponds to a porous condition or a different solid phase.

The initial particle velocity UP0 is used in the calculation of reflected shocks. For a single shock Hugoniot, where the material is initially at rest, UP0 is set to 0. For a reflected shock, UP0 is set to the particle velocity for the first shock. (The reflected wave is assumed to move backward into the first shock, so the shock and particle velocities of the reflected shock decrease with increasing temperature and energy.)

The parameter IEP is used to include elastic-plastic effects in the Hugoniot calculation. Before specifying this option, the instruction SET STR (Sec. 15.3) must be used to enter the parameters for calculating the yield strength  $Y$  and the shear modulus. The calculation assumes plane geometry, with an elastic precursor propagating at the longitudinal sound speed, and a plastic wave in which the stress is offset from the hydrostatic pressure by  $(2/3)Y$ . If IEP=1, the code computes and prints the conditions for the elastic precursor as well as for the plastic wave. (*Note:* When material strength is included, the variable that is labeled P(GPA) on the output and plot files is actually stress, *not* hydrostatic pressure.

## 12.7 Chapman-Jouguet State

The Chapman-Jouguet (CJ) point for an explosive corresponds to the final state of the detonation products at the front of an ideal steady-state detonation wave [69] [73]. Mathematically, this state is the point on the Hugoniot for the detonation products at which the shock velocity is a minimum. The instruction *CJ MODTYP* is used to compute the CJ state from the EOS of the detonation products and the initial state of the unreacted explosive. No parameters are entered on the input line. The user is prompted as follows.

ENTER RZRO, PZRO, AND EZRO FOR UNBURNED EXPLOSIVE

The user responds by entering the initial density, pressure, and energy of the unreacted explosive. The code prints out the CJ density, temperature, pressure, internal energy, particle velocity, and detonation velocity. If a *plct* file has been opened, these variables will be sent to that file, along with the entropy, specific volume, loading density (RZRO), and free energy. The code continues to read additional lines of input until the user specifies a zero density.

*Note:* The energy for the unburned explosive must be consistent with the energy zero of the detonation products and must give the correct amount of energy for the chemical reaction. For example, these conditions can be satisfied if the energy zeros of both the reacted and unreacted explosives are given relative to the elements in their standard states.

## 12.8 Vaporization Curve

The instruction *VAP MODTYP* is used to generate the vapor pressure and properties of the vapor and the condensed phase as a function of temperature. (*Note:* Some solid models do not give realistic behavior at low densities and should not be used with this option.) No parameters are entered on the input line. The user is prompted as follows.

ENTER T1, T2, NT, AND GUESSES OF RVAP AND RLIQ

The code computes the vaporization curve at *NT* equally spaced points on the temperature interval from *T1* to *T2*. It then reads in the same parameters for another temperature interval, continuing until the user specifies *NT*=0. *RVAP* and *RLIQ* are guesses of the vapor and liquid densities at temperature *T1*. These parameters are required for the first temperature interval. Thereafter, the code takes the densities from the last temperature as guesses unless those values are overridden by user input. PANDA prints out the

temperature, vapor pressure, vapor and liquid densities, and vapor and liquid energies. If a plot file has been opened, these variables will be sent to that file, along with the entropies, enthalpies, and the liquid pressure.

Although the pressures of the two phases should be equal, the *liquid* pressure can be inaccurate at low temperatures, where the vapor pressures are small ( $10^{-6}$  or less), because small changes in the liquid density cause changes in the liquid pressure that are large compared with the vapor pressure. In such cases, the other properties are still computed accurately, and the user should simply ignore the liquid pressure.

## 12.9 Spinodal Points

Spinodals are points on an isotherm where  $(\partial P/\partial \rho)_T = 0$  (see Sec. 13.5). They give the extreme limits for metastability of the phases inside a two-phase coexistence region, such as a supercooled vapor or superheated liquid. The instruction `SPN MODTYP` is used to locate spinodal points. No parameters are entered on the input line. The user is prompted as follows.

ENTER T1, T2, NT, AND GUESSES OF RVAP AND RLIQ

The code locates the spinodals at NT equally spaced temperatures on the interval from T1 to T2. It then reads in the same parameters for another temperature interval, continuing until the user specifies NT=0. RVAP and RLIQ are guesses of the vapor (low density) and liquid (high density) spinodal densities at temperature T1. These parameters are required for the first temperature interval. Thereafter, the code takes the densities from the last temperature as guesses unless those values are overridden by user input. PANDA prints out the temperature, vapor and liquid spinodal pressures, vapor and liquid spinodal densities, and the vapor spinodal energy. If a plot file has been opened, these variables will be sent to that file, along with the liquid energy, the entropies, and the enthalpies.

Because the spinodal finder assumes the EOS surface to be perfectly smooth, it may encounter problems with some of the complicated models that employ numerical procedures of limited accuracy. In such cases, it is preferable to use the higher accuracy Cray machine. It may be possible to eliminate the difficulties by specifying higher accuracy when defining the model parameters. In other situations, it may be necessary to smooth the pressure by generating and working with a tabular EOS.

## 12.10 Critical Point

A critical point can be defined as a density and temperature at which  $(\partial P/\partial \rho)_T = (\partial^2 P/\partial \rho^2)_T = 0$ . However, this definition is of little practical use for many of the models

in PANDA, for which the limitations on numerical accuracy result in pressure derivatives that are not perfectly continuous and smooth. For this reason, PANDA makes an estimate of the critical point by extrapolating the spinodal data. The following quantities are defined.

$$\rho_a(T) = .5[\rho_v(T) + \rho_l(T)], \quad (12.6)$$

and

$$K(T) = \rho_v(T)\rho_l(T)/\rho_a(T)^2, \quad (12.7)$$

where  $\rho_v(T)$  and  $\rho_l(T)$  are the vapor and liquid spinodal densities, respectively. The critical temperature  $T_c$  is determined by extrapolating data for  $T < T_c$  to the condition  $K(T_c) = 1.0$ . Then the critical density is calculated by extrapolating to  $\rho_c = \rho_a(T_c)$ . This method is similar to one that is used in estimating the critical point from experimental data [72], except that the spinodal densities are used instead of the densities on the coexistence boundary.

The CRIT instruction is used to estimate the critical point. This command has the form

CRIT   *MODTYP*   *parameters*

where *parameters* is a list of five quantities, of which the first three are required. If they are not entered on the command line, the user is prompted with a list, as follows.

ENTER TST, GUESSES OF RVAP AND RLIQ, EPS, AND TFAC

where	<div style="display: flex; justify-content: space-between; align-items: flex-start;"> <div style="width: 150px;">TST</div> <div>- lower limit on critical temperature</div> </div> <div style="display: flex; justify-content: space-between; align-items: flex-start;"> <div style="width: 150px;">RVAP,RLIQ</div> <div>- spinodal densities at temperature TST</div> </div> <div style="display: flex; justify-content: space-between; align-items: flex-start;"> <div style="width: 150px;">EPS</div> <div>- <math>\epsilon</math> = error criterion on temperature (default is 0.01)</div> </div> <div style="display: flex; justify-content: space-between; align-items: flex-start;"> <div style="width: 150px;">TFAC</div> <div>- factor used in temperature extrapolation (default is 0.9)</div> </div>
-------	---

PANDA estimates the critical point from the the spinodal densities at two temperatures,  $T_1 < T_c$  and  $T_2 = \text{TFAC} \cdot T_1$ . It starts with  $T_1 = \text{TST}$ , then does a binary search on  $T_1$ , iterating until  $T_c - T_1 \leq \epsilon T_c$ . As in calculating the spinodals, problems can be encountered with some of the more complicated models. In order to obtain good results, it may be necessary to use the Cray machine and to specify very high accuracy when defining the model parameters. In some cases, it may be necessary to smooth the pressure by generating and working with a tabular EOS. The code prints out the density, temperature, pressure, internal energy, entropy, and volume at the estimated critical point. If a plot file has been opened, these data are also sent to that file, along with the free energy.

## 12.11 Melting Curve

The instruction MELT is used to generate the melting curve as a function of temperature, using the one-component solid and liquid models. (This option does apply to MODTYP = MIX, TRN, or USE.) No parameters are entered on the input line. The user is prompted as follows.

ENTER T1, T2, NT, AND GUESSES OF RLIQ AND RSOL

The code computes the melting curve at NT equally spaced points on the temperature interval from T1 to T2. It then reads in the same parameters for another temperature interval, continuing until the user specifies NT=0. RLIQ and RSOL are guesses of the liquid and solid densities at temperature T1. These parameters are required for the first temperature interval. Thereafter, the code takes the densities from the last temperature as guesses unless those values are overridden by user input. PANDA prints out the temperature, liquid pressure, liquid and solid densities, and liquid and solid energies. If a plot file has been opened, these variables will be sent to that file, along with the entropies, enthalpies, and the solid pressure. (The liquid and solid pressures should be equal to within the accuracy of the calculation.)

*Note:* The algorithm that is used to find the melting point assumes that the liquid is less dense than the solid. This assumption is usually correct, but exceptions do occur. In such cases, the more general and powerful phase transition model (Ch. 11) should be employed.

## 13. EOS Tables and Libraries

### 13.1 Structure of Sesame Files

The Sesame library [8]-[10] is a general-purpose system for storing, accessing, and using equations of state, opacities, and other material properties. These data are stored in tabular form, on files that are accessed by computer codes [11]-[14]. Those files that are accessed frequently are written in a binary format, which may be either sequential or random. In addition, ASCII files are used to transfer data between computing systems. This chapter describes the general features of Sesame tables and how to construct them. Chapter 14 describes the structure of library files in more detail and discusses the commands that are used to update and maintain a Sesame data base.

A *data record* is the fundamental unit of information in a Sesame library. A *catalog number* identifies the type of data and the table format. PANDA can be used to construct five types of records, which are listed in Table 12.1. A *material file* consists of one or more data records for a specific material, together with an *index record*. Each material is assigned a *material number* that is used for accessing the data. Finally, a binary *library file* consists of one or more material files, preceded by a *directory file*.

The most important data type shown in Table 12.1, catalog number 301, contains tables of pressure, internal energy, and entropy at discrete points on a rectangular grid of densities and temperatures. 301 tables define the EOS that are used in hydrocode calculations [11]-[14] and are also used as input to PANDA in several models (Chs. 2, 10, and 11). In the first version of PANDA [15], the Helmholtz free energy was tabulated instead of the entropy. If the entropy is computed from the relation  $S = (E - A)/T$ ,  $S$  is undefined at  $T = 0$ . By tabulating the entropy explicitly, this problem has been eliminated. Tables 303 and 304 have the same format as the 301 table, but they are used for partial EOS quantities. In PANDA, a “300 table” designates a group of three tables: 301, 303, and 304.) Tables 201 and 401 are used for special purposes.

### 13.2 Constructing Sesame Tables

Sesame tables are constructed using the instruction SLIB *MODTYP*, where *MODTYP* is one of the keywords used for the five models (SOL, LIQ, MIX, TRN, or USE). The following is prompt is given.

```
ENTER ID NUMBER FOR TABLE TYPE
```



**Table 13.1.** Format of Sesame Data Records

Table No.	Word No.	Symbol	Description
201: Basic Data	1	$Z$	formula number
	2	$W$	formula weight
	3	$\rho_0$	normal density
	4	$\beta_0$	bulk modulus
	5	$T_0$	std. temperature
301: Total EOS	1	$n_r$	no. of densities
	2	$n_t$	no. of temperatures
	3	$\rho(i), i = 1, n_r$	density mesh
303: Ion EOS	$3 + n_r$	$T(j), j = 1, n_t$	temperature mesh
303: Electron EOS	$3 + n_r + n_t$	$(P(ij), i = 1, n_r), j = 1, n_t$	pressure
	$3 + n_r + n_t + n_r n_t$	$(E(ij), i = 1, n_r), j = 1, n_t$	internal energy
	$3 + n_r + n_t + 2n_r n_t$	$(S(ij), i = 1, n_r), j = 1, n_t$	entropy
401: Vaporization	1	$n_t$	no. of temperatures
	2	$P(i), i = 1, n_t$	pressure
	$2 + n_t$	$T(i), i = 1, n_t$	temperature
	$2 + 2n_t$	$\rho_v(i), i = 1, n_t$	vapor density
	$2 + 3n_t$	$\rho_l(i), i = 1, n_t$	liquid density
	$2 + 4n_t$	$E_v(i), i = 1, n_t$	vap. internal energy
	$2 + 5n_t$	$E_l(i), i = 1, n_t$	liq. internal energy

The user responds by entering the catalog number for the type of table (201, 301, 300, or 401) to be created. The code then requests additional information (which depends upon the type of table), constructs the table and saves it, but does not create any files. Then it prompts the user to enter another table number, and the above process is repeated. Hence several types of data tables can be built using one SLIB command. If the user specifies a table number that was already entered, the table constructed previously is destroyed.

The process is concluded when the user enters zero in response to a request for a table number. Then the code responds as follows.

ENTER MATID, DATE, BINLIB, AND ASCLIB



where	MATID	- material number (integer) to be assigned to EOS
	DATE	- 6 digit integer specifying the current date
	BINLIB	- file name (character) for binary library
	ASCLIB	- file name (character) for ASCII update file

The binary file that is created has the Sesame library format, consisting of one material file and a directory. Hence the user should specify a different binary file name each time the SLIB instruction is given. These binary files can be merged into a single library file using the UPDATE command, as discussed in Sec. 14.3. The ASCII file has the format that is used mainly to transfer data between different computing systems, as described in Sec. 14.4. The user *can* specify the same ASCII file name in different SLIB commands; the code will reopen an existing file and add new data at the end. (No file is created if the user does not give a file name.)

### 13.3 The 201 Table

A 201 table consists of the five parameters given in Table 12.1. If a 201 table is requested as the table type, the code gives the following prompt.

ENTER FZ, FW, PREF, TREF, AND GUESS FOR RHOREF

where	FZ	- $Z$ = formula number (number of electrons in molecule)
	FW	- $W$ = formula weight
	PREF	- $P_0$ = reference pressure
	TREF	- $T_0$ = reference temperature
	RHOREF	- $\rho_0$ = normal density at $P_0$ and $T_0$

Here  $P_0$  and  $T_0$  specify a “reference state” that is often used as the default initial condition in hydrodynamic code calculations [14]. The code solves for  $\rho_0$  and the bulk modulus  $\beta_0$  and prints out the results. When making 201 tables, it is recommended that the following conventions be used to define properties of the reference state.

- If the substance is a solid or a liquid at room temperature (defined as  $298^\circ K$ ), the reference state should be  $P_0 = 0$ ,  $T_0 = 298^\circ K$ .
- If the substance is a vapor at room temperature, the reference state should be the liquid at the triple point.
- The reference state should also be the zero of energy for the 301 table, *i.e.*, the internal energy should be zero at the reference state.

## 13.4 Mesh for a 301 Table

When constructing a 301, 303, or 304 table, the user must specify a rectangular grid of density and temperature points. PANDA provides the commands MESH *MODTYP*, READ MESH, and SAVE MESH for this purpose. When the user instructs the code to make a 301 or 300 table with an SLIB command, the mesh entered previously is used. If no mesh has yet been entered, PANDA requests one by issuing the same prompts as if the MESH command had been given.

The MESH command instructs the code to set up a density grid and a temperature grid, each consisting of one or more sections. The type of mesh for a given section is denoted by the parameter MTYPE.

1. MTYPE=1 is linear. Values of the density or temperature are equally spaced on the specified interval.
2. MTYPE=2 is exponential. The logarithms of the density or temperature are equally spaced on the specified interval. (This option must not be used if the interval includes zero.)
3. For MTYPE=3, mesh points are chosen so that the logarithm of the pressure is equally spaced on the specified interval. In this case, the pressures are computed along a reference isotherm or isochore, using model *MODTYP*. This option is useful when the EOS table covers a wide density and temperature range, because it provides an accurate tabulation of the EOS with fewer points than the linear and exponential options [24].

The density mesh is constructed first. PANDA prompts the user as follows.

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF

The user enters the lower and upper limits of the density interval, the number of points on the interval, and the type of mesh. If MTYPE=3, the parameter TREF specifies which isotherm is used for computing the pressures. Next the code prompts the user to enter a second section of mesh, a third section, and so on, until MTYPE=0 is specified. PANDA sorts the densities and eliminates identical values; hence the different sections of mesh can overlap and can be entered in any order. Then PANDA prompts the user for a temperature mesh.

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF

As before, the user enters the lower and upper limits, the number of points, and the type of mesh for the interval. For `MTYPE=3`, `RREF` specifies which isochore is used for computing the pressures. Several sections can be entered and the process terminates if `MTYPE=0`.

The commands `READ MESH FNAME` and `SAVE MESH FNAME` instruct PANDA to read in the mesh or to write it out for future use, using an ASCII file called “fname”. (There is no default for the file name; if no name is given, a prompt is issued.) The format of this file is as follows.

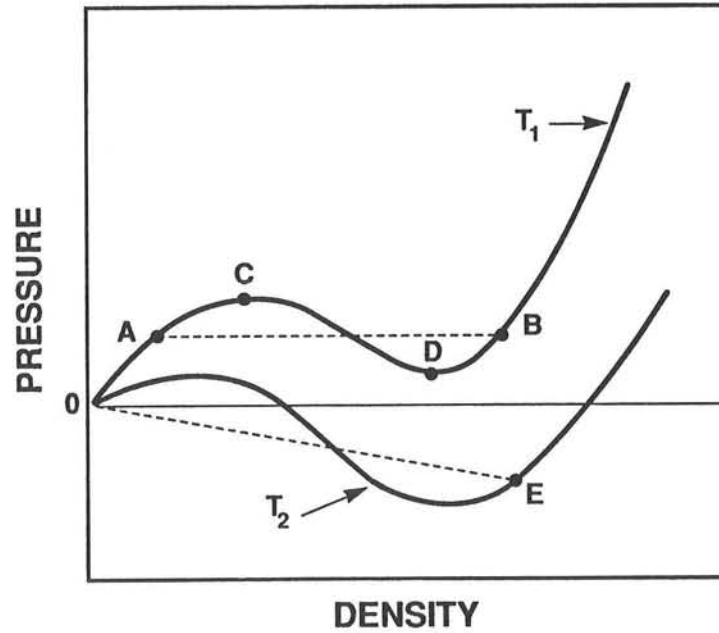
- The first line gives  $n_r$  (number of densities) and  $n_t$  (number of temperatures).
- The next few lines give  $n_r$  values of the density. PANDA sorts the densities, so they can be entered in any order.
- The last few lines give  $n_t$  values of the temperature. PANDA also sorts the temperatures.

An example of a mesh file is shown in Ref. [15]. A sample file can also be created with test problem 1 (see Sec. 16.1).

*Note:* When constructing the density mesh, it is usually desirable to include a zero density point in order to avoid extrapolating off the table at low densities. At zero density, PANDA will set the pressure to zero and set the energy and entropy to the same values as the lowest finite density in the mesh.

## 13.5 The 301 Table: Maxwell Constructions

At sufficiently low temperatures, isotherms calculated using the models in PANDA display van der Waals loops, indicating a vapor-liquid coexistence region and a critical point. After a 301 or 300 table has been generated on the density-temperature grid, the user must specify how this two-phase region should be treated. If left as is, the EOS table can be used to describe metastable states: supercooled vapor and superheated liquid [74]. However, the user can instruct the code to include Maxwell constructions [55] that describe the true equilibrium state, a liquid-vapor mixture. In the latter case, the user can choose to have a nonequilibrium tension region at low temperatures, so that the EOS can be used in hydrodynamic code calculations that treat spallation phenomena. In certain models, the EOS may have a complicated structure that results in more than one coexistence region [58]; PANDA allows for this possibility by having the user specify different density and temperature regions where the Maxwell constructions are to be made.



**Figure 13.1.** Typical pressure isotherms in the vapor-liquid coexistence region, showing van der Waals loops and Maxwell constructions.

Typical pressure isotherms are illustrated in Fig. 13.1. Consider first the highest temperature isotherm, denoted by  $T_1$ . Points C and D are called “spinodals”. Points A and B are states that have both the same pressure and the same Gibbs free energy. For densities  $\rho_A \leq \rho \leq \rho_B$ , the fluid at equilibrium will separate into an inhomogeneous mixture of vapor at state A and liquid at state B. Because the two components of the mixture are in mechanical equilibrium, the pressure is constant in the two-phase region, as shown by the dashed line. The volumes of the two phases are additive. Hence the fraction of vapor,  $f_v$ , is given by

$$f_v = (\rho_B/\rho - 1)/(\rho_B/\rho_A - 1). \quad (13.1)$$

The internal energy in the two-phase region is given by

$$E(\rho, T) = f_v E(\rho_A, T) + (1 - f_v) E(\rho_B, T). \quad (13.2)$$

Similar relations hold for the free energy and entropy.

In PANDA, the user can specify that a tension region be created at temperatures below some value TSPALL. In this regime, the isotherms have the form shown by curve  $T_2$  in Fig. 13.1. RSPALL is defined to be the liquid density at  $T = \text{TSPALL}$  and  $P = 0$ . For  $T \leq \text{TSPALL}$ , an isotherm is allowed to go into tension for densities above point E, where  $\rho_E = \text{RSPALL}$ . For  $\rho \leq \rho_E$ , the internal energy, free energy, and entropy are taken to be constant, while the pressure is given by

$$P(\rho, T) = P(\rho_E, T) \rho / \rho_E, \quad (13.3)$$

as shown by the dotted line from 0 to E in Fig. 13.1. The above relation was chosen to give reasonable values for the sound velocity in hydrocode calculations. Of course, the EOS is fictitious for  $T \leq TSPALL$  and  $\rho \leq RSPALL$ , but this region must be included to make a rectangular table.

When a 301 or 300 table type is requested with the SLIB command, the code first generates the nonequilibrium table and then gives the following prompt.

MAKE MAXWELL CONSTRUCTIONS? (YES/NO)

If the user enters “yes” (or just “y”), the code sends the following message.

ENTER TSPALL AND GUESS OF RSPALL

The user responds by entering the boundary of the tension region, as defined above, and a guess of the liquid density at that temperature. (If  $TSPALL < 0$ , no tension region will be created.) Finally, the code prompts the user to make the Maxwell constructions in sections, as follows.

ENTER TMIN, TMAX, AND GUESSES FOR RLO AND RUP

Here the user responds by giving the lower and upper temperature limits of the region. RLO and RUP are guesses for the lower and upper densities on the coexistence boundary at for the lowest isotherm within the region. PANDA then locates the boundaries at each temperature, printing out the results for each isotherm as it goes. If the code cannot locate the coexistence boundaries for a particular temperature, it prompts the user to enter guesses, then proceeds. (In some cases, it may still fail to find a solution and continue prompting the user. In that case, zeros should be entered; the Maxwell constructions will not be made and an error message will result.) PANDA continues to prompt the user to enter another temperature section until both  $TMIN = 0$  and  $TMAX = 0$  are specified.

## 13.6 The 303 and 304 Tables

For the one-component solid and liquid models, a two-temperature table is generated by specifying a table ID number of 300. In this case, PANDA will simultaneously generate the 301 (total EOS), 303 (ion EOS), and 304 (electron EOS) tables on identical density-temperature meshes. Input to the code (to set up the mesh and to include Maxwell constructions) is the same as for a 301 table.

If Maxwell constructions are selected, the total EOS table is treated as described above. The vapor density  $\rho_A$  and the liquid density  $\rho_B$  are determined on the boundaries of the coexistence curve, and the fraction of vapor,  $f_v$ , is defined by Eq. 13.1. Inside the coexistence region, the ion pressure and energy are defined by

$$P_{ion}(\rho, T) = f_v P(\rho_A, T) + (1 - f_v) P(\rho_B, T), \quad (13.4)$$

and

$$E_{ion}(\rho, T) = f_v E(\rho_A, T) + (1 - f_v) E(\rho_B, T). \quad (13.5)$$

The ion free energy and entropy and the electron EOS quantities are similarly partitioned inside the coexistence region. The user should be aware that these equations do not guarantee thermodynamic consistency. According to this prescription, only the total EOS obeys the thermodynamic relations in the region of Maxwell constructions.

## 13.7 The 401 Table

The 401 table provides the vapor pressure and other properties on the coexistence curve as a function of temperature, as shown in Table 12.1. If a 401 table is specified under the SLIB command, PANDA prompts the user to enter the temperature mesh for this table.

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE

The user responds by entering the lower and upper limits and the number of points on the temperature interval. There are two mesh options, MTYPE=1 (linear) and MTYPE=2 (exponential). Then the code prompts the user to enter a second section of mesh, and so on until MTYPE=0 is received. PANDA sorts the temperatures and eliminates duplicated values, so the sections of mesh can overlap and can be entered in any order.

Next the code prompts the user to enter the temperature and density at the critical point.

ENTER TCRIT AND RHOCRIT

The critical point should be determined before making the table, using other options in the code (see Ch. 12). This point will appear as the highest temperature in the 401 table. The code will ignore any supercritical temperatures specified by the user when constructing the mesh.

Next the user is prompted to enter guesses of the vapor and liquid densities at the first (lowest) temperature in the table. The code iterates to obtain the exact densities,

the vapor pressure, and the other coexistence properties. PANDA makes its own guesses of the vapor and liquid densities at higher temperatures and prompts the user only if it cannot find solutions on its own. If the user enters zero for either the vapor or liquid density when prompted, the attempt to make a 401 table is terminated and an error message is sent to the TTY. PANDA prints out the coexistence data while it is making the 401 table.



## 14. Maintaining a Sesame Data Base

### 14.1 Structure of Binary and ASCII Files

The procedures for generating, storing, and accessing EOS tables in a Sesame data base are simple to carry out if the user employs standard software packages that have been provided for that purpose [8]-[14]. This chapter discusses the PANDA commands that are provided for maintaining a Sesame data base. In order to understand the use of these commands, it is necessary to explain certain features pertaining to Sesame files. However, it is not necessary to know the details of the file structure unless one chooses to write new routines.

A Sesame data base uses two kinds of computer files - unformatted (binary) and formatted (ASCII). Because they are more compact and faster to read, binary files are used for those procedures that involve direct access to data in the library. For example, PANDA reads from binary files when loading EOS tables for the solid, liquid, mixture, and phase transition models. The commands to list, update, and modify a Sesame file (Secs. 14.2 and 14.3) also assume the binary structure. The ASCII file format was developed to transfer data between different computing systems. The SLIB command (Ch. 13) generates both types of files. The ASC2BIN command (Sec. 14.4) is used to process an ASCII file and generate a binary file. For example, this command is used when EOS tables generated on a Cray machine are sent to a VAX or PC.

A binary library file consists of one or more material files, preceded by a directory file. As discussed in Ch. 13, each material file consists of several types of records, or data types; in addition, the first record in each material file is an index to that file. The directory file at the beginning of the library contains the information needed to read through and access data from the library.

Two kinds of binary files are in common use - sequential and random access. PANDA works exclusively with the sequential file structure in order to avoid the use of system-dependent routines. The sequential files are written with unformatted WRITE statements, which insert record marks on the file; hence these files must be read with unformatted READ statements. In addition, the standard Sesame procedures insert special fiducial marks after the directory and material files, in order to simplify the problem of accessing data. In earlier programs, an END FILE statement was used to generate this fiducial. That procedure has been abandoned in the present version of PANDA because it is not standard FORTRAN. In its place, the code writes the one-word integer record -777777. The new procedures should be able to read files written with the old structure.

However, older subroutine packages will not be able to read the new files unless a slight change to the INBUF routine is made.

## 14.2 Listing a Sesame Library File

The instruction LIST is used to obtain a list of materials and table types on a Sesame (binary) library file. The command form is

LIST    *filename*

where *filename* is the name of the Sesame library file. A prompt is given if no name is entered on the command line.) For each material on the library, PANDA prints out a table of the material number, formula number FZ, formula weight FW, reference density RHOREF, reference temperature TREF, and the types of material records on the file. (The parameters FZ, FW, RHOREF, and TREF are obtained from the 201 table if one is available.) The LIST command also performs certain checks on the file; it compares the information in the directory with the material indexes and compares the material indexes with the material records, printing messages if discrepancies are found. Examples of this command are shown in test problems 1 and 2 (Ch. 16).

## 14.3 The UPDATE, DELETE, and EXTRACT Commands

The instruction UPDATE is used to add data to an existing (binary) library file. The command form is

UPDATE    *oldfile*    *updfile*    *newfile*    *date*

Here *oldfile* is the file name for the old library and *updfile* is name of an update file (binary) containing the EOS data to be added to the library. If the update file contains a data table that is *already* on the library, the new data will replace the old. *newfile* is the file name for the new library file that is created. A prompt will be given if the three file names are not entered on the command line. *date* is an optional 6-digit real number specifying the current date to be put into the directory of the new library. Examples of this command are shown in test problem 2 (Sec. 16.2).

The instruction DELETE is used to remove specified data tables from a library file. The command form is

DELETE   *oldfile*   *newfile*   *date*

Here *oldfile* is the file name for the old library and *newfile* is the file name for the new library that is created. A prompt will be given if the two file names are not entered on the command line. The 6-digit date is optional. After entering the command, the user is prompted as follows.

ENTER MATERIAL NUMBER AND TABLE TYPES TO DELETE

The user responds by entering the material ID number, followed by the catalog numbers for each of the data types to be removed from the library. If no data types are entered, the entire material will be deleted from the library. PANDA continues to prompt the user until a material number of zero is entered.

The EXTRACT instruction is similar to DELETE, except that the user specifies those data tables that are to be included in the new file. The command form is

EXTRACT   *oldfile*   *newfile*   *date*

Here *oldfile* is the file name for the old library and *newfile* is the file name for the new library that is created. A prompt will be given if the two file names are not entered on the command line. The 6-digit date is optional. After entering the command, the user is prompted as follows.

ENTER MATERIAL NUMBER AND TABLE TYPES TO EXTRACT

The user responds by entering the material ID number, followed by the catalog numbers for each of the data types to be included in the library. If no data types are entered, the entire material will be included in the library. PANDA continues to prompt the user until a material number of zero is entered.

## 14.4   Converting Between ASCII and Binary Files

The instruction ASC2BIN is used to read an ASCII data file, like one generated by an SLIB command (Ch. 13) and generate a Sesame binary library file. The command form is

ASC2BIN   *ascfile*   *binfile*   *date*

Here *ascfile* is the name of the input ASCII file, and *binfile* is the name of the binary file that is to be created. A prompt will be given if the two file names are not entered on the command line. The 6-digit date is optional.

The instruction BIN2ASC is used to generate an ASCII file from a binary library. The command form is

BIN2ASC   *binfile*   *ascfile*

Here *binfile* is the name of the input binary file, and *ascfile* is the name of the ASCII file that is to be created. A prompt will be given if the two file names are not entered on the command line. No date is specified in this case because that information is obtained from the binary file.

The ASCII file format used in the above PANDA commands is different from the one that was developed at Los Alamos National Laboratory for transmitting the Sesame library between various computing systems [8] [9]. The new format was chosen because when it was found that the CHARACTER operations available under FORTRAN 77 make it easier to achieve the same goal with a much simpler file structure. The TRANS ASC command provides a way to convert files from the old to the new format, so that data received from Los Alamos can be processed by PANDA. The command form is

TRANS ASC   *oldfile*   *newfile*

Here *oldfile* is the name for the ASCII file having the old format, and *newfile* is the name for the new ASCII file that is created. A prompt will be given if the two file names are not entered on the command line. After entering the command, the user is prompted as follows.

#### ENTER MATERIAL NUMBER AND CATALOG NUMBERS

The user responds by entering the material ID number, followed by up to ten catalog numbers for each of the data types to be included in the output file. Alternately, the user may enter the word "ALL" instead of the catalog numbers in order to obtain all data types. (However, the PANDA commands do not support the use of Hollerith data types, catalog numbers 101-199). The code prints out a message stating whether or not the requested data was located. PANDA continues to prompt the user until a material number of zero is entered.

## 15. Miscellaneous Options

### 15.1 User-Defined Models

PANDA has two dummy routines, BUSE and BUSEI, that can be replaced with a model constructed by the user. The function of routine BUSEI is to prompt the user for input, read the data, and perform any preliminary calculations that are needed to set up the model. This routine is called when the PANDA instruction MOD USE is entered. Routine BUSE should calculate the pressure, internal energy, and entropy as functions of density and temperature. This routine is called by various commands listed in Tables 1.3 and 1.4, such as EOS USE, ISOT USE, SLIB USE, *etc.* The general structure of these routines can be patterned after that in the standard PANDA options. Two examples of this option are discussed in this chapter.

ANEOS [38] is a sophisticated analytic equation of state package that was developed for use in wave propagation codes at Sandia and other laboratories. The ANEOS model was interfaced to PANDA so that it could be used to generate EOS tables in the Sesame format. These tabular versions of the ANEOS models can be used with Sesame tabular EOS packages for hydrocodes [13] [14]. To install the ANEOS user option in PANDA, obtain file /u0/gkerley/panda/aneos.f (Cray) or /u3/gkerley/panda/aneos.f (SUN). Remove subroutines BUSE and BUSEI from the source code, add the routines from this file, compile, and load the code. The ANEOS routines were taken from the CTH code [14] [75], and the input lines are the same as for CTH.

### 15.2 Making a File of Experimental Hugoniot Data

The instruction SHOCK DATA is used to make a file of experimental Hugoniot data for plotting and comparing with theoretical calculations. These data can either be entered at the terminal or retrieved from two compendia of shock-wave data that are described in Refs. [76] and [77]. For the Cray, the data files are available from IFS, under the following node names:

/e00024305/libs/hugs/hugla - Los Alamos compendium [76],

/e00024305/libs/hugs/hugl3 - Lawrence Livermore compendium [77],

/e00024305/libs/hugs/hgndx - listing of material names.

On the SUN, the corresponding files are:

/u3/gkerley/libs/hugs/hugla - Los Alamos compendium,  
/u3/gkerley/libs/hugs/hugla - Lawrence Livermore compendium,  
/u3/gkerley/libs/hugs/hgndx - listing of material names.

These data files were obtained from Los Alamos and have the same format that is described in Ref. [78]. However, the names of the materials on the files have been revised to simplify user input under the SHOCK DATA option. A list of the material names on these two files is given on the index file hgndx.

Before using this option, the user must open a plot file as described in Sec. 1.5. Next, the command line has the form

SHOCK DATA *fname*

where *fname* is either “tty” or the name of a data file having the special format discussed above. A prompt is issued if no name is given on the command line.

If the data are to be obtained from a file, the user is prompted as follows.

ENTER MATERIAL DESCRIPTION

The user responds by entering the first 30 characters of the material name, for the section of data to be retrieved, as given in file hgndx. If the material is located, PANDA prints out the initial density, and the particle velocity, shock velocity, density, pressure, and internal energy at each point on the Hugoniot. These same data are sent to the plot file, along with the initial and final specific volumes. The average initial density is also printed before the user is prompted to enter a label for the plot file. Error messages are given if the material cannot be located or if a plot file has not been defined.

If the data are to be entered at the terminal, the user is prompted as follows.

ENTER RZRO, US, AND UP, TERMINATING WITH ZEROS

The user responds by entering the initial density and the shock and particle velocities for each Hugoniot point, each point on a separate line. Input terminates when the user enters an initial density of zero. The output is the same as described above.

## 15.3 Defining a Material Strength Model

In calculating the Hugoniot for a solid (Sec. 12.6), it is possible to include the effects of elastic-plastic flow (assuming plane geometry). The command SET STR is used to



set the material strength parameters using the model of Steinberg, *et. al.* [80]. This command has the form

SET STR *parameters*

where *parameters* is a list of the eight constants used in the model. If no parameters are specified on the input line, the user is prompted with a list of the constants, as follows.

MATERIAL STRENGTH - ENTER G0,Y0,YX,BY,PY,EY,GP,GT

where	<p>G0 - <math>G_0</math> = shear modulus (GPa) at room temperature and pressure</p> <p>Y0 - <math>Y_0</math> = yield strength (GPa) at room temperature and pressure</p> <p>YX - <math>Y_{max}</math> = limit on yield in work hardening formula</p> <p>BY - <math>\beta_y</math> = constant in work hardening term</p> <p>PY - <math>p_y</math> = constant in work hardening term</p> <p>EY - <math>\varepsilon_{pi}</math> = initial plastic strain</p> <p>GP - <math>G_P</math> = coefficient for pressure dependence (<math>\text{GPa}^{-1}</math>)</p> <p>GT - <math>G_T</math> = coefficient for temperature dependence (<math>^{\circ}\text{K}^{-1}</math>)</p>
-------	--

All of the above parameters have a default value of zero except for  $Y_{max}$ , for which the default is 1.0E+10.

The PANDA code uses the following constitutive equations of Ref. [80], which describe the pressure and temperature dependence of the shear modulus  $G$  and yield strength  $Y$  and also the effect of work hardening on the yield strength.

$$G = G_0[1 + G_P P / \eta^{1/3} + G_T(T - 298)], \quad (15.1)$$

and

$$Y = Y_0[1 + \beta_y(\varepsilon_p - \varepsilon_{pi})]^{p_y}[1 + G_P P / \eta^{1/3} + G_T(T - 298)], \quad (15.2)$$

subject to the limitation that

$$Y_0[1 + \beta_y(\varepsilon_p - \varepsilon_{pi})]^{p_y} \leq Y_{max}. \quad (15.3)$$

Here  $\eta = \rho / \rho_{ref}$ , where  $\rho_{ref}$  is the reference density defined using the SET BAS command (Sec. 2.2). (This instruction will be executed automatically, if those data have not been entered previously.) For plane geometry, the “equivalent plastic strain”  $\varepsilon_p$  is given by [81]

$$\varepsilon_p = 0.5443(1 - 1/\eta). \quad (15.4)$$



## 15.4 Monte Carlo Calculations

The Monte Carlo (MC) method [82]-[84] is a numerical technique for computing the EOS for a classical system of particles from specified intermolecular potentials. The internal energy and pressure are calculated for a finite number of particles in a box with periodic boundary conditions. Starting from an initial configuration, the random sampling technique introduced by Metropolis, *et. al.* [82], is used to generate a chain of new configurations. For a chain of sufficient length, the average of the energy and pressure over all configurations in the chain approximates the Boltzmann-weighted average. The MC method is different from the molecular dynamics (MD) method [83], which involves solution of the Newtonian equations of motion; however, the two methods give similar results for equilibrium properties.

MC and MD calculations are sometimes termed “computer experiments” or “numerical simulations” because they provide results which are exact, except that they are subject to both statistical and systematic errors. Like experimental data, these numerical calculations are useful for testing the predictions of simpler EOS models. However, the methods are too expensive to be used in constructing a global EOS surface.

In PANDA, the MC option [84] can be used to compute the pressure and internal energy as functions of temperature and volume (the canonical ensemble), for a binary equimolar mixture of two particle types. Three options for the intermolecular potential are available. Upon entering the command MONTE CARLO, the user is prompted as follows.

INITIAL SETUP - ENTER NX,NY,NZ,IMIX,IPOT,OUTFILE

	NX	- number of particles along x-axis
	NY	- number of particles along y-axis
	NZ	- number of particles along z-axis
	IMIX	- initial mixture configuration
	ICLD=0,	NaCl lattice
where	ICLD=1,	heterogeneous mixture
	IPOT	- type of intermolecular potential
	IPOT=0,	inverse-power potential
	IPOT=1,	Lennard-Jones (6-12) potential
	IPOT=2,	exponential-6 potential
	OUTFILE	- name of configuration file

The initial configuration is a simple cubic lattice with parameters NX, NY, and NZ giving the number of particles (lattice points) in the x, y, and z directions, respectively. If IMIX=0, the particle labels alternate on the various lattice sites, as in the NaCl lattice, giving a homogeneous initial distribution of particle types. If IMIX=1, the particle labels

are separated into two layers lying perpendicular to the z-axis, giving a heterogeneous initial distribution of particle types. If a name is given for OUTFILE, the configurations are saved on that file and are available for subsequent editing. However, this file is not used in PANDA at the present time, and no discussion of it will be given in this manual. (*Note:* The Monte Carlo option uses the same storage array that is used for EOS tables in several other options. When the MC option is invoked, the user is given a warning message that anything in that array will be destroyed.)

If IPOT=0, the intermolecular potentials have the inverse-power form,

$$\phi_{ij}(r) = \epsilon(r_{ij}^*/r)^{p_{ij}}, \quad (15.5)$$

where  $i$  and  $j$  are the particle labels,  $r$  is the intermolecular distance, and  $\epsilon = 1^\circ K$ . The following prompt is given.

INVERSE POWER POTENTIAL - ENTER RU,PU,I=1,2,3

The user responds by entering the parameters  $r_{11}^*$ ,  $p_{11}$ ,  $r_{22}^*$ ,  $p_{22}$ ,  $r_{12}^*$ , and  $p_{12}$ .

If IPOT=1, the intermolecular potentials have the Lennard-Jones form,

$$\phi_{ij}(r) = 4\epsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]. \quad (15.6)$$

The following prompt is given.

LJ POTENTIAL - ENTER EU,SU,I=1,2,3

The user responds by entering the parameters  $\epsilon_{11}$ ,  $\sigma_{11}$ ,  $\epsilon_{22}$ ,  $\sigma_{22}$ ,  $\epsilon_{12}$ , and  $\sigma_{12}$ .

If IPOT=2, the intermolecular potentials have the exponential-6 form,

$$\phi_{ij}(r) = \frac{\epsilon_{ij}}{\alpha_{ij} - 6} (6 \exp[\alpha_{ij}(1 - r/r_{ij}^*)] - \alpha_{ij}(r_{ij}^*/r)^6). \quad (15.7)$$

The following prompt is given.

EXP6 POTENTIAL - ENTER AU,EU,RU,I=1,2,3

The user responds by entering the parameters  $\alpha_{11}$ ,  $\epsilon_{11}$ ,  $r_{11}^*$ ,  $\alpha_{22}$ ,  $\epsilon_{22}$ ,  $r_{22}^*$ ,  $\alpha_{12}$ ,  $\epsilon_{12}$ , and  $r_{12}^*$ .

After the potential parameters have been entered, the user is prompted to enter the temperatures and volumes to be computed.

ENTER TEMPERATURE, VOLUME, NCHN, NMAX, RFC

	TEMPERATURE	- temperature in $^{\circ}K$
	VOLUME	- volume in cc/mole
where	NCHN	- number of chains (default is 25)
	NMAX	- number of configurations per chain (default is 1000)
	RFC	- pair sphere radius divided by lattice constant

The total number of configurations is divided into NCHN chains, in order to provide statistical information about the calculation. The code prints out the average energy and pressure for each chain, along with the cumulative averages over all chains. The cumulative averages should fluctuate about the value for an infinite number of chains, diminishing in magnitude as the number of chains increases. Hence the fluctuations about the final average values provide a measure of the precision of the calculation.

In computing the energy and pressure per particle, only those neighbors that are within a certain radius (the "pair sphere") are considered explicitly; a correction for the neighbors outside the pair sphere is computed by assuming a uniform pair distribution function. The pair sphere radius is given by RFC times the lattice constant. The default value for RFC is determined by the distance from the center of the box to its closest face, *i.e.*  $RFC = \text{MIN}(NX, NY, NZ)/2$ . The user can specify a smaller value for RFC but cannot exceed the default value.

The code continues to prompt the user for temperature-volume points until a zero temperature is entered. The last configuration for the previous point is used as the starting configuration for the new point, except that the distances are scaled to account for any change in volume. When a zero temperature is entered, the code prompts the user for new potential parameters, once again keeping the last configuration as the starting one for any new points. The calculation terminates if a zero is given for the first potential parameter.

The Monte Carlo option can be used on the Cray, VAX, SUN, or PC. However, these calculations involve considerable computing time, and big jobs will run most efficiently on the Cray/YMP which has hardware "gather" features that enhance vectorization. The computing time required for a system of 216 particles ( $NX=NY=NZ=6$ ) is about 400  $\mu s$  per particle per configuration on the Cray/YMP. Because of system differences, a different random number generator is used on each computing machine.

The PANDA output file shown on the following page is an example of a Monte Carlo run for a mixture of particles with  $1/r^{12}$  potentials [85]. At the conclusion of each calculation, the code prints out the temperature, volume, average internal energy, and average pressure. It also gives the energy and pressure contributions from outside the pair sphere radius, along with some statistical information. The standard deviations refer to variations in the averages for each chain about the final average values. The crossing frequency is the number of times a chain average value crosses the final average value, divided by the number of chains.

THE PANDA CODE, CTSS VERSION 2.01, 11/15/89  
SANDIA NATIONAL LABORATORIES, ALBUQUERQUE, NM 87185

PROBLEM: SS12\_MIX DATE: 12/04/89

OPTION?

monte carlo

WARNING - ANY DATA IN /TABLK/ WILL BE DESTROYED

INITIAL SETUP - ENTER NX,NY,NZ,IMIX,IPOT,OUTFILE

8 8 8 0 0

INVERSE POWER POTENTIAL - ENTER RU,PU,I=1,2,3

1 12 .3333333333 12 .6666666667 12

ENTER TEMPERATURE, VOLUME, NCHN, NMAX, RFC

1 .747046 25 4000 2.25

I	EI	PI	EAV	PAV
1	1.5691e-02	2.8366e-02	1.5691e-02	2.8366e-02
2	1.5694e-02	2.8385e-02	1.5693e-02	2.8375e-02
3	1.5686e-02	2.8342e-02	1.5690e-02	2.8364e-02
4	1.5705e-02	2.8443e-02	1.5694e-02	2.8384e-02
5	1.5688e-02	2.8351e-02	1.5693e-02	2.8377e-02
6	1.5687e-02	2.8346e-02	1.5692e-02	2.8372e-02
7	1.5709e-02	2.8461e-02	1.5694e-02	2.8385e-02
8	1.5710e-02	2.8470e-02	1.5696e-02	2.8395e-02
9	1.5716e-02	2.8498e-02	1.5698e-02	2.8407e-02
10	1.5712e-02	2.8477e-02	1.5700e-02	2.8414e-02
11	1.5695e-02	2.8386e-02	1.5699e-02	2.8411e-02
12	1.5686e-02	2.8338e-02	1.5698e-02	2.8405e-02
13	1.5694e-02	2.8383e-02	1.5698e-02	2.8404e-02
14	1.5684e-02	2.8332e-02	1.5697e-02	2.8398e-02
15	1.5696e-02	2.8395e-02	1.5697e-02	2.8398e-02
16	1.5710e-02	2.8469e-02	1.5698e-02	2.8403e-02
17	1.5695e-02	2.8389e-02	1.5698e-02	2.8402e-02
18	1.5695e-02	2.8390e-02	1.5697e-02	2.8401e-02
19	1.5696e-02	2.8392e-02	1.5697e-02	2.8401e-02
20	1.5691e-02	2.8368e-02	1.5697e-02	2.8399e-02
21	1.5678e-02	2.8296e-02	1.5696e-02	2.8394e-02
22	1.5695e-02	2.8390e-02	1.5696e-02	2.8394e-02
23	1.5693e-02	2.8375e-02	1.5696e-02	2.8393e-02
24	1.5705e-02	2.8442e-02	1.5696e-02	2.8395e-02
25	1.5703e-02	2.8434e-02	1.5697e-02	2.8397e-02

TEMPERATURE = 1.0000e+00 KELVIN

VOLUME = 7.4705e-01 CC/MOLE

AVERAGE ENERGY = 1.5697e-02 MJ/KG-MOLE

AVERAGE PRESSURE = 2.8397e-02 GPA

E FOR R>RCO = 4.2105e-07 MJ/KG-MOLE

P FOR R>RCO = 2.2545e-06 GPA

STD. DEV. (E) = 9.5550e-06 MJ/KG-MOLE

STD. DEV. (P) = 5.1161e-05 GPA

XING FREQ. (E) = 2.8000e-01

XING FREQ. (P) = 2.8000e-01

ENTER TEMPERATURE, VOLUME, NCHN, NMAX, RFC

0

INVERSE POWER POTENTIAL - ENTER RU,PU,I=1,2,3

0

OPTION?

end

## 16. Test Problems

Four problems have been constructed that demonstrate use of the models and options in PANDA. They can be run from an input file, using the @FNAME option. The files for these problems can be obtained in subdirectories /u0/gkerley/panda/tests (Cray) and /u3/gkerley/panda/tests (SUN). The conventions used in file nomenclature should be evident from the following examples.

tplinp - input file to run test problem 1.

tplout - output file generated by test problem 1.

tplplt - plot file generated by test problem 1.

aesps - file of EOS tables (ASCII format) for test problem 4.

The output files for these four test problems are listed in Appendices E - H. The code output lines and prompts are shown in upper case, while the user input lines are in lower case. Problem 1 was run on the Cray under CTSS. Problem 2 was run on the Cray under UNICOS. Problem 3 was run on the VAX under VMS. Problem 4 was run on the SUN under UNIX. Some of the calculations in problem 1 do not give satisfactory results on the VAX and the SUN, because of the lower precision. The other three problems give satisfactory results even on the lower precision machines.

### 16.1 Test Problem 1: Aluminum EOS

This problem uses the one-component solid and liquid models for aluminum. The  $0^\circ K$  curve is computed from the Hugoniot; this option is not the best one for aluminum, but it has been selected as a test problem because it is the most complicated of all the options. The TFD option is used for the thermal electronic term. A more elaborate model for aluminum is described in Ref. [58]. The code computes isobars, isentropes, Hugoniots, melting, and vaporization curves. The code also constructs an EOS table for the fluid phase, creating both a binary and an ASCII file, as well as a file for the density-temperature mesh. The EOS table is read back in and several quantities are recomputed for comparison with the exact calculations.

The output file TP1OUT for this example is listed in Appendix E. Figure 16.1 shows the Hugoniot, release isentrope, and the solid and liquid melting densities; this plot was made from the plot file TP1PLT, using the GRAPH utility [20]. Portions of the plot file are also listed in Table 12.1, Ch. 12.

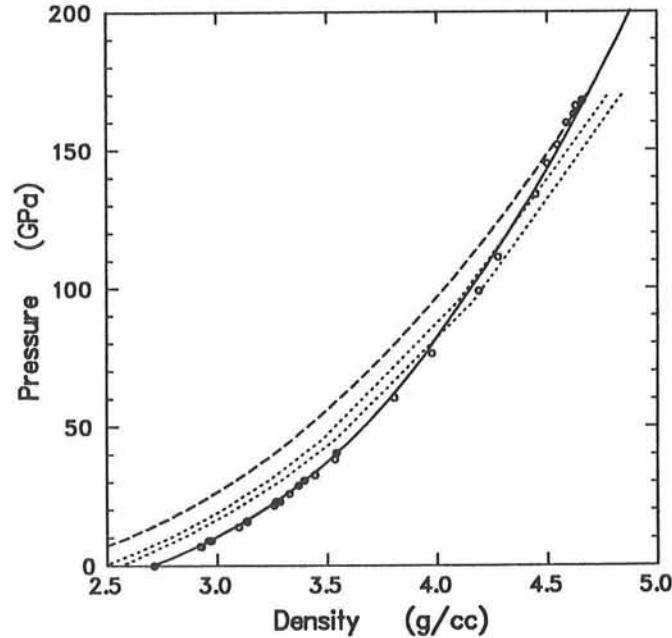
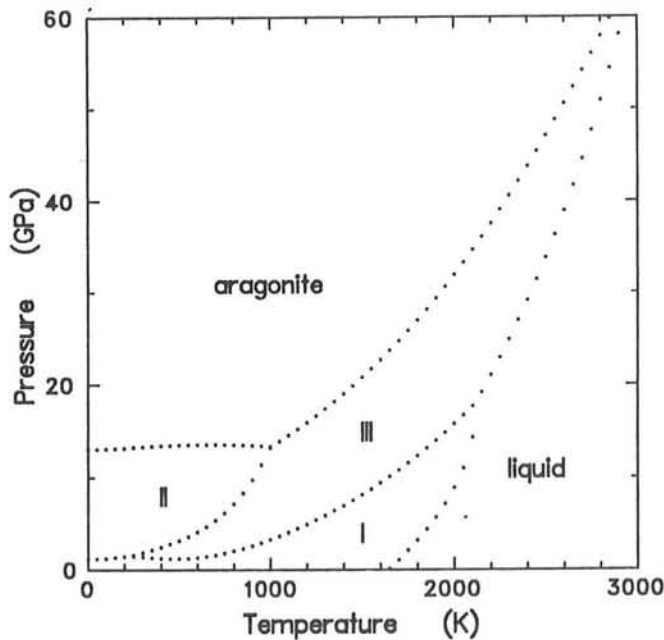


Figure 16.1. EOS calculations for aluminum, from test problem 1. The full curve is the computed Hugoniot; the circles are experimental shock data from Refs. [76] and [86]. The dashed curve is the computed release isentrope from a 173 GPa shock state. The dotted curves show the solid and liquid densities on the melt boundary.

## 16.2 Test Problem 2: Multiphase EOS for Calcium Carbonate

This problem tests the phase transition model as well as several other options; the theory is discussed in Ref. [87]. EOS tables are generated for four solid phases and the liquid phase of  $\text{CaCO}_3$ . These models use both the analytic EXP-N and the tabular cold curve options. They also include density and temperature dependence in the internal vibrational degrees of freedom, for treatment of the optical lattice vibrational modes. The phase transition model is called to compute the phase diagram and to generate a multiphase EOS table. The phase diagram is sent to plot file TP2PLT. The UPDATE option is used to generate a binary library containing the EOS tables for the individual phases and the multiphase EOS. An ASCII library is also produced. The RESET command is used so that all calculations can be done within a single code run.

The output file TP2OUT for this example is listed in Appendix F. Figure 16.2 shows a plot of the calculated phase diagram, made from the plot file with the GRAPH utility. Other examples of the model are given in Ref. [87].

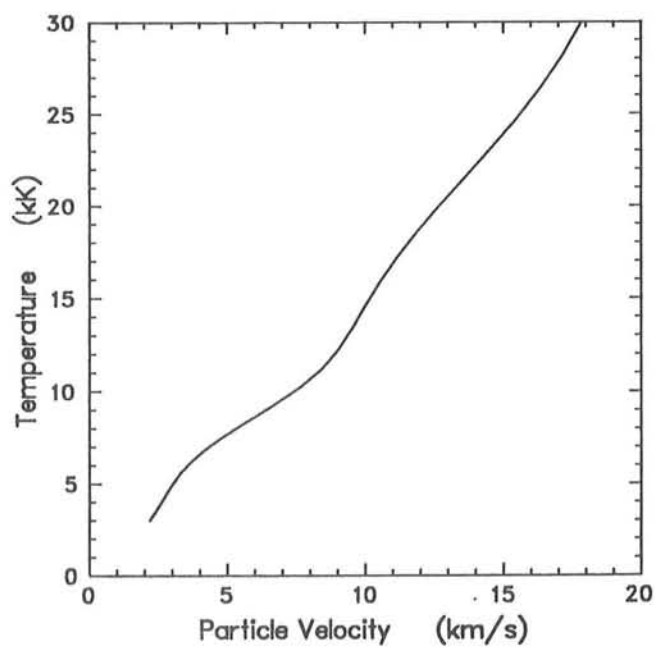


**Figure 16.2.** Calculated phase diagram for calcium carbonate, from test problem 2. The dots show the pressure-temperature points actually computed using the MOD TRN option.

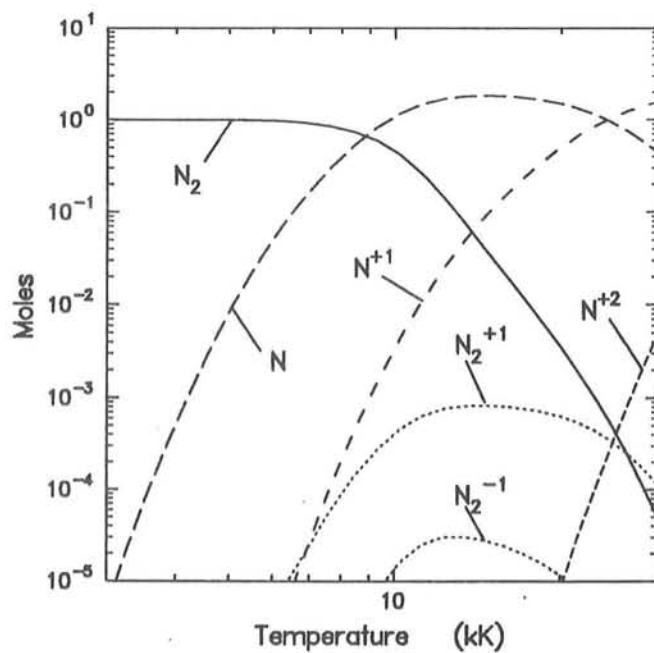
### 16.3 Test Problem 3: Chemical Equilibrium in Nitrogen Gas

This calculation uses the mixture-chemical equilibrium model to compute the EOS for shocked nitrogen gas, allowing for both dissociation and ionization. Chemical species  $N_2$ ,  $N_2^{+1}$ ,  $N_2^{-1}$ ,  $N$ ,  $N^{+1}$ , and  $N^{+2}$  are allowed to form. (Higher states of ionization would be required at higher temperatures.) In addition, ionization is included by treating the electrons as another chemical species. The analytic option is used for each of the species; therefore, no libraries are required for execution. The Hugoniot is calculated for an initial state of 300°K and 2 psi and sent to plot file TP3PLT. The option CONC PLOT is used to compute the molar composition of the gas as a function of temperature on the Hugoniot and send it to the plot file.





**Figure 16.3.** Calculated Hugoniot temperature vs. particle velocity for shocked nitrogen gas, from test problem 3.



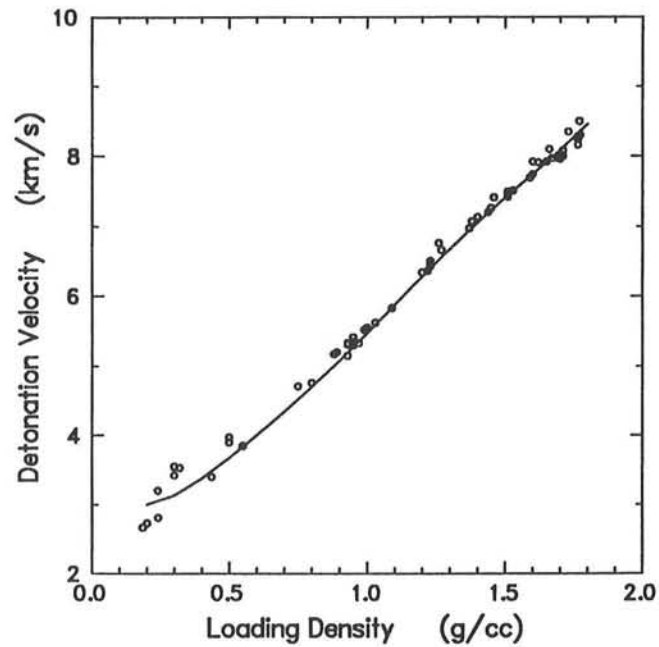
**Figure 16.4.** Calculated molecular concentrations vs. Hugoniot temperature for shocked nitrogen gas, from test problem 3.

The output file TP3OUT for this example is listed in Appendix G. Figures 16.3 and 16.4 show plots of the calculated Hugoniot temperature and concentrations made from the plot file with the GRAPH utility.

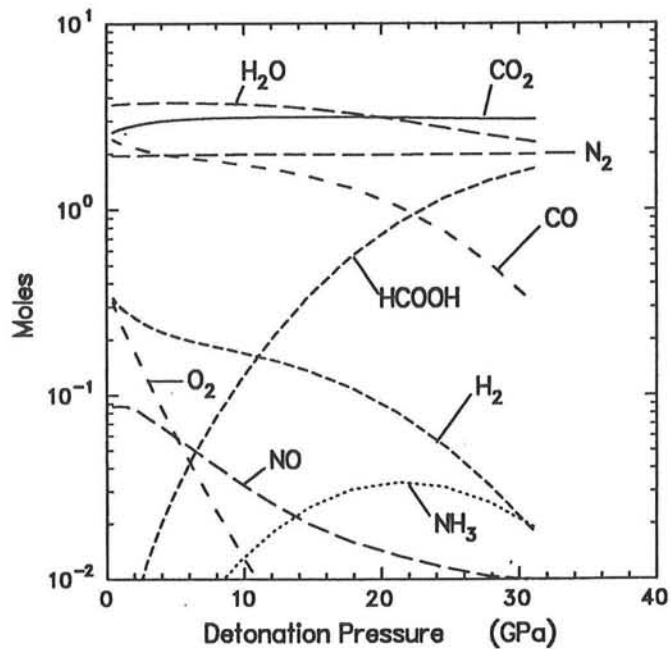
## 16.4 Test Problem 4: Detonation Properties of an Explosive

This calculation uses the mixture-equilibrium model to compute the EOS for the detonation products of the explosive PETN; the theory is described in Refs. [68] and [88]. Ten chemical species are allowed to form in the mixture - carbon dioxide ( $\text{CO}_2$ ), nitrogen ( $\text{N}_2$ ), water ( $\text{H}_2\text{O}$ ), carbon monoxide ( $\text{CO}$ ), formic acid ( $\text{HCOOH}$ ), oxygen ( $\text{O}_2$ ), hydrogen ( $\text{H}_2$ ), nitric oxide ( $\text{NO}$ ), ammonia ( $\text{NH}_3$ ), and methane ( $\text{CH}_4$ ). In this example, EOS tables are used for the mixture components; these tables are obtained from the ASCII file AESPS, which is first converted to the binary form using the ASC2BIN option. (The EOS tables on this file were also constructed using the PANDA code.) The code first computes the CJ state as a function of loading density. Then it computes the molar concentrations as a function of CJ pressure.

The output file TP4OUT for this example is listed in Appendix H. Figures 16.5 and 16.6 show plots of the calculated detonation velocity and concentrations made from the plot file with the GRAPH utility. The theoretical predictions are in very good agreement with the experimental detonation velocity data. Other examples of the model and calculations for other explosives are discussed in Refs. [68] and [88].



**Figure 16.5.** Detonation velocity vs. loading density for PETN explosive, from test problem 4. The solid curve is the calculated result. The circles are experimental data from Ref. [89].



**Figure 16.6.** Molar concentrations of detonation products for PETN as functions of detonation pressure, from test problem 4.

## 17. Acknowledgements

Development of the PANDA code and the theoretical models therein has extended over a period of more than 20 years. During that time, I have been blessed with the opportunity to collaborate with many capable scientists, to benefit from numerous discussions with both theoreticians and experimentalists, and to receive encouragement and support from several particularly fine individuals. The complete list of names is much too long to be printed here. Besides, I do not want to risk leaving someone off of it! However, I must give credit to G. T. Rood and S. P. Lyon, who worked with me in developing the phase transition and mixture-chemical equilibrium models. I am also grateful to A. Farnsworth and T. G. Trucano for their critical reviews of the manuscript. Finally, the love and support of my wife Donna have been indispensable to me in this work, just as in everything else I do.

# Appendix A

## Separation of Degrees of Freedom

The PANDA model for one-component solids and fluids assumes that the various degrees of freedom can be decoupled from one another in computing thermodynamic properties. In certain cases, this approximation results in an EOS that is the sum of several terms, each of which is computed separately from the others. In other cases, such as the liquid model, the decoupling leads to a more complicated result. This approximation is much poorer when chemical reactions and phase transitions are present, and the MIX and TRN models are available for such cases.

This Appendix discusses the conditions under which two “subsystems” can be decoupled in the computation of thermal averages (ensemble averages in statistical mechanics). These ideas are applied to the separation between electronic and nuclear degrees of freedom [26] and to the separation between translational and vibrational-rotational degrees of freedom [54].

### A.1 Decoupling of Two Subsystems

The first step in the problem is to group the coordinates of the system into two subsystems, having coordinates  $\vec{x}$  and  $\vec{y}$ , respectively. The only cases considered are those where the quantum-mechanical Hamiltonian has the following form.

$$H = K_1(\vec{x}) + K_2(\vec{y}) + U(\vec{x}, \vec{y}), \quad (\text{A.1})$$

where  $K_1$  and  $K_2$  are the kinetic energy operators for the two subsystems and  $U$  is a potential energy function that couples them. (For example, let  $\vec{x}$  be the coordinates of the nuclei and let  $\vec{y}$  be the coordinates of the electrons.)

The partition function for the system is defined by

$$Q = \text{Tr}[\exp(-\beta H)], \quad (\text{A.2})$$

where  $\text{Tr}$  denotes the trace. Because any set of basis functions can be used in Eq. A.2, the trace can be computed in two steps. An operator  $Z$  is defined by

$$Q = \sum_n \int \Psi_n^*(\vec{x}) \exp(-\beta Z) \Psi_n(\vec{x}) d\vec{x} = \text{Tr}_1[\exp(-\beta Z)], \quad (\text{A.3})$$

where

$$\exp(-\beta Z) = Tr_2[\exp(-\beta H)]. \quad (\text{A.4})$$

Here the  $\Psi_n(\vec{x})$  are any complete set of functions on the subspace of coordinates  $\vec{x}$ , and  $Tr_1$  denotes the trace over that subspace.  $Tr_2$  denotes the trace over the subspace of coordinates  $\vec{y}$ .  $Z$  operates only on the coordinates  $\vec{x}$ , but it contains all information about the subspace  $\vec{y}$  needed for computing ensemble averages.

The following definitions are made.

$$H_2 = K_2(\vec{y}) + U(\vec{x}, \vec{y}) \quad (\text{A.5})$$

and

$$\exp(-\beta A_2) = Tr_2[\exp(-\beta H_2)]. \quad (\text{A.6})$$

$H_2$  is the Hamiltonian for a system in which the coordinates  $\vec{x}$  are held fixed, and  $A_2$  is the Helmholtz free energy for this system. Note that  $A_2$  depends parametrically both on  $\beta$  and on the coordinates  $\vec{x}$ . The average value of an operator  $F$  on subspace 2 is defined as

$$\langle F \rangle = Tr_2[\exp(\beta W_2)F] \quad (\text{A.7})$$

and

$$W_2 = H_2 - A_2. \quad (\text{A.8})$$

Now an expansion variable  $\xi$  is introduced so that

$$\exp[-\beta \xi Z(\xi)] = \langle \exp(\beta \xi W_2) \exp(-\beta \xi H) \rangle. \quad (\text{A.9})$$

$Z(\xi)$  is expanded as a power series

$$Z(\xi) = \sum_{k=0}^{\infty} \xi^k Z_k, \quad (\text{A.10})$$

where the limit  $\xi \rightarrow 1$  recovers Eq. A.4. From Eq. A.9 it is found that the  $k = 0$  term vanishes. To obtain higher order terms, the exponentials on both sides of Eq. A.9 are expanded, and terms having equal powers of  $\xi$  are equated. The leading term in  $Z$  is

$$Z_1 = K_1(\vec{x}) + A_2(\vec{x}; \beta). \quad (\text{A.11})$$

The remaining terms in the expansion involve the commutators of  $K_1$  with  $U$  and  $A_2$ . For example, the second order term is

$$Z_2 = -\frac{\beta}{2} \langle K_1 W_2 - W_2 K_1 \rangle. \quad (\text{A.12})$$

$Z_2$  and higher order terms in Eq. A.10 form a power series in  $\beta h^2$ . Hence they vanish at high temperatures ( $\beta \rightarrow 0$ ). They also vanish if the coordinates  $\vec{x}$  of subsystem 1 can be treated classically ( $h \rightarrow 0$ ), even in cases where a fully quantum-mechanical treatment of

subsystem 2 must be retained. This conclusion is important for the separation between electronic and nuclear degrees of freedom [26].

The above results show that, if two subsystems are chosen in the proper way, they can be decoupled in the calculation of thermal averages. Holding the coordinates  $\vec{y}$  fixed, the energy levels, the partition function, and the free energy  $A_2$  of subsystem 2 are determined. Then  $Z$ , defined by Eq. A.11, is used as the effective Hamiltonian for subsystem 1 and a second ensemble average is done. This approach is similar to the Born-Oppenheimer approximation [90], which applies to a single quantum state of the system.

## A.2 Separating Electronic and Nuclear Motions

Thermal averages over the electronic and nuclear degrees of freedom can be decoupled by letting  $\vec{x}$  be the coordinates of the nuclei and  $\vec{y}$  be the coordinates of the electrons. The Helmholtz free energy of the electrons,  $A_2(\vec{x}, \beta)$ , is calculated with the positions of the nuclei held fixed, and this free energy function serves as the effective potential for motion of the nuclei. Hence the electrons and nuclei are coupled mechanically but not thermally. An important result, also obtained by Zwanzig [26], is that the classical limit can be applied to the nuclear degrees of freedom while the electrons are still treated quantum-mechanically.

According to the above analysis, the effective forces between the nuclei depend upon temperature. Unfortunately, there is no complete theory for calculating this temperature dependence at the present time, and it is necessary to make additional approximations. Two cases are considered, one in which the effect of temperature is very important and one in which it is not.

When *chemical reactions* occur, the resulting changes in the electronic structure of the system have a profound effect upon the motion of the nuclei. If a molecule dissociates, vibrational and rotational degrees of freedom are converted into translational degrees of freedom, and the effect upon the thermodynamic properties is significant. In this case, it is useful to regard the system as a mixture of several chemical species. A change in the chemical composition is actually a change in the electronic state of the system as a whole, and a simple separation of the electronic and nuclear terms cannot be made. However, such systems can be treated by the methods of chemical equilibrium, using the MIX option in PANDA that is described in Ch. 10. The dimer model (Ch. 7) is also a simple example of a chemical equilibrium model.

With the exception of the dimer corrections, the one-component solid and liquid models apply to a *single chemical species*. In this case, it is useful to write

$$A_2 = \Phi(\vec{x}) + A_\theta(\vec{x}; \beta), \quad (\text{A.13})$$



where  $\Phi$  is the energy of the ground electronic state of the system, and  $A_\theta$  is the contribution from thermal electronic excitation and ionization. The thermal term  $A_\theta$  is usually small for temperatures  $< \approx 10^4 K$ . Hence the motion of the nuclei is determined mostly by the electronic ground state at low temperatures.

For the purpose of discussion, define coordinates  $\vec{x}_0$  that describe “average” positions of the nuclei. Then

$$A_\theta(\vec{x}; \beta) = A_e(\rho, \beta) + \Delta A_\theta(\vec{x}; \beta), \quad (\text{A.14})$$

$$A_e(\rho, \beta) = A_\theta(\vec{x}_0; \beta). \quad (\text{A.15})$$

Here  $A_e$  is a “static” term, which does not affect the nuclear motion. This quantity can be computed using the PANDA ionization equilibrium model discussed in Ch. 9 or another electronic structure model such as INFERNO [57]. However, the calculation of  $\Delta A_\theta$ , which depends upon displacements of the nuclei about their average positions, is a difficult problem that has not been solved in any general way. As noted above, this term is not important at low temperatures. Furthermore, the detailed structure of the potential is not important at high temperatures, where the ideal gas limit is reached. Therefore, for lack of a better approximation, the term  $\Delta A_e$  is ignored in PANDA.

Using the results derived above, the partition function for the system is given by

$$Q = \exp(-\beta A_e) \text{Tr}_1[\exp(-\beta H_n)] = \exp[-\beta(A_n + A_e)] \quad (\text{A.16})$$

and

$$H_n = K_1(\vec{x}) + \Phi(\vec{x}) + \Delta A_\theta(\vec{x}; \beta) \approx K_1(\vec{x}) + \Phi(\vec{x}). \quad (\text{A.17})$$

Here  $\text{Tr}_1$  denotes the trace over the subspace of the nuclear coordinates,  $H_n$  is the effective nuclear Hamiltonian, and  $A_n$  is the corresponding free energy of the nuclei.

In certain cases, it is useful to split  $A_n$  into a “cold curve”, or static term, and a “nuclear” term, in a manner analogous to Eq. A.14. For solids, the usual method is to expand the potential  $\Phi$  in a Taylor series about the equilibrium nuclear positions in the lattice. This approach is not useful for fluids, for which there are no equilibrium lattice positions. Therefore, PANDA does not define separate cold curve and nuclear positions in the fluid EOS model.

### A.3 The Two-Temperature EOS

As noted above, the Helmholtz free energy of a single chemical species can be written as the sum of a nuclear and and electronic term.

$$A(\rho, \beta) = A_n(\rho, \beta) + A_e(\rho, \beta). \quad (\text{A.18})$$

The two subsystems are coupled *mechanically*, in that the electronic motions determine the effective forces between the nuclei. However, they are not coupled *thermally*, because both  $A_n$  and  $A_e$  are given by averages of a Boltzmann factor over their respective

subspaces. Therefore it is reasonable to consider cases where the two subsystems have different thermal equilibria and hence different characteristic temperatures [25].

$$A(\rho, \beta_n, \beta_e) = A_n(\rho, \beta_n) + A_e(\rho, \beta_e). \quad (\text{A.19})$$

Here  $A_e$  includes only the static part of the thermal electronic contribution to the EOS. Because  $A_n$  is determined by the ground state function  $\Phi$ , this term corresponds to a system where the nuclei can become excited but the electrons remain in the ground state.

It is not clear how to extend these conclusions to cases where chemical reactions occur; such problems are beyond the scope of this report.

## A.4 Separating Vibrational-Rotational and Translational Motions

The preceding arguments can also be used to decouple translational degrees of freedom. This problem is discussed in Ref. [54], and only the conclusions are given here. The first step is to hold the molecular centers of mass fixed and calculate the vibrational and rotational free energy  $A_{vr}$ .  $A_{vr}$  can be split into an unperturbed part, which corresponds to noninteracting molecules, and a perturbed part, which is the effective potential for the molecular centers of mass. Hence the translational contribution to the EOS has the same form as the EOS for a system of spherical molecules. Effects from hindered vibration and rotation are included in the effective potential. This potential is independent of temperature, if the temperature is high enough to disorder the molecular orientations. At low temperatures, where rotational motion is hindered, the temperature dependence may be important.

# Appendix B

## Calculation of Cold Curves From Hugoniot Data

This Appendix discusses the methods used in PANDA to estimate zero-temperature isotherms from shock-wave measurements (see Sec. 3.2). These techniques are similar to those described by Rice, *et. al.* [27] and by Grover *et. al.* [28]. A Mie-Grüneisen EOS is assumed, which relates pressure, internal energy, and density as follows.

$$P(\rho, E) = P_c(\rho) + \rho\gamma(\rho)[E - E_c(\rho)]. \quad (\text{B.1})$$

The Grüneisen parameter  $\gamma$  depends only on density. It is related to the Debye or Einstein temperature  $\Theta$  by Eq. 4.17 (see Sec. 4.5). The pressure and energy on the cold curve are related by

$$P_c(\rho) = \rho^2(dE_c/d\rho). \quad (\text{B.2})$$

On the Hugoniot, the shock velocity  $U_s$ , particle velocity  $U_p$ , and the pressure, energy, and density are related by the conservation laws of mass, momentum, and energy. These relations yield

$$U_s = \rho U_p / (\rho - \rho_0), \quad (\text{B.3})$$

$$P_H = P_0 + \rho_0 U_s U_p, \quad (\text{B.4})$$

and

$$E_H = E_0 + (1/2)(P_H + P_0)(1/\rho_0 - 1/\rho), \quad (\text{B.5})$$

where  $\rho_0$ ,  $P_0$ , and  $E_0$  are the initial conditions. In PANDA,  $\rho_0$  is taken to be the reference density RHOREF, specified with the SET BAS command (Sec. 2.2),  $P_0 = 0$ , and  $E_0$  is computed from RHOREF and TREF using the solid lattice vibration model specified by the user. The Hugoniot curve is given by the polynomial, Eq. 3.1. Note that these equations do not give a physically meaningful solution for  $P_H$  and  $E_H$  above a certain density limit. The high-density portion of the cold curve must be constructed by some other technique such as the TFD match (Sec. 3.10).

### B.1 Analytic Formula for $\gamma$ and $\Theta$

When  $\gamma$  and  $\Theta$  are specified by analytic expressions ( $\text{IGRN} = 2, 3$ , or  $4$  in Ch. 4), the zero-temperature isotherm is computed as follows. Equations 4.17, B.1, and B.2 can

be written

$$P_H - \rho\gamma E_H = P_c - \rho\gamma E_c = \rho^2 \frac{d}{d\rho} \left( \frac{E_c}{\Theta} \right). \quad (\text{B.6})$$

Integrating the above gives

$$E_c(\rho) = \Theta(\rho) \left[ \frac{E_c(\rho_0)}{\Theta(\rho_0)} + \int_{\rho_0}^{\rho} \frac{P_H(x) - x\gamma(x)E_H(x)}{x^2\Theta(x)} dx \right]. \quad (\text{B.7})$$

The quantities  $E_c$  and  $P_c$  are tabulated on a standard grid, along with interpolation coefficients obtained by fitting a local polynomial to the data. Integration of Eq. B.7 as a function of density continues until the Hugoniot asymptote is reached or until the third derivative of the pressure becomes negative. (*Note:* In certain cases, the formula specified for  $\gamma$  and  $\Theta$  will be inconsistent with the shock data. Then no solution to the problem will exist.) Finally, the code sets the energy zero, in accordance with the convention, and computes the solid binding energy for extrapolating off the table.

## B.2 Cold Curve Formula for $\gamma$ and $\Theta$

If the user specifies the cold curve formula for  $\gamma$  and  $\Theta$  (IGRN=1 in Ch. 4), a self-consistent solution for  $\gamma$ ,  $\Theta$ ,  $P_c$ , and  $E_c$  is required. Using Eqs. 4.19 and B.1,

$$\frac{P_H - P_c}{\rho(E_H - E_c)} = \gamma = -\frac{1}{6} + \frac{1}{2} \frac{\beta'_c - 2\tau_g\beta_c/3}{\beta_c - 2\tau_gP_c/3}. \quad (\text{B.8})$$

The energy, pressure, and derivatives are obtained at points on a standard density grid. The interpolation formulas for energy and pressure are given by Eqs. 3.14 and 3.15. The terms  $P_c(\rho_i)$ ,  $A_1(i)$ , and  $A_2(i)$  are determined by requiring that the pressure and two of its derivatives be continuous functions, and  $A_3(i)$  is obtained from Eq. B.8. In this way, Eq. B.8 is integrated from point to point along the density grid until the Hugoniot asymptote is reached or the third derivative of the pressure becomes negative. Finally, the code sets the energy zero and determines the binding energy.

## B.3 Interpolation and Extrapolation

To compute the cold curve from the calculated tables, the code interpolates using Eqs. 3.14 and 3.15. At low densities, it extrapolates off the tables. The LJ match (Sec. 3.8) should be used to guarantee that the cold curve has the correct behavior in this region. For high densities, the TFD match (Sec. 3.7) is done automatically. If the user sets  $\rho_{TFD} = 0$ , the match is made at  $\rho_{MAX}$ , the highest density reached in the integration. The user can specify a different value, but the code will insure that  $\rho_{TFD} \leq \rho_{MAX}$ .

# Appendix C

## Corrections to the Einstein and Debye Models

The standard Einstein and Debye models are derived using the harmonic approximation for the lattice vibration model [39]. This approximation breaks down for highly excited states, where the amplitudes of vibration are large and the lattice is unstable. This appendix describes a model in which these unstable levels are excluded in calculating thermodynamic properties.

The energy levels of a harmonic oscillator are given by

$$\epsilon_n = (n + 1/2)h\omega. \quad (\text{C.1})$$

Consider a molecule of mass  $W$  oscillating within its Wigner-Seitz cell. The cell radius is given by

$$4\pi N_0 r_s^3 / 3 = W / \rho. \quad (\text{C.2})$$

The potential energy at the cell boundary is

$$u(r_s) = 2\pi^2 W \omega^2 r_s^2. \quad (\text{C.3})$$

Define  $n_c$  to be the quantum number for which  $\epsilon_n = u(r_s)$ . Then

$$n_c \approx \frac{2\pi^2 k}{h^2} \Theta W \left( \frac{3W}{4\pi N_0 \rho} \right)^{2/3} = 5.5638 \times 10^{-3} \frac{\Theta W^{5/3}}{\rho^{2/3}}, \quad (\text{C.4})$$

where  $\Theta = h\omega/k$ . A level with  $n > n_c$  would be unstable because the molecule would have sufficient energy to escape from its Wigner-Seitz cell. In this model, the sum over vibrational levels is cut off for quantum numbers  $n > \lambda n_c$ , where  $\lambda$  is chosen so that the solid is always less stable than the fluid at high temperatures. Because the cutoff corrections so obtained turn out to be very small for temperatures below the melting curve, the exact choice for  $\lambda$  makes little difference in the solid regime.

### C.1 The Einstein Model

In the Einstein model, a lattice of  $N_0$  molecules has  $3N_0$  degrees of freedom, each of which has the same frequency. The partition function is

$$Q = q_\omega^{3N_0} \quad (\text{C.5})$$

and

$$q_\omega = \sum_{n < \lambda n_c} \exp[-\beta(n + 1/2)h\omega] = \exp(-\beta h\omega/2) \frac{1 - \exp(-\lambda n_c \beta h\omega)}{1 - \exp(-\beta h\omega)}. \quad (\text{C.6})$$

The Helmholtz free energy is

$$A = -\frac{1}{\beta} \ln Q = \frac{R}{W} \left[ \frac{3}{2} \Theta + 3T \ln(1 - e^{-\Theta/T}) - 3T \ln(1 - e^{-T_\lambda/T}) \right], \quad (\text{C.7})$$

where

$$T_\lambda = \lambda n_c \Theta = 5.5638 \times 10^{-3} \lambda \frac{\Theta^2 W^{5/3}}{\rho^{2/3}}. \quad (\text{C.8})$$

The internal energy and pressure are found from the thermodynamic relations

$$E = A - T \left( \frac{\partial A}{\partial T} \right)_\rho = \frac{R}{W} \left( \frac{3}{2} \Theta + \frac{3\Theta}{e^{\Theta/T} - 1} - \frac{3T_\lambda}{e^{T_\lambda/T} - 1} \right), \quad (\text{C.9})$$

and

$$P = \rho^2 \left( \frac{\partial A}{\partial \rho} \right)_T = \frac{R}{W} \rho \left[ \gamma \left( \frac{3}{2} \Theta + \frac{3\Theta}{e^{\Theta/T} - 1} \right) - \left( 2\gamma - \frac{2}{3} \right) \frac{3T_\lambda}{e^{T_\lambda/T} - 1} \right], \quad (\text{C.10})$$

where  $\gamma$  is the Grüneisen function, given by Eq. 4.17. The entropy is given by Eq. 4.12.

$T_\lambda$  has the same density dependence as the Lindemann melting temperature [91] but is  $\approx 100$ -200 times higher. At high temperatures ( $T \approx T_\lambda$ ) the energy and pressure reach a maximum and begin to decrease, as they would if the lattice structure and potential energy wells for the molecules were to break down. In this region, PANDA switches to formulas similar to those for an ideal gas.

$$A = \frac{RT}{W} [\alpha_0 - \ln(W/\rho) - \frac{3}{2} \ln(WT)], \quad (\text{C.11})$$

$$E = 3RT/2W, \quad (\text{C.12})$$

and

$$P = RT\rho/W. \quad (\text{C.13})$$

The switch to these gas formulas is made at  $T = 0.795905T_\lambda$ , which makes E and P continuous. The free energy and entropy are made continuous by setting  $\alpha_0 = 9.13465 - 1.5 \ln \lambda$ . Choosing  $\lambda = 0.5$  insures that the free energy is always greater than that for the fluid. *Note:* Derivatives of the thermodynamic functions are not continuous at the switchover point.

## C.2 The Debye Model

In the Debye model, the  $3N_0$  oscillators do not have the same frequency. The free energy becomes

$$A = -\frac{3N_0}{\beta} \int f_\omega \ln q_\omega d\omega, \quad (\text{C.14})$$

where  $f_\omega$  is the normalized phonon frequency spectrum,

$$\int f_\omega d\omega = 1. \quad (\text{C.15})$$

Making the usual approximation [39] that  $f_\omega \propto \omega^2$  for  $\omega \leq \omega_D$ , along with Eq. C.6, then

$$A = \frac{R}{W} \left[ \frac{9}{8} \Theta + TF(\Theta/T) - TF(T_\lambda/T) \right], \quad (\text{C.16})$$

where

$$F(x) = \frac{9}{x^3} \int_0^x y^2 \ln(1 - e^{-y}) dy = 3 \ln(1 - e^{-x}) - D(x), \quad (\text{C.17})$$

and  $D(x)$  is given by Eq. 4.5. The internal energy and pressure are

$$E = \frac{R}{W} \left[ \frac{9}{8} \Theta + 3TD(\Theta/T) - 3TD(T_\lambda/T) \right], \quad (\text{C.18})$$

$$P = \frac{R\rho}{W} (\gamma [\frac{9}{8} \Theta + 3TD(\Theta/T)] - (6\gamma - 2)TD(T_\lambda/T)). \quad (\text{C.19})$$

The high-temperature behavior is similar to that for the Einstein model. PANDA switches over to the ideal gas expressions, Eqs. C.11 - C.13, for  $T \geq 0.584597T_\lambda$ , making the internal energy and pressure continuous. The free energy and entropy are made continuous by setting  $\alpha_0 = 8.69060 - 1.5 \ln \lambda$ .



## Appendix D

### Monomer-Dimer Equilibrium

Dimer corrections to the EOS of a one-component fluid (Chs. 2 and 7) are computed using a simplified model that is exact in the low density limit. Consider an ideal gas, consisting of  $N_1$  monomer atoms and  $N_2$  dimer molecules in a volume  $V$ . The partition function for this system is [92]

$$Q = \frac{1}{N_1!N_2!} [V(\frac{2\pi W_1 kT}{h^2})^{3/2} q_e]^{N_1} [V(\frac{2\pi W_2 kT}{h^2})^{3/2} q_{vr}]^{N_2}, \quad (\text{D.1})$$

where  $q_e$  is the electronic partition function for the monomer,  $q_{vr}$  is the vibration-rotation partition function for the dimer,  $W_1$  is the atomic weight, and  $W_2 = 2W_1$  is the molecular weight. The total number of atomic nuclei in the system is

$$N = N_1 + 2N_2. \quad (\text{D.2})$$

The monomer fraction is defined as the number of atomic nuclei in the monomer form.

$$f = N_1/N. \quad (\text{D.3})$$

For a fully dissociated gas,  $f = 1$ , Eq. D.1 becomes

$$Q \rightarrow [\frac{eV}{N}(\frac{2\pi W_1 kT}{h^2})^{3/2} q_e]^N \equiv \exp[-\beta A_M(\rho, T)], \quad (\text{D.4})$$

where  $A_M(\rho, T)$  is the Helmholtz free energy of a monomer gas. For  $f = 0$ , Eq. D.1 becomes

$$Q \rightarrow [\frac{2eV}{N}(\frac{2\pi W_2 kT}{h^2})^{3/2} q_{vr}]^{N/2} \equiv \exp[-\beta A_D(\rho, T)], \quad (\text{D.5})$$

where  $A_D(\rho, T)$  is the Helmholtz free energy of a dimer gas. Hence Eq. D.1 can be written

$$Q = \frac{\exp[-f\beta A_M - (1-f)\beta A_D]}{f^f N^f (1-f)^{(1-f)N/2}}. \quad (\text{D.6})$$

The free energy for the mixture is

$$A(\rho, T) = fA_M(\rho, T) + (1-f)A_D(\rho, T) + \frac{RT}{W_1} [f \ln f + \frac{1}{2} \ln(1-f)]. \quad (\text{D.7})$$

The monomer fraction is obtained by minimizing the free energy.

$$(\partial A / \partial f)_{\rho, T} = 0. \quad (\text{D.8})$$

The result is

$$f = \frac{1}{2}(\sqrt{x^2 + 4x} - x) \quad (\text{D.9})$$

and

$$x = \exp [2W_1(A_D - A_M)/RT - 1]. \quad (\text{D.10})$$

The internal energy and pressure are

$$E(\rho, T) = A - T(\partial A / \partial T)_\rho = f E_M(\rho, T) + (1 - f) E_D(\rho, T) \quad (\text{D.11})$$

and

$$P(\rho, T) = \rho^2(\partial A / \partial \rho)_T = f P_M(\rho, T) + (1 - f) P_D(\rho, T). \quad (\text{D.12})$$

In Eqs. D.11 and D.12, terms containing derivatives of  $f$  drop out because of Eq. D.8.

The electron partition function,  $q_e$ , can have a significant effect upon the amount of dimer formation. In sodium vapor, for example,  $q_e = 2$  at low temperatures where the valence 3s electron can have two spin states. In this limit,  $q_e$  does not affect the energy  $E_M$  or the pressure  $P_M$  of the monomer component, but it does affect the formation of molecules. In PANDA, Eq. D.7 is rewritten

$$A(\rho, T) = f A_M(\rho, T) + (1 - f)[A_D(\rho, T) + \frac{RT}{W_1} \ln Q_e] + \frac{RT}{W_1} [f \ln f + \frac{1}{2} \ln (1 - f)], \quad (\text{D.13})$$

where  $Q_e$ , a constant, is an approximation to the electron partition function. Including this term puts the electron spin factor into the dimer EOS instead of the monomer. The monomer fraction is given by Eq. D.9, and Eq. D.10 becomes

$$x = \exp [2W_1(A_D - A_M)/RT + 2 \ln Q_e - 1]. \quad (\text{D.14})$$

If the electronic term has been included in constructing the monomer EOS, then the electron factor should be set  $Q_e = 1$ . If an electron term was not included, the parameter  $Q_e$  provides a simple way to obtain the correct amount of dissociation.

Although the above equations have been derived for the case of an ideal gas, they are used in PANDA for the entire fluid range. This approximation gives reasonable results for hydrogen, even at high densities [62]. It should be satisfactory for calculating dimer corrections to the EOS, because the molecules form only at low densities where both the monomer and dimer components are almost perfect gases.

# Appendix E

## Output File for Test Problem 1

THE PANDA CODE, CTSS VERSION 2.01, 12/06/89  
SANDIA NATIONAL LABORATORIES, ALBUQUERQUE, NM 87185

PROBLEM: TESTPROB\_1 DATE: 12/06/89

OPTION?

@tp1inp

```
!
! PANDA Test Problem 1 - Aluminum equation of state.
! Sets up both solid and fluid models. Computes cold curve from the
! Hugoniot, using Debye model and Chart-D formula for the Gruneisen
! parameter. Uses TFD model for thermal electronic contribution.
! Computes EOS point, Hugoniots, etc., for both models.
! Generates tabular EOS for the fluid. Reads fluid EOS back in and
! recomputes various things.
!
! In addition to the output file, this problem produces a plot file, a
! mesh file called 'almsh', a binary library file called 'b3711', and
! an ASCII library file called 'a3711'.
!
! Setup for solid and fluid
mod sol crv=1 nuc=1 tel=1
SOLID-LIQUID MODEL - ENTER MOLECULAR FORMULA
al
  MOLES = 1.0000e+00, Z = 1.3000e+01, AW = 2.6982e+01
  FZ = 1.3000e+01, FW = 2.6982e+01, ZAV = 1.3000e+01
ENTER ECHO,RHOREF,TREF,GAMREF,DEBREF,CB,PSSN
12.12 2.7 298 2.15 395
COLD CURVE - ENTER ICLD,RTFD,RLJ,FACLJ
1 0 2.3 1.0
LATTICE VIBRATION MODEL- ENTER INPT,IGRN,RV,TG,GAML
1 3 0 0 .6666666667
ENTER 3-PARAMETER FIT TO US-UP CURVE
5.31 1.39
ELECTRONIC TERM - ENTER ENTROPY FILE NAME OR OPTION
tfd
OPTION?
mod liq crs=1 tel=1
CRIS MODEL - ENTER BEXP,EFAC,QFAC,TMIN,NGS,NZI,EPS,DR,DT,XG
0 .6688
  BFAC,BEXP,EFAC,QFAC = 4.908e+00 4.908e+00 6.688e-01 0.000e+00
  TMIN,RFAC,NGS,NZI = 8.175e+02 6.296e-01 1000 1
  EPS,DR,DT,XG = 1.000e-05 1.000e-02 1.000e-02 4.000e-01
OPTION?
! Solid and fluid EOS at a few points
eos sol
  RHO(G/CC) T(K) P(GPA) E(MJ/KG) S(MJ/KGK) CS(KM/S)
ENTER DENSITY (G/CC) AND TEMPERATURE (K)
2.7 298
  2.7000e+00 2.9800e+02 2.4939e-03 3.0833e-01 1.0232e-03 5.3095e+00
2.7 1000
  2.7000e+00 1.0000e+03 3.6995e+00 9.5870e-01 2.1342e-03 5.5704e+00
3.5 298
  3.5000e+00 2.9800e+02 3.4059e+01 1.3295e+00 6.2582e-04 7.7086e+00
3.5 1000
  3.5000e+00 1.0000e+03 3.7683e+01 1.9516e+00 1.6779e-03 7.8292e+00
```

```

OPTION?
eos liq
  RHO(G/CC)      T(K)      P(GPA)      E(MJ/KG)      S(MJ/KGK)      CS(KM/S)
ENTER DENSITY (G/CC) AND TEMPERATURE (K)
2.4 1000
  2.4000e+00  1.0000e+03 -1.5034e+00  1.2340e+00  2.4507e-03  4.6210e+00
2.4 5000
  2.4000e+00  5.0000e+03  8.6554e+00  5.1155e+00  3.9915e-03  5.3224e+00
2.4 10000
  2.4000e+00  1.0000e+04  2.0330e+01  1.0476e+01  4.7295e-03  6.0445e+00
3.5 1000
  3.5000e+00  1.0000e+03  4.2976e+01  2.6454e+00  2.0113e-03  8.0086e+00
3.5 5000
  3.5000e+00  5.0000e+03  5.6705e+01  6.6264e+00  3.6186e-03  8.3952e+00
3.5 10000
  3.5000e+00  1.0000e+04  7.2974e+01  1.2081e+01  4.3702e-03  8.7588e+00

OPTION?
! Isobars for solid and fluid
isob sol 0 298 933.25 2 2.7
  RHO(G/CC)      T(K)      E(MJ/KG)      S(MJ/KGK)      H(MJ/KG)      A(MJ/KG)
  2.6999e+00  2.9800e+02  3.0835e-01  1.0233e-03  3.0835e-01  3.4205e-03
  2.5629e+00  9.3325e+02  9.6297e-01  2.1748e-03  9.6297e-01 -1.0666e+00

OPTION?
isob liq 0 933.25 0 1 2.5
  RHO(G/CC)      T(K)      E(MJ/KG)      S(MJ/KGK)      H(MJ/KG)      A(MJ/KG)
  2.4786e+00  9.3325e+02  1.1288e+00  2.3524e-03  1.1287e+00 -1.0666e+00

OPTION?
! Vaporization curve and critical point
vap liq
  T(K)      PV(GPA)      RV(G/CC)      RL(G/CC)      EV(MJ/KG)      EL(MJ/KG)
ENTER T1, T2, NT, AND GUESSES FOR RVAP AND RLIQ
3000 7000 9 1.e-4 2
  3.0000e+03  4.2759e-04  3.6790e-04  2.1959e+00  1.4806e+01  3.3512e+00
  3.5000e+03  2.0295e-03  1.5341e-03  2.1132e+00  1.5062e+01  3.9675e+00
  4.0000e+03  6.6147e-03  4.5260e-03  2.0249e+00  1.5321e+01  4.6169e+00
  4.5000e+03  1.6876e-02  1.0794e-02  1.9305e+00  1.5565e+01  5.3048e+00
  5.0000e+03  3.6585e-02  2.2732e-02  1.8284e+00  1.5771e+01  6.0405e+00
  5.5000e+03  7.1286e-02  4.5292e-02  1.7170e+00  1.5905e+01  6.8372e+00
  6.0000e+03  1.3020e-01  8.9090e-02  1.5934e+00  1.5929e+01  7.7149e+00
  6.5000e+03  2.2667e-01  1.6357e-01  1.4541e+00  1.5859e+01  8.7025e+00
  7.0000e+03  3.6889e-01  2.6580e-01  1.2912e+00  1.5696e+01  9.8558e+00

OPTION?
crit liq 7000 .26 1.3
      ESTIMATE OF CRITICAL POINT PARAMETERS
  RHO(G/CC)      T(K)      P(GPA)      E(MJ/KG)      S(MJ/KGK)      VOL(CC/G)
  7.2657e-01  7.8461e+03  7.1806e-01  1.3629e+01  5.4502e-03  1.3763e+00

OPTION?
plot tp1plt
OPTION?
! Melting curve
melt
TYPE SKIP OR ENTER LABEL FOR PLOT FILE
Theoretical melting curve for aluminum
  T(K)      PL(GPA)      RL(G/CC)      RS(G/CC)      EL(MJ/KG)      ES(MJ/KG)
ENTER T1, T2, NT, AND GUESSES FOR RLIQ AND RSOL
950 0 1 2.5 2.6
  9.5000e+02  2.2858e-01  2.4866e+00  2.5692e+00  1.1411e+00  9.7425e-01
1000 2000 6
  1.0000e+03  9.5784e-01  2.5119e+00  2.5897e+00  1.1786e+00  1.0078e+00
  1.2000e+03  4.7570e+00  2.6360e+00  2.6992e+00  1.3593e+00  1.1512e+00
  1.4000e+03  1.0628e+01  2.8032e+00  2.8595e+00  1.6340e+00  1.3561e+00
  1.6000e+03  1.9292e+01  3.0099e+00  3.0646e+00  2.0746e+00  1.7051e+00
  1.8000e+03  3.1059e+01  3.2417e+00  3.2982e+00  2.7292e+00  2.2602e+00
  2.0000e+03  4.5836e+01  3.4838e+00  3.5440e+00  3.6017e+00  3.0359e+00

```

```

2500 5000 6
2.5000e+03 9.4849e+01 4.0928e+00 4.1619e+00 6.6301e+00 5.8285e+00
3.0000e+03 1.7056e+02 4.7850e+00 4.8465e+00 1.1314e+01 1.0145e+01
3.5000e+03 1.9232e+03 1.1488e+01 1.1535e+01 8.9275e+01 8.7291e+01
4.0000e+03 2.9442e+03 1.3745e+01 1.3819e+01 1.2338e+02 1.2138e+02
4.5000e+03 3.9788e+03 1.5644e+01 1.5736e+01 1.5372e+02 1.5163e+02
5.0000e+03 5.0821e+03 1.7402e+01 1.7509e+01 1.8288e+02 1.8066e+02
6000 10000 5
6.0000e+03 7.5471e+03 2.0713e+01 2.0845e+01 2.4012e+02 2.3758e+02
7.0000e+03 1.0401e+04 2.3899e+01 2.4051e+01 2.9746e+02 2.9456e+02
8.0000e+03 1.3663e+04 2.7024e+01 2.7194e+01 3.5546e+02 3.5219e+02
9.0000e+03 1.7360e+04 3.0128e+01 3.0315e+01 4.1450e+02 4.1084e+02
1.0000e+04 2.1608e+04 3.3299e+01 3.3503e+01 4.7603e+02 4.7195e+02

```

OPTION?

! Hugoniot calculations

hug sol 2.6999 0 .30835 305 2320 12

TYPE SKIP OR ENTER LABEL FOR PLOT FILE

Theoretical Hugoniot for solid aluminum

RHO(G/CC)	T(K)	P(GPA)	E(MJ/KG)	UP(KM/S)	US(KM/S)
2.7296e+00	3.0500e+02	8.5487e-01	3.1007e-01	5.8726e-02	5.3917e+00
2.7973e+00	3.2165e+02	2.9269e+00	3.2723e-01	1.9431e-01	5.5790e+00
2.9550e+00	3.7161e+02	8.4807e+00	4.4391e-01	5.2069e-01	6.0326e+00
3.1139e+00	4.5488e+02	1.5221e+01	6.8313e-01	8.6579e-01	6.5115e+00
3.2524e+00	5.7145e+02	2.2144e+01	1.0050e+00	1.1804e+00	6.9484e+00
3.3748e+00	7.2132e+02	2.9165e+01	1.3884e+00	1.4698e+00	7.3496e+00
3.4855e+00	9.0450e+02	3.6317e+01	1.8243e+00	1.7412e+00	7.7253e+00
3.5875e+00	1.1210e+03	4.3648e+01	2.3084e+00	2.0000e+00	8.0833e+00
3.6829e+00	1.3708e+03	5.1187e+01	2.8384e+00	2.2495e+00	8.4280e+00
3.7728e+00	1.6539e+03	5.8948e+01	3.4127e+00	2.4917e+00	8.7623e+00
3.8582e+00	1.9703e+03	6.6951e+01	4.0307e+00	2.7285e+00	9.0883e+00
3.9400e+00	2.3200e+03	7.5213e+01	4.6922e+00	2.9611e+00	9.4079e+00

OPTION?

huge liq 2.6999 0 .30835 7.2907 20.0 12

TYPE SKIP OR ENTER LABEL FOR PLOT FILE

Theoretical Hugoniot for liquid aluminum

RHO(G/CC)	T(K)	P(GPA)	E(MJ/KG)	UP(KM/S)	US(KM/S)
4.2024e+00	2.5850e+03	1.0545e+02	7.2907e+00	3.7369e+00	1.0452e+01
4.2122e+00	2.6368e+03	1.0660e+02	7.3957e+00	3.7649e+00	1.0487e+01
4.2410e+00	2.7934e+03	1.1000e+02	7.7108e+00	3.8477e+00	1.0589e+01
4.2875e+00	3.0573e+03	1.1561e+02	8.2360e+00	3.9819e+00	1.0753e+01
4.3498e+00	3.4315e+03	1.2333e+02	8.9713e+00	4.1624e+00	1.0974e+01
4.4255e+00	3.9213e+03	1.3306e+02	9.9166e+00	4.3837e+00	1.1243e+01
4.5123e+00	4.5296e+03	1.4470e+02	1.1072e+01	4.6398e+00	1.1551e+01
4.6081e+00	5.2591e+03	1.5816e+02	1.2437e+01	4.9253e+00	1.1894e+01
4.7109e+00	6.1120e+03	1.7336e+02	1.4013e+01	5.2354e+00	1.2264e+01
4.8189e+00	7.0904e+03	1.9022e+02	1.5799e+01	5.5660e+00	1.2658e+01
4.9308e+00	8.1988e+03	2.0869e+02	1.7794e+01	5.9137e+00	1.3071e+01
5.0452e+00	9.4384e+03	2.2874e+02	2.0000e+01	6.2756e+00	1.3500e+01

OPTION?

! Release isentrope

isen liq 6112 4.7109 2.5 25 1 5.2354

TYPE SKIP OR ENTER LABEL FOR PLOT FILE

Release isentrope for fluid aluminum through 173 GPa shock point

RHO(G/CC)	T(K)	P(GPA)	E(MJ/KG)	S(MJ/KGK)	CS(KM/S)
4.7109e+00	6.1120e+03	1.7336e+02	1.4013e+01	3.5738e-03	1.1112e+01
4.6188e+00	6.0216e+03	1.6217e+02	1.3303e+01	3.5738e-03	1.0927e+01
4.5267e+00	5.9302e+03	1.5136e+02	1.2613e+01	3.5738e-03	1.0741e+01
4.4345e+00	5.8369e+03	1.4091e+02	1.1942e+01	3.5738e-03	1.0554e+01
4.3424e+00	5.7425e+03	1.3084e+02	1.1293e+01	3.5738e-03	1.0363e+01
4.2503e+00	5.6465e+03	1.2113e+02	1.0664e+01	3.5738e-03	1.0166e+01
4.1582e+00	5.5486e+03	1.1179e+02	1.0058e+01	3.5738e-03	9.9651e+00
4.0661e+00	5.4489e+03	1.0283e+02	9.4732e+00	3.5738e-03	9.7591e+00
3.9739e+00	5.3465e+03	9.4247e+01	8.9117e+00	3.5738e-03	9.5471e+00
3.8818e+00	5.2417e+03	8.6040e+01	8.3738e+00	3.5738e-03	9.3321e+00
3.7897e+00	5.1353e+03	7.8202e+01	7.8599e+00	3.5738e-03	9.1126e+00
3.6976e+00	5.0269e+03	7.0741e+01	7.3708e+00	3.5738e-03	8.8852e+00

3.6055e+00	4.9164e+03	6.3657e+01	6.9068e+00	3.5738e-03	8.6520e+00
3.5133e+00	4.8038e+03	5.6949e+01	6.4687e+00	3.5738e-03	8.4132e+00
3.4212e+00	4.6885e+03	5.0616e+01	6.0570e+00	3.5738e-03	8.1687e+00
3.3291e+00	4.5713e+03	4.4655e+01	5.6722e+00	3.5738e-03	7.9183e+00
3.2370e+00	4.4523e+03	3.9064e+01	5.3148e+00	3.5738e-03	7.6611e+00
3.1448e+00	4.3312e+03	3.3841e+01	4.9854e+00	3.5738e-03	7.3974e+00
3.0527e+00	4.2081e+03	2.8982e+01	4.6845e+00	3.5738e-03	7.1283e+00
2.9606e+00	4.0833e+03	2.4479e+01	4.4126e+00	3.5738e-03	6.8530e+00
2.8685e+00	3.9568e+03	2.0329e+01	4.1701e+00	3.5738e-03	6.5710e+00
2.7764e+00	3.8282e+03	1.6524e+01	3.9576e+00	3.5738e-03	6.2828e+00
2.6842e+00	3.6979e+03	1.3056e+01	3.7753e+00	3.5738e-03	5.9879e+00
2.5921e+00	3.5661e+03	9.9180e+00	3.6238e+00	3.5738e-03	5.6854e+00
2.5000e+00	3.4323e+03	7.1007e+00	3.5035e+00	3.5738e-03	5.3703e+00

OPTION?

! Compute TFD cold curve

tfd curve 100

TYPE SKIP OR ENTER LABEL FOR PLOT FILE

Aluminum cold curve from TFD theory

RHO(G/CC)	P(GPA)	P(FIT)	VOL(CC/G)	Z0
4.2408e+00	1.0000e+02	9.9999e+01	2.3580e-01	1.3000e+01
5.4876e+00	2.1544e+02	2.1544e+02	1.8223e-01	1.3000e+01
7.2020e+00	4.6416e+02	4.6416e+02	1.3885e-01	1.3000e+01
9.5842e+00	1.0000e+03	1.0000e+03	1.0434e-01	1.3000e+01
1.2928e+01	2.1544e+03	2.1544e+03	7.7349e-02	1.3000e+01
1.7669e+01	4.6416e+03	4.6415e+03	5.6595e-02	1.3000e+01
2.4453e+01	1.0000e+04	9.9999e+03	4.0894e-02	1.3000e+01
3.4250e+01	2.1544e+04	2.1545e+04	2.9197e-02	1.3000e+01
4.8515e+01	4.6416e+04	4.6415e+04	2.0612e-02	1.3000e+01
6.9464e+01	1.0000e+05	1.0000e+05	1.4396e-02	1.3000e+01

OPTION?

no plot

OPTION?

! Set up a mesh for a 301 table

mesh sol

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF

! Densities

1.e-6 1.e-4 7 2

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF

1.e-4 .74 15 2

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF

.74 2.6999 15 1

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF

2.72 5 15 3 298

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF

5 10 5 3 298

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF

10 1000 4 2

DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF

! Temperatures

0 298 4 1

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF

298 7600 16 1

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF

7300 7500 2 1

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF

8000 1.e4 4 1

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF

1.e4 1.e6 9 3 2.7

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF

1.e6 1.e8 7 2

TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF

OPTION?

save mesh alms



```

OPTION?
! Make Sesame EOS table for fluid
slib liq
ENTER ID NUMBER FOR TABLE TYPE
201
ENTER FZ, FW, PREF, TREF, AND GUESS FOR RHOREF
13 26.98154 0 933.25 2.4
COMPUTED STANDARD STATE - RHOREF, BREF = 2.47858e+00 5.62205e+01
ENTER ID NUMBER FOR TABLE TYPE
301
MAKE MAXWELL CONSTRUCTIONS? (YES/NO)
y
ENTER TSPALL AND GUESS OF RSPALL
2500 2
      T(K)      RV(G/CC)      RL(G/CC)      PV(GPA)      PL(GPA)
ENTER TMIN, TMAX, AND GUESSES FOR RLO AND RUP
2500 7855 1.e-4 2
2.7320e+03 1.3799e-04 2.2380e+00 1.4772e-04 9.5969e-05
3.2188e+03 7.2672e-04 2.1604e+00 8.9710e-04 9.3506e-04
3.7056e+03 2.4735e-03 2.0776e+00 3.4215e-03 3.4287e-03
4.1924e+03 6.4511e-03 1.9894e+00 9.7147e-03 9.7029e-03
4.6792e+03 1.4240e-02 1.8949e+00 2.2610e-02 2.2582e-02
5.1660e+03 2.8667e-02 1.7926e+00 4.6089e-02 4.6012e-02
5.6528e+03 5.5744e-02 1.6807e+00 8.6137e-02 8.6102e-02
6.1396e+03 1.0688e-01 1.5563e+00 1.5281e-01 1.5285e-01
6.6264e+03 1.8665e-01 1.4158e+00 2.5816e-01 2.5818e-01
7.1132e+03 2.9445e-01 1.2491e+00 4.0803e-01 4.0805e-01
7.3000e+03 3.4762e-01 1.1733e+00 4.7740e-01 4.7740e-01
7.5000e+03 4.1815e-01 1.0778e+00 5.5907e-01 5.5907e-01
7.6000e+03 4.6244e-01 1.0209e+00 6.0253e-01 6.0252e-01
ENTER TMIN, TMAX, AND GUESSES FOR RLO AND RUP

ENTER ID NUMBER FOR TABLE TYPE
0
ENTER MATID, DATE, BINLIB, AND ASCLIB
3711 120489 b3711 a3711
OPTION?
list b3711
      1 MATERIALS ON B3711 FILE, DATED 120489, VERSION 1
      ID      FZ      FW      RHOREF      TREF      TABLE TYPES
3711 1.300e+01 2.698e+01 2.479e+00 9.333e+02 201. 301.
OPTION?
! Read table back in and recompute various things for comparison
mod liq crs=0 tel=0 tab=1
ENTER MATERIAL NUMBER AND FILE NAME FOR EOS TABLE
3711 b3711
OPTION?
eos liq
      RHO(G/CC)      T(K)      P(GPA)      E(MJ/KG)      S(MJ/KGK)      CS(KM/S)
ENTER DENSITY (G/CC) AND TEMPERATURE (K)
2.4 1000
2.4000e+00 1.0000e+03 -1.5148e+00 1.2376e+00 2.4412e-03 4.6721e+00
2.4 5000
2.4000e+00 5.0000e+03 8.6547e+00 5.1154e+00 3.9914e-03 5.3216e+00
2.4 10000
2.4000e+00 1.0000e+04 2.0329e+01 1.0476e+01 4.7295e-03 6.0485e+00
3.5 1000
3.5000e+00 1.0000e+03 4.2942e+01 2.6480e+00 1.9849e-03 8.0162e+00
3.5 5000
3.5000e+00 5.0000e+03 5.6703e+01 6.6263e+00 3.6186e-03 8.3960e+00
3.5 10000
3.5000e+00 1.0000e+04 7.2975e+01 1.2081e+01 4.3702e-03 8.7612e+00

OPTION?
isob liq 0 933.25 0 1 2.5
      RHO(G/CC)      T(K)      E(MJ/KG)      S(MJ/KGK)      H(MJ/KG)      A(MJ/KG)
2.4790e+00 9.3325e+02 1.1321e+00 2.3449e-03 1.1322e+00 -1.0562e+00

```



OPTION?

huge liq 2.6999 0 .30835 7.2907 20.0 12

RHO(G/CC)	T(K)	P(GPA)	E(MJ/KG)	UP(KM/S)	US(KM/S)
4.2024e+00	2.5854e+03	1.0545e+02	7.2907e+00	3.7369e+00	1.0452e+01
4.2122e+00	2.6370e+03	1.0660e+02	7.3957e+00	3.7649e+00	1.0487e+01
4.2410e+00	2.7930e+03	1.1000e+02	7.7108e+00	3.8477e+00	1.0589e+01
4.2875e+00	3.0564e+03	1.1561e+02	8.2360e+00	3.9819e+00	1.0753e+01
4.3498e+00	3.4306e+03	1.2333e+02	8.9713e+00	4.1624e+00	1.0974e+01
4.4255e+00	3.9203e+03	1.3306e+02	9.9166e+00	4.3837e+00	1.1243e+01
4.5123e+00	4.5298e+03	1.4470e+02	1.1072e+01	4.6398e+00	1.1551e+01
4.6081e+00	5.2598e+03	1.5816e+02	1.2437e+01	4.9253e+00	1.1894e+01
4.7109e+00	6.1100e+03	1.7336e+02	1.4013e+01	5.2354e+00	1.2264e+01
4.8190e+00	7.0885e+03	1.9022e+02	1.5799e+01	5.5660e+00	1.2658e+01
4.9308e+00	8.1974e+03	2.0869e+02	1.7794e+01	5.9137e+00	1.3070e+01
5.0452e+00	9.4398e+03	2.2874e+02	2.0000e+01	6.2756e+00	1.3500e+01

OPTION?

isen liq 6112 4.7109 2.5 25 1 5.2354

RHO(G/CC)	T(K)	P(GPA)	E(MJ/KG)	S(MJ/KGK)	CS(KM/S)
4.7109e+00	6.1120e+03	1.7336e+02	1.4015e+01	3.5741e-03	1.1109e+01
4.6188e+00	6.0231e+03	1.6218e+02	1.3304e+01	3.5741e-03	1.0928e+01
4.5267e+00	5.9321e+03	1.5136e+02	1.2614e+01	3.5741e-03	1.0742e+01
4.4345e+00	5.8388e+03	1.4092e+02	1.1944e+01	3.5741e-03	1.0554e+01
4.3424e+00	5.7442e+03	1.3084e+02	1.1295e+01	3.5741e-03	1.0362e+01
4.2503e+00	5.6481e+03	1.2113e+02	1.0666e+01	3.5741e-03	1.0166e+01
4.1582e+00	5.5499e+03	1.1180e+02	1.0059e+01	3.5741e-03	9.9647e+00
4.0661e+00	5.4492e+03	1.0284e+02	9.4747e+00	3.5741e-03	9.7587e+00
3.9739e+00	5.3467e+03	9.4254e+01	8.9133e+00	3.5741e-03	9.5480e+00
3.8818e+00	5.2427e+03	8.6043e+01	8.3749e+00	3.5741e-03	9.3326e+00
3.7897e+00	5.1367e+03	7.8207e+01	7.8611e+00	3.5741e-03	9.1120e+00
3.6976e+00	5.0281e+03	7.0746e+01	7.3723e+00	3.5741e-03	8.8850e+00
3.6055e+00	4.9175e+03	6.3662e+01	6.9080e+00	3.5741e-03	8.6523e+00
3.5133e+00	4.8047e+03	5.6953e+01	6.4696e+00	3.5741e-03	8.4143e+00
3.4212e+00	4.6897e+03	5.0618e+01	6.0581e+00	3.5741e-03	8.1687e+00
3.3291e+00	4.5727e+03	4.4659e+01	5.6734e+00	3.5741e-03	7.9181e+00
3.2370e+00	4.4534e+03	3.9066e+01	5.3159e+00	3.5741e-03	7.6615e+00
3.1448e+00	4.3322e+03	3.3844e+01	4.9863e+00	3.5741e-03	7.3976e+00
3.0527e+00	4.2091e+03	2.8984e+01	4.6855e+00	3.5741e-03	7.1281e+00
2.9606e+00	4.0844e+03	2.4483e+01	4.4138e+00	3.5741e-03	6.8528e+00
2.8685e+00	3.9575e+03	2.0332e+01	4.1711e+00	3.5741e-03	6.5718e+00
2.7764e+00	3.8289e+03	1.6525e+01	3.9582e+00	3.5741e-03	6.2829e+00
2.6842e+00	3.6987e+03	1.3059e+01	3.7762e+00	3.5741e-03	5.9869e+00
2.5921e+00	3.5670e+03	9.9217e+00	3.6249e+00	3.5741e-03	5.6859e+00
2.5000e+00	3.4330e+03	7.1023e+00	3.5042e+00	3.5741e-03	5.3742e+00

OPTION?

end

# Appendix F

## Output File for Test Problem 2

THE PANDA CODE, UCOS VERSION 2.01, 04/23/91  
SANDIA NATIONAL LABORATORIES, ALBUQUERQUE, NM 87185

PROBLEM: TESTPROB\_2 DATE: 04/23/91

OPTION?

@tp2inp

```
!
! PANDA Test Problem 2 - Equation of state for dry calcium carbonate.
! EOS tables are generated for 4 solid phases and for the liquid phase
! of CaCO3. Then the phase transition option (MOD TRN) is called to
! compute the phase diagram and generate a multiphase EOS table. The
! RESET command is used to do the entire calculation in a single run.
!
```

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!
! Several files are generated during the calculation. The file TP2PLT
! is a plot file of the phase diagram. Files BINLIB and ASCLIB are
! binary and ASCII libraries containing EOS tables for the individual
! phases and for the multiphase EOS. Temporary binary library files and
! a file for the density-temperature mesh are also created.
!
```

```
! EOS for calcite I.
!
```

mod sol crv=1 nuc=1 vrt=1 esft=-.1746997

SOLID-LIQUID MODEL - ENTER MOLECULAR FORMULA

ca[1]c[1]o[3]

MOLES = 1.0000E+00, Z = 2.0000E+01, AW = 4.0080E+01

MOLES = 1.0000E+00, Z = 6.0000E+00, AW = 1.2011E+01

MOLES = 3.0000E+00, Z = 8.0000E+00, AW = 1.5999E+01

FZ = 5.0000E+01, FW = 1.0009E+02, ZAV = 1.0669E+01

ENTER ECOH,RHOREF,TREF,GAMREF,DEBREF,CB,PSSN

28 2.71 298 .50 310

COLD CURVE - ENTER ICLD,RTFD,RLJ,FACLJ

3 6

ENTER EXP-N CONSTANTS - EBZPE,RZRO,BZRO,A4

28 2.721 73.6 .3333333333

LATTICE VIBRATION MODEL- ENTER INPT,IGRN,RV,TG,GAML

-1 2

ROTATIONAL TERM - ENTER IRT,BRT,SRT,WRT

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

105 1 100 .90 1

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

150 2 100 .90 1 2500

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

310 3 50 .50 1

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

1086 1 25 .50 1

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

872 1 25 .50 1

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

1420 2 25 .50 1

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

712 2 25 .50 1

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

```

OPTION?
isob sol 0 298 0 1 3
  RHO(G/CC)      T(K)      E(MJ/KG)      S(MJ/KGK)      H(MJ/KG)      A(MJ/KG)
  2.7101E+00    2.9800E+02  4.8566E-08  9.1651E-04  2.4845E-06  -2.7312E-01
OPTION?
eos sol
  RHO(G/CC)      T(K)      P(GPA)      E(MJ/KG)      S(MJ/KGK)      CS(KM/S)
ENTER DENSITY (G/CC) AND TEMPERATURE (K)
2.71 298
  2.7100E+00    2.9800E+02 -3.8799E-03  8.0407E-06  9.1653E-04  5.1747E+00
OPTION?
mesh sol
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.1 2.7 4 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.71 2.75 5 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.75 4.1 28 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
0 0 0 0
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 298 5 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
400 2500 15 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 0 0 0
OPTION?
slib sol
ENTER ID NUMBER FOR TABLE TYPE
301
MAKE MAXWELL CONSTRUCTIONS? (YES/NO)
n
ENTER ID NUMBER FOR TABLE TYPE
0
ENTER MATID, DATE, BINLIB, AND ASCLIB
401 030689 b401 asclib
OPTION?
!
! EOS for calcite II.
!
reset
OPTION?
mod sol crv=1 nuc=1 vrt=1 esft=-.1567141
SOLID-LIQUID MODEL - ENTER MOLECULAR FORMULA
ca[1]c[1]o[3]
  MOLES = 1.0000E+00, Z = 2.0000E+01, AW = 4.0080E+01
  MOLES = 1.0000E+00, Z = 6.0000E+00, AW = 1.2011E+01
  MOLES = 3.0000E+00, Z = 8.0000E+00, AW = 1.5999E+01
  FZ = 5.0000E+01, FW = 1.0009E+02, ZAV = 1.0669E+01
ENTER ECOH,RHOREF,TREF,GAMREF,DEBREF,CB,PSSN
28 2.71 298 0.5 260
COLD CURVE - ENTER ICLD,RTFD,RLJ,FACLJ
4 5.5 1.2 .3333333333
ENTER NAME OF INPUT FILE
tty
ENTER DENSITY AND PRESSURE, POINT BY POINT
! Tabular cold curve follows
! First section of curve - EBZPE=28, RZR0=2.75, BZR0=30, PWR=1/3
  1.0000E+00 -5.9870E+00
  1.1250E+00 -6.4457E+00
  1.2500E+00 -6.7745E+00
  1.3750E+00 -6.9683E+00
  1.5000E+00 -7.0240E+00
  1.6250E+00 -6.9400E+00
  1.7500E+00 -6.7157E+00
  1.8750E+00 -6.3513E+00

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2.0000E+00 -5.8478E+00
2.1250E+00 -5.2066E+00
2.2500E+00 -4.4292E+00
2.3750E+00 -3.5176E+00
2.5000E+00 -2.4741E+00
2.6250E+00 -1.3007E+00
2.7500E+00 -5.2452E-06
! Second section of curve - EBZPE=28, RZR0=2.80, BZR0=66, PWR=1/3
3.0546E+00 6.9745E+00
3.2174E+00 1.2501E+01
3.3889E+00 1.9270E+01
3.5695E+00 2.7496E+01
3.7598E+00 3.7423E+01
3.9602E+00 4.9332E+01
4.1713E+00 6.3541E+01
4.3937E+00 8.0409E+01
4.6279E+00 1.035E+02
4.8746E+00 1.2382E+02
5.1344E+00 1.5134E+02
5.4081E+00 1.8350E+02
5.6964E+00 2.2097E+02
6.0000E+00 2.6446E+02
0 0
LATTICE VIBRATION MODEL- ENTER INPT,IGRN,RV,TG,GAML
! Nuclear terms
-1 2
ROTATIONAL TERM - ENTER IRT,BRT,SRT,WRT

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
105 1 100 .90 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
150 2 100 .90 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
310 3 50 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
1086 1 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
872 1 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
1420 2 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
712 2 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

OPTION?
isob sol 0 298 0 1 3
RHO(G/CC) T(K) E(MJ/KG) S(MJ/KGK) H(MJ/KG) A(MJ/KG)
2.7252E+00 2.9800E+02 1.3674E-02 9.3770E-04 1.3678E-02 -2.6576E-01
OPTION?
isob sol 1.45 298 0 1 3
RHO(G/CC) T(K) E(MJ/KG) S(MJ/KGK) H(MJ/KG) A(MJ/KG)
2.8209E+00 2.9800E+02 1.6775E-02 9.2076E-04 5.3079E-01 -2.5761E-01
OPTION?
isob sol 2 298 0 1 3
RHO(G/CC) T(K) E(MJ/KG) S(MJ/KGK) H(MJ/KG) A(MJ/KG)
2.8494E+00 2.9800E+02 2.1415E-02 9.1587E-04 7.2332E-01 -2.5151E-01
OPTION?
eos sol
RHO(G/CC) T(K) P(GPA) E(MJ/KG) S(MJ/KGK) CS(KM/S)
ENTER DENSITY (G/CC) AND TEMPERATURE (K)
2.8 298
2.8000E+00 2.9800E+02 1.0768E+00 1.4520E-02 9.2439E-04 4.1621E+00
- -
OPTION?
mesh sol
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.70 2.75 6 1

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DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.75 4.3 32 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
0 0 0 0
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 298 5 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
400 2500 15 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
2650 1.e4 22 2
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 0 0 0
OPTION?
slib sol
ENTER ID NUMBER FOR TABLE TYPE
301
MAKE MAXWELL CONSTRUCTIONS? (YES/NO)
n
ENTER ID NUMBER FOR TABLE TYPE
0
ENTER MATID, DATE, BINLIB, AND ASCLIB
402 030689 b402 asclib
OPTION?
!
! EOS for calcite III.
!
reset
OPTION?
mod sol crv=1 nuc=1 vrt=1 esft=-.1568141
SOLID-LIQUID MODEL - ENTER MOLECULAR FORMULA
ca[1]c[1]o[3]
  MOLES = 1.0000E+00, Z = 2.0000E+01, AW = 4.0080E+01
  MOLES = 1.0000E+00, Z = 6.0000E+00, AW = 1.2011E+01
  MOLES = 3.0000E+00, Z = 8.0000E+00, AW = 1.5999E+01
  FZ = 5.0000E+01, FW = 1.0009E+02, ZAV = 1.0669E+01
ENTER ECOH,RHOREF,TREF,GAMREF,DEBREF,CB,PSSN
28 2.845 298 2.3 380
COLD CURVE - ENTER ICLD,RTFD,RLJ,FACLJ
3 6
ENTER EXP-N CONSTANTS - EBZPE,RZRO,BZRO,A4
28 2.899 67.5 .333333333
LATTICE VIBRATION MODEL- ENTER INPT,IGRN,RV,TG,GAML
-1 2
ROTATIONAL TERM - ENTER IRT,BRT,SRT,WRT

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
105 1 100 1.0 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
155 2 100 1.0 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
244 3 50 2.3 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
1100 1 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
860 1 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
1510 2 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
718 2 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

OPTION?
isob sol 0 298 0 1 3
  RHO(G/CC)    T(K)      E(MJ/KG)    S(MJ/KGK)    H(MJ/KG)    A(MJ/KG)
  2.8576E+00  2.9800E+02  2.4727E-02  8.9067E-04  2.4728E-02  -2.4069E-01
OPTION?
isob sol 1.74 298 0 1 3

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      RHO(G/CC)      T(K)      E(MJ/KG)      S(MJ/KGK)      H(MJ/KG)      A(MJ/KG)
2.9328E+00  2.9800E+02  2.2224E-02  8.5673E-04  6.1553E-01  -2.3308E-01
OPTION?
isob sol 2 298 0 1 3
      RHO(G/CC)      T(K)      E(MJ/KG)      S(MJ/KGK)      H(MJ/KG)      A(MJ/KG)
2.9434E+00  2.9800E+02  2.3142E-02  8.5205E-04  7.0263E-01  -2.3077E-01
OPTION?
eos sol
      RHO(G/CC)      T(K)      P(GPA)      E(MJ/KG)      S(MJ/KGK)      CS(KM/S)
ENTER DENSITY (G/CC) AND TEMPERATURE (K)
2.845 298
2.8450E+00  2.9800E+02  -2.7770E-01  2.6703E-02  8.9658E-04  4.7382E+00
2.933 298
2.9330E+00  2.9800E+02  1.7460E+00  2.2241E-02  8.5662E-04  4.9844E+00
2.943 298
2.9430E+00  2.9800E+02  1.9895E+00  2.3099E-02  8.5224E-04  5.0120E+00
- -
OPTION?
mesh sol
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.71 2.75 5 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.75 4.1 28 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
0 0 0 0
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 298 5 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
400 2500 15 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 0 0 0
OPTION?
slib sol
ENTER ID NUMBER FOR TABLE TYPE
301
MAKE MAXWELL CONSTRUCTIONS? (YES/NO)
n
ENTER ID NUMBER FOR TABLE TYPE
0
ENTER MATID, DATE, BINLIB, AND ASCLIB
403 030689 b403 asclib
OPTION?
!
! EOS for aragonite.
!
reset
OPTION?
mod sol crv=1 nuc=1 vrt=1 esft=-.1882141
SOLID-LIQUID MODEL - ENTER MOLECULAR FORMULA
ca[1]c[1]o[3]
      MOLES = 1.0000E+00, Z = 2.0000E+01, AW = 4.0080E+01
      MOLES = 1.0000E+00, Z = 6.0000E+00, AW = 1.2011E+01
      MOLES = 3.0000E+00, Z = 8.0000E+00, AW = 1.5999E+01
      FZ = 5.0000E+01, FW = 1.0009E+02, ZAV = 1.0669E+01
ENTER ECOH,RHOREF,TREF,GAMREF,DEBREF,CB,PSSN
28 2.93 298 2.3 420
COLD CURVE - ENTER ICLD,RTFD,RLJ,FACLJ
3 6
ENTER EXP-N CONSTANTS - EBZPE,RZRO,BZRO,A4
28 2.973 69 .3333333333
LATTICE VIBRATION MODEL- ENTER INPT,IGRN,RV,TG,GAML
-1 2
ROTATIONAL TERM - ENTER IRT,BRT,SRT,WRT

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
105 1 100 1.0 1

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VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
155 2 100 1.0 1 7500
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
244 3 50 2.3 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
1100 1 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
860 1 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
1510 2 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
718 2 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

OPTION?
isob sol 0 298 0 1 3
  RHO(G/CC)      T(K)      E(MJ/KG)      S(MJ/KGK)      H(MJ/KG)      A(MJ/KG)
  2.9298E+00    2.9800E+02 -4.0345E-03  8.7937E-04 -4.0270E-03 -2.6609E-01
OPTION?
eos sol
  RHO(G/CC)      T(K)      P(GPA)      E(MJ/KG)      S(MJ/KGK)      CS(KM/S)
ENTER DENSITY (G/CC) AND TEMPERATURE (K)
2.93 298
  2.9300E+00    2.9800E+02  3.8108E-03 -4.0576E-03  8.7929E-04  4.7659E+00

OPTION?
mesh sol
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.71 2.75 5 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.75 4.1 28 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
4.1 9.7 10 3 298
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
9.7 64 7 3 298
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
64 1000 4 2
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
0 0 0 0
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 298 5 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
400 2500 15 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
2650 1.e4 22 2
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
1.e4 1.e6 9 2
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 0 0 0
OPTION?
slib sol
ENTER ID NUMBER FOR TABLE TYPE
301
MAKE MAXWELL CONSTRUCTIONS? (YES/NO)
n
ENTER ID NUMBER FOR TABLE TYPE
0
ENTER MATID, DATE, BINLIB, AND ASCLIB
406 030689 b406 asclib
OPTION?
!
! Make mesh for calcite table - use aragonite for pressure increments
!
mesh sol
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
.05 1.3 3 1

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DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
1.3 2.7 8 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.71 2.75 5 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
2.75 4.1 28 1
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
4.1 9.7 10 3 298
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
9.7 64 7 3 298
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
64 1000 4 2
DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE,TREF
0 0 0 0
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 298 5 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
400 2500 15 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
2650 1.e4 22 2
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
1.e4 1.e6 9 2
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE,RREF
0 0 0 0
OPTION?
save mesh mshdat
OPTION?
!
! EOS for liquid CaCO3.
!
reset
OPTION?
! first calculate rotational constant for CO3 ion
brot
ENTER SYMBOL AND COORDINATES FOR EACH ATOM
c 0 0 0
o 0 1.280 0
o 1.1085 -.64 0
o -1.1085 -.64 0

ROTATIONAL CONSTANT = 3.40286E-01 1/CM
OPTION?
mod liq crs=1 vrt=1 esft=-.1746997
SOLID-LIQUID MODEL - ENTER MOLECULAR FORMULA
ca[.5]c[.5]o[1.5]
MOLES = 5.0000E-01, Z = 2.0000E+01, AW = 4.0080E+01
MOLES = 5.0000E-01, Z = 6.0000E+00, AW = 1.2011E+01
MOLES = 1.5000E+00, Z = 8.0000E+00, AW = 1.5999E+01
FZ = 2.5000E+01, FW = 5.0045E+01, ZAV = 1.0669E+01
ENTER ECOH,RHOREF,TREF,GAMREF,DEBREF,CB,PSSN
28 2.75 298
COLD CURVE - ENTER ICLD,RTFD,RLJ,FAC LJ
3 6
ENTER EXP-N CONSTANTS - EBZPE,RZRO,BZRO,A4
28 2.75 60.8 .3333333333
CRIS MODEL - ENTER BEXP,EFAC,QFAC,TMIN,NGS,NZI,EPS,DR,DT,XG
- .025 - 1500 10
BFAC,BEXP,EFAC,QFAC = 4.287E+00 4.287E+00 2.500E-02 0.000E+00
TMIN,RFAC,NGS,NZI = 1.500E+03 6.182E-01 10 1
EPS,DR,DT,XG = 1.000E-05 1.000E-02 1.000E-02 4.000E-01
ROTATIONAL TERM - ENTER IRT,BRT,SRT,WRT
2 .34 3 .5
ROTATIONAL TERM - ENTER IRT,BRT,SRT,WRT

VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
! note that degeneracies of vibrational modes are multiplied by 1/2

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1086 .5 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
872 .5 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
1420 1 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB
712 1 25 .50 1
VIBRATIONAL TERM - ENTER WVB,GVB,FVB,GAM,PVB,TVB

OPTION?
read mesh mshdat
OPTION?
slib liq
ENTER ID NUMBER FOR TABLE TYPE
301
MAKE MAXWELL CONSTRUCTIONS? (YES/NO)
n
ENTER ID NUMBER FOR TABLE TYPE
0
ENTER MATID, DATE, BINLIB, AND ASCLIB
407 030689 b407 asclib
OPTION?
!
! Compute multiphase EOS.
!
reset
OPTION?
mod trn
ENTER PHASE SEARCH PARAMETERS - RREF,RCRT,TCRT,PCPS,NCPS,ERR

ENTER MATERIAL NUMBER, FILE NAME, AND ENERGY SHIFT
401 b401
ENTER MATERIAL NUMBER, FILE NAME, AND ENERGY SHIFT
402 b402
ENTER MATERIAL NUMBER, FILE NAME, AND ENERGY SHIFT
403 b403
ENTER MATERIAL NUMBER, FILE NAME, AND ENERGY SHIFT
406 b406 .1255
ENTER MATERIAL NUMBER, FILE NAME, AND ENERGY SHIFT
407 b407
ENTER MATERIAL NUMBER, FILE NAME, AND ENERGY SHIFT

5 PHASES SUCCESSFULLY LOADED FOR MODEL
OPTION?
plot tp2plt
OPTION?
phase diag
TYPE SKIP OR ENTER LABEL FOR PLOT FILE
Calcite phase diagram including metastable phases
      T(K)      P(GPA)      N1      N2      RH01(G/CC)  RH02(G/CC)
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE
0 5000 101 1
TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE

0.0000E+00  1.1931E+00  1.0000E+00  3.0000E+00  2.7624E+00  2.9385E+00
0.0000E+00  1.3096E+01  3.0000E+00  4.0000E+00  3.3312E+00  3.4074E+00
5.0000E+01  1.2114E+00  1.0000E+00  3.0000E+00  2.7628E+00  2.9388E+00
5.0000E+01  1.3095E+01  3.0000E+00  4.0000E+00  3.3310E+00  3.4071E+00
1.0000E+02  1.2509E+00  1.0000E+00  3.0000E+00  2.7633E+00  2.9382E+00
1.0000E+02  1.3123E+01  3.0000E+00  4.0000E+00  3.3308E+00  3.4070E+00
1.5000E+02  1.3532E+00  1.0000E+00  3.0000E+00  2.7653E+00  2.9375E+00
1.5000E+02  1.3156E+01  3.0000E+00  4.0000E+00  3.3290E+00  3.4052E+00
2.0000E+02  1.4561E+00  1.0000E+00  3.0000E+00  2.7670E+00  2.9354E+00
2.0000E+02  1.3199E+01  3.0000E+00  4.0000E+00  3.3265E+00  3.4026E+00
2.5000E+02  1.5027E+00  1.0000E+00  2.0000E+00  2.7665E+00  2.8272E+00
2.5000E+02  1.5992E+00  2.0000E+00  3.0000E+00  2.8322E+00  2.9343E+00
2.5000E+02  1.3276E+01  3.0000E+00  4.0000E+00  3.3242E+00  3.4003E+00

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3.0000E+02	1.4023E+00	1.0000E+00	2.0000E+00	2.7607E+00	2.8182E+00
3.0000E+02	1.8632E+00	2.0000E+00	3.0000E+00	2.8424E+00	2.9375E+00
3.0000E+02	1.3338E+01	3.0000E+00	4.0000E+00	3.3209E+00	3.3969E+00
3.5000E+02	1.3204E+00	1.0000E+00	2.0000E+00	2.7554E+00	2.8097E+00
3.5000E+02	2.1475E+00	2.0000E+00	3.0000E+00	2.8530E+00	2.9412E+00
3.5000E+02	1.3396E+01	3.0000E+00	4.0000E+00	3.3172E+00	3.3930E+00
4.0000E+02	1.2584E+00	1.0000E+00	2.0000E+00	2.7506E+00	2.8020E+00
4.0000E+02	2.4569E+00	2.0000E+00	3.0000E+00	2.8643E+00	2.9457E+00
4.0000E+02	1.3448E+01	3.0000E+00	4.0000E+00	3.3131E+00	3.3887E+00
4.5000E+02	1.2254E+00	1.0000E+00	2.0000E+00	2.7467E+00	2.7955E+00
4.5000E+02	2.7984E+00	2.0000E+00	3.0000E+00	2.8766E+00	2.9512E+00
4.5000E+02	1.3493E+01	3.0000E+00	4.0000E+00	3.3085E+00	3.3839E+00
5.0000E+02	1.2247E+00	1.0000E+00	2.0000E+00	2.7438E+00	2.7908E+00
5.0000E+02	3.1796E+00	2.0000E+00	3.0000E+00	2.8901E+00	2.9581E+00
5.0000E+02	1.3528E+01	3.0000E+00	4.0000E+00	3.3035E+00	3.3787E+00
5.5000E+02	1.2568E+00	1.0000E+00	2.0000E+00	2.7421E+00	2.7878E+00
5.5000E+02	3.6079E+00	2.0000E+00	3.0000E+00	2.9051E+00	2.9667E+00
5.5000E+02	1.3556E+01	3.0000E+00	4.0000E+00	3.2981E+00	3.3731E+00
6.0000E+02	1.3344E+00	1.0000E+00	2.0000E+00	2.7418E+00	2.7874E+00
6.0000E+02	4.1005E+00	2.0000E+00	3.0000E+00	2.9220E+00	2.9776E+00
6.0000E+02	1.3574E+01	3.0000E+00	4.0000E+00	3.2923E+00	3.3670E+00
6.5000E+02	1.4530E+00	1.0000E+00	2.0000E+00	2.7430E+00	2.7893E+00
6.5000E+02	4.6771E+00	2.0000E+00	3.0000E+00	2.9416E+00	2.9915E+00
6.5000E+02	1.3582E+01	3.0000E+00	4.0000E+00	3.2861E+00	3.3606E+00
7.0000E+02	1.6089E+00	1.0000E+00	2.0000E+00	2.7455E+00	2.7933E+00
7.0000E+02	5.3573E+00	2.0000E+00	3.0000E+00	2.9642E+00	3.0091E+00
7.0000E+02	1.3581E+01	3.0000E+00	4.0000E+00	3.2796E+00	3.3538E+00
7.5000E+02	1.8104E+00	1.0000E+00	2.0000E+00	2.7494E+00	2.7998E+00
7.5000E+02	6.1785E+00	2.0000E+00	3.0000E+00	2.9908E+00	3.0314E+00
7.5000E+02	1.3570E+01	3.0000E+00	4.0000E+00	3.2726E+00	3.3466E+00
8.0000E+02	2.0480E+00	1.0000E+00	2.0000E+00	2.7546E+00	2.8081E+00
8.0000E+02	7.1663E+00	2.0000E+00	3.0000E+00	3.0217E+00	3.0591E+00
8.0000E+02	1.3549E+01	3.0000E+00	4.0000E+00	3.2653E+00	3.3389E+00
8.5000E+02	2.3126E+00	1.0000E+00	2.0000E+00	2.7607E+00	2.8176E+00
8.5000E+02	8.3578E+00	2.0000E+00	3.0000E+00	3.0578E+00	3.0930E+00
8.5000E+02	1.3519E+01	3.0000E+00	4.0000E+00	3.2576E+00	3.3309E+00
9.0000E+02	2.6094E+00	1.0000E+00	2.0000E+00	2.7677E+00	2.8284E+00
9.0000E+02	9.7700E+00	2.0000E+00	3.0000E+00	3.0990E+00	3.1331E+00
9.0000E+02	1.3477E+01	3.0000E+00	4.0000E+00	3.2494E+00	3.3225E+00
9.5000E+02	-8.4594E+00	5.0000E+00	1.0000E+00	1.7393E+00	2.1703E+00
9.5000E+02	2.9348E+00	1.0000E+00	2.0000E+00	2.7757E+00	2.8403E+00
9.5000E+02	1.1406E+01	2.0000E+00	3.0000E+00	3.1444E+00	3.1787E+00
9.5000E+02	1.3425E+01	3.0000E+00	4.0000E+00	3.2409E+00	3.3137E+00
1.0000E+03	-8.1170E+00	5.0000E+00	1.0000E+00	1.8334E+00	2.1976E+00
1.0000E+03	3.2849E+00	1.0000E+00	2.0000E+00	2.7843E+00	2.8529E+00
1.0000E+03	1.3243E+01	2.0000E+00	3.0000E+00	3.1930E+00	3.2284E+00
1.0000E+03	1.3363E+01	3.0000E+00	4.0000E+00	3.2320E+00	3.3045E+00
1.0500E+03	-7.7179E+00	5.0000E+00	1.0000E+00	1.9071E+00	2.2279E+00
1.0500E+03	3.6611E+00	1.0000E+00	2.0000E+00	2.7936E+00	2.8662E+00
1.0500E+03	1.3939E+01	2.0000E+00	3.0000E+00	3.2091E+00	3.3146E+00
1.1000E+03	-7.2730E+00	5.0000E+00	1.0000E+00	1.9719E+00	2.2595E+00
1.1000E+03	4.0614E+00	1.0000E+00	2.0000E+00	2.8036E+00	2.8801E+00
1.1000E+03	1.4580E+01	2.0000E+00	3.0000E+00	3.2235E+00	3.3266E+00
1.1500E+03	-6.7911E+00	5.0000E+00	1.0000E+00	2.0306E+00	2.2915E+00
1.1500E+03	4.4836E+00	1.0000E+00	2.0000E+00	2.8142E+00	2.8944E+00
1.1500E+03	1.5247E+01	2.0000E+00	3.0000E+00	3.2384E+00	3.3391E+00
1.2000E+03	-6.2655E+00	5.0000E+00	1.0000E+00	2.0856E+00	2.3244E+00
1.2000E+03	4.9325E+00	1.0000E+00	2.0000E+00	2.8254E+00	2.9093E+00
1.2000E+03	1.5942E+01	2.0000E+00	3.0000E+00	3.2539E+00	3.3524E+00
1.2500E+03	-5.6950E+00	5.0000E+00	1.0000E+00	2.1380E+00	2.3581E+00
1.2500E+03	5.4058E+00	1.0000E+00	2.0000E+00	2.8372E+00	2.9246E+00
1.2500E+03	1.6667E+01	2.0000E+00	3.0000E+00	3.2698E+00	3.3663E+00
1.3000E+03	-5.0943E+00	5.0000E+00	1.0000E+00	2.1878E+00	2.3915E+00
1.3000E+03	5.9014E+00	1.0000E+00	2.0000E+00	2.8495E+00	2.9402E+00
1.3000E+03	1.7424E+01	2.0000E+00	3.0000E+00	3.2864E+00	3.3809E+00

1.3500E+03	-4.4856E+00	5.0000E+00	1.0000E+00	2.2335E+00	2.4232E+00
1.3500E+03	6.4245E+00	1.0000E+00	2.0000E+00	2.8623E+00	2.9564E+00
1.3500E+03	1.8213E+01	2.0000E+00	4.0000E+00	3.3035E+00	3.3962E+00
1.4000E+03	-3.8294E+00	5.0000E+00	1.0000E+00	2.2789E+00	2.4556E+00
1.4000E+03	6.9740E+00	1.0000E+00	2.0000E+00	2.8758E+00	2.9730E+00
1.4000E+03	1.9035E+01	2.0000E+00	4.0000E+00	3.3211E+00	3.4121E+00
1.4500E+03	-3.0705E+00	5.0000E+00	1.0000E+00	2.3276E+00	2.4912E+00
1.4500E+03	7.5480E+00	1.0000E+00	2.0000E+00	2.8897E+00	2.9898E+00
1.4500E+03	1.9894E+01	2.0000E+00	4.0000E+00	3.3393E+00	3.4289E+00
1.5000E+03	-2.3167E+00	5.0000E+00	1.0000E+00	2.3724E+00	2.5243E+00
1.5000E+03	8.1510E+00	1.0000E+00	2.0000E+00	2.9042E+00	3.0072E+00
1.5000E+03	2.0788E+01	2.0000E+00	4.0000E+00	3.3581E+00	3.4463E+00
1.5500E+03	-1.5435E+00	5.0000E+00	1.0000E+00	2.4154E+00	2.5566E+00
1.5500E+03	8.7828E+00	1.0000E+00	2.0000E+00	2.9192E+00	3.0249E+00
1.5500E+03	2.1720E+01	2.0000E+00	4.0000E+00	3.3774E+00	3.4645E+00
1.6000E+03	-7.2578E-01	5.0000E+00	1.0000E+00	2.4582E+00	2.5892E+00
1.6000E+03	9.4418E+00	1.0000E+00	2.0000E+00	2.9346E+00	3.0431E+00
1.6000E+03	2.2692E+01	2.0000E+00	4.0000E+00	3.3973E+00	3.4833E+00
1.6500E+03	1.1313E-01	5.0000E+00	1.0000E+00	2.4993E+00	2.6210E+00
1.6500E+03	1.0131E+01	1.0000E+00	2.0000E+00	2.9506E+00	3.0618E+00
1.6500E+03	2.3702E+01	2.0000E+00	4.0000E+00	3.4178E+00	3.5029E+00
1.7000E+03	1.0595E+00	5.0000E+00	1.0000E+00	2.5435E+00	2.6556E+00
1.7000E+03	1.0850E+01	1.0000E+00	2.0000E+00	2.9671E+00	3.0809E+00
1.7000E+03	2.4753E+01	2.0000E+00	4.0000E+00	3.4388E+00	3.5231E+00
1.7500E+03	2.1298E+00	5.0000E+00	1.0000E+00	2.5912E+00	2.6931E+00
1.7500E+03	1.1599E+01	1.0000E+00	2.0000E+00	2.9840E+00	3.1005E+00
1.7500E+03	2.5845E+01	2.0000E+00	4.0000E+00	3.4603E+00	3.5441E+00
1.8000E+03	3.2171E+00	5.0000E+00	1.0000E+00	2.6369E+00	2.7292E+00
1.8000E+03	1.2376E+01	1.0000E+00	2.0000E+00	3.0013E+00	3.1203E+00
1.8000E+03	2.6978E+01	2.0000E+00	4.0000E+00	3.4824E+00	3.5656E+00
1.8500E+03	4.4005E+00	5.0000E+00	1.0000E+00	2.6841E+00	2.7667E+00
1.8500E+03	1.3186E+01	1.0000E+00	2.0000E+00	3.0191E+00	3.1406E+00
1.8500E+03	2.8152E+01	2.0000E+00	4.0000E+00	3.5049E+00	3.5878E+00
1.9000E+03	5.7080E+00	5.0000E+00	1.0000E+00	2.7338E+00	2.8065E+00
1.9000E+03	1.4029E+01	1.0000E+00	2.0000E+00	3.0373E+00	3.1613E+00
1.9000E+03	2.9369E+01	2.0000E+00	4.0000E+00	3.5279E+00	3.6106E+00
1.9500E+03	7.1852E+00	5.0000E+00	1.0000E+00	2.7871E+00	2.8494E+00
1.9500E+03	1.4894E+01	1.0000E+00	2.0000E+00	3.0556E+00	3.1820E+00
1.9500E+03	3.0627E+01	2.0000E+00	4.0000E+00	3.5513E+00	3.6339E+00
2.0000E+03	8.9068E+00	5.0000E+00	1.0000E+00	2.8462E+00	2.8970E+00
2.0000E+03	1.5799E+01	1.0000E+00	2.0000E+00	3.0746E+00	3.2035E+00
2.0000E+03	3.1927E+01	2.0000E+00	4.0000E+00	3.5752E+00	3.6578E+00
2.0500E+03	1.1052E+01	5.0000E+00	1.0000E+00	2.9161E+00	2.9535E+00
2.0500E+03	1.6739E+01	1.0000E+00	2.0000E+00	3.0939E+00	3.2255E+00
2.0500E+03	3.3269E+01	2.0000E+00	4.0000E+00	3.5994E+00	3.6821E+00
2.1000E+03	1.4297E+01	5.0000E+00	1.0000E+00	3.0151E+00	3.0337E+00
2.1000E+03	1.7704E+01	1.0000E+00	2.0000E+00	3.1135E+00	3.2478E+00
2.1000E+03	3.4651E+01	2.0000E+00	4.0000E+00	3.6240E+00	3.7069E+00
2.1500E+03	1.9214E+01	5.0000E+00	2.0000E+00	3.1518E+00	3.2834E+00
2.1500E+03	3.6074E+01	2.0000E+00	4.0000E+00	3.6490E+00	3.7321E+00
2.2000E+03	2.1033E+01	5.0000E+00	2.0000E+00	3.1969E+00	3.3255E+00
2.2000E+03	3.7537E+01	2.0000E+00	4.0000E+00	3.6742E+00	3.7577E+00
2.2500E+03	2.2922E+01	5.0000E+00	2.0000E+00	3.2422E+00	3.3677E+00
2.2500E+03	3.9040E+01	2.0000E+00	4.0000E+00	3.6997E+00	3.7836E+00
2.3000E+03	2.4913E+01	5.0000E+00	2.0000E+00	3.2883E+00	3.4108E+00
2.3000E+03	4.0580E+01	2.0000E+00	4.0000E+00	3.7254E+00	3.8098E+00
2.3500E+03	2.6988E+01	5.0000E+00	2.0000E+00	3.3349E+00	3.4543E+00
2.3500E+03	4.2159E+01	2.0000E+00	4.0000E+00	3.7514E+00	3.8363E+00
2.4000E+03	2.9141E+01	5.0000E+00	2.0000E+00	3.3816E+00	3.4979E+00
2.4000E+03	4.3774E+01	2.0000E+00	4.0000E+00	3.7775E+00	3.8631E+00
2.4500E+03	3.1419E+01	5.0000E+00	2.0000E+00	3.4295E+00	3.5428E+00
2.4500E+03	4.5426E+01	2.0000E+00	4.0000E+00	3.8037E+00	3.8900E+00
2.5000E+03	3.3806E+01	5.0000E+00	2.0000E+00	3.4781E+00	3.5882E+00
2.5000E+03	4.7112E+01	2.0000E+00	4.0000E+00	3.8301E+00	3.9172E+00
2.5500E+03	3.6299E+01	5.0000E+00	2.0000E+00	3.5273E+00	3.6343E+00
2.5500E+03	4.8832E+01	2.0000E+00	4.0000E+00	3.8566E+00	3.9444E+00
2.6000E+03	3.8920E+01	5.0000E+00	2.0000E+00	3.5774E+00	3.6812E+00
2.6000E+03	5.0584E+01	2.0000E+00	4.0000E+00	3.8831E+00	3.9718E+00



2.6500E+03	4.1688E+01	5.0000E+00	2.0000E+00	3.6287E+00	3.7293E+00
2.6500E+03	5.2370E+01	2.0000E+00	4.0000E+00	3.9098E+00	3.9993E+00
2.7000E+03	4.4598E+01	5.0000E+00	2.0000E+00	3.6811E+00	3.7784E+00
2.7000E+03	5.4184E+01	2.0000E+00	4.0000E+00	3.9364E+00	4.0268E+00
2.7500E+03	4.7675E+01	5.0000E+00	2.0000E+00	3.7348E+00	3.8286E+00
2.7500E+03	5.6030E+01	2.0000E+00	4.0000E+00	3.9631E+00	4.0545E+00
2.8000E+03	5.0939E+01	5.0000E+00	2.0000E+00	3.7900E+00	3.8803E+00
2.8000E+03	5.7906E+01	2.0000E+00	4.0000E+00	3.9898E+00	4.0821E+00
2.8500E+03	5.4407E+01	5.0000E+00	2.0000E+00	3.8469E+00	3.9336E+00
2.8500E+03	5.9809E+01	2.0000E+00	4.0000E+00	4.0165E+00	4.1098E+00
2.9000E+03	5.8108E+01	5.0000E+00	2.0000E+00	3.9059E+00	3.9888E+00
2.9000E+03	6.1741E+01	2.0000E+00	4.0000E+00	4.0431E+00	4.1374E+00
2.9500E+03	6.2078E+01	5.0000E+00	2.0000E+00	3.9671E+00	4.0461E+00
2.9500E+03	6.3700E+01	2.0000E+00	4.0000E+00	4.0698E+00	4.1650E+00
3.0000E+03	6.5987E+01	5.0000E+00	4.0000E+00	4.0255E+00	4.1975E+00
3.0500E+03	6.9109E+01	5.0000E+00	4.0000E+00	4.0705E+00	4.2424E+00
3.1000E+03	7.2315E+01	5.0000E+00	4.0000E+00	4.1156E+00	4.2875E+00
3.1500E+03	7.5596E+01	5.0000E+00	4.0000E+00	4.1608E+00	4.3326E+00
3.2000E+03	7.8951E+01	5.0000E+00	4.0000E+00	4.2060E+00	4.3777E+00
3.2500E+03	8.2387E+01	5.0000E+00	4.0000E+00	4.2513E+00	4.4228E+00
3.3000E+03	8.5924E+01	5.0000E+00	4.0000E+00	4.2970E+00	4.4684E+00
3.3500E+03	8.9569E+01	5.0000E+00	4.0000E+00	4.3430E+00	4.5143E+00
3.4000E+03	9.3325E+01	5.0000E+00	4.0000E+00	4.3895E+00	4.5607E+00
3.4500E+03	9.7180E+01	5.0000E+00	4.0000E+00	4.4363E+00	4.6074E+00
3.5000E+03	1.0110E+02	5.0000E+00	4.0000E+00	4.4829E+00	4.6538E+00
3.5500E+03	1.0510E+02	5.0000E+00	4.0000E+00	4.5294E+00	4.7002E+00
3.6000E+03	1.0917E+02	5.0000E+00	4.0000E+00	4.5760E+00	4.7464E+00
3.6500E+03	1.1334E+02	5.0000E+00	4.0000E+00	4.6226E+00	4.7929E+00
3.7000E+03	1.1763E+02	5.0000E+00	4.0000E+00	4.6698E+00	4.8398E+00
3.7500E+03	1.2206E+02	5.0000E+00	4.0000E+00	4.7175E+00	4.8873E+00
3.8000E+03	1.2663E+02	5.0000E+00	4.0000E+00	4.7657E+00	4.9354E+00
3.8500E+03	1.3129E+02	5.0000E+00	4.0000E+00	4.8140E+00	4.9835E+00
3.9000E+03	1.3601E+02	5.0000E+00	4.0000E+00	4.8621E+00	5.0314E+00
3.9500E+03	1.4082E+02	5.0000E+00	4.0000E+00	4.9101E+00	5.0792E+00
4.0000E+03	1.4571E+02	5.0000E+00	4.0000E+00	4.9581E+00	5.1270E+00
4.0500E+03	1.5070E+02	5.0000E+00	4.0000E+00	5.0061E+00	5.1747E+00
4.1000E+03	1.5581E+02	5.0000E+00	4.0000E+00	5.0544E+00	5.2228E+00
4.1500E+03	1.6107E+02	5.0000E+00	4.0000E+00	5.1033E+00	5.2715E+00
4.2000E+03	1.6650E+02	5.0000E+00	4.0000E+00	5.1529E+00	5.3209E+00
4.2500E+03	1.7208E+02	5.0000E+00	4.0000E+00	5.2030E+00	5.3709E+00
4.3000E+03	1.7775E+02	5.0000E+00	4.0000E+00	5.2529E+00	5.4206E+00
4.3500E+03	1.8349E+02	5.0000E+00	4.0000E+00	5.3027E+00	5.4703E+00
4.4000E+03	1.8932E+02	5.0000E+00	4.0000E+00	5.3524E+00	5.5197E+00
4.4500E+03	1.9525E+02	5.0000E+00	4.0000E+00	5.4021E+00	5.5692E+00
4.5000E+03	2.0126E+02	5.0000E+00	4.0000E+00	5.4516E+00	5.6186E+00
4.5500E+03	2.0737E+02	5.0000E+00	4.0000E+00	5.5011E+00	5.6679E+00
4.6000E+03	2.1361E+02	5.0000E+00	4.0000E+00	5.5509E+00	5.7175E+00
4.6500E+03	2.2004E+02	5.0000E+00	4.0000E+00	5.6014E+00	5.7678E+00
4.7000E+03	2.2667E+02	5.0000E+00	4.0000E+00	5.6526E+00	5.8190E+00
4.7500E+03	2.3347E+02	5.0000E+00	4.0000E+00	5.7042E+00	5.8706E+00
4.8000E+03	2.4035E+02	5.0000E+00	4.0000E+00	5.7557E+00	5.9220E+00
4.8500E+03	2.4733E+02	5.0000E+00	4.0000E+00	5.8071E+00	5.9734E+00
4.9000E+03	2.5440E+02	5.0000E+00	4.0000E+00	5.8584E+00	6.0246E+00
4.9500E+03	2.6157E+02	5.0000E+00	4.0000E+00	5.9096E+00	6.0757E+00
5.0000E+03	2.6882E+02	5.0000E+00	4.0000E+00	5.9606E+00	6.1266E+00

OPTION?

read mesh mshdat

OPTION?

slib trn

ENTER ID NUMBER FOR TABLE TYPE

201

ENTER FZ, FW, PREF, TREF, AND GUESS FOR RHOREF

10 20.018 0 298 2.71

COMPUTED STANDARD STATE - RHOREF, BREF = 2.71015E+00 7.23492E+01

ENTER ID NUMBER FOR TABLE TYPE

301

MAKE MAXWELL CONSTRUCTIONS? (YES/NO)

n

ENTER ID NUMBER FOR TABLE TYPE

0

ENTER MATID, DATE, BINLIB, AND ASCLIB

450 030689 b450 asclib

OPTION?

update b401 b402 t1

OPTION?

update b403 b406 t2

OPTION?

update b407 b450 t3

OPTION?

update t1 t2 t4

OPTION?

update t3 t4 binlib 030689

OPTION?

list binlib

6 MATERIALS ON BINLIB FILE, DATED 30689, VERSION 3

ID	FZ	FW	RHOREF	TREF	TABLE TYPES
401	0.000E+00	0.000E+00	0.000E+00	0.000E+00	301.
402	0.000E+00	0.000E+00	0.000E+00	0.000E+00	301.
403	0.000E+00	0.000E+00	0.000E+00	0.000E+00	301.
406	0.000E+00	0.000E+00	0.000E+00	0.000E+00	301.
407	0.000E+00	0.000E+00	0.000E+00	0.000E+00	301.
450	1.000E+01	2.002E+01	2.710E+00	2.980E+02	201. 301.

OPTION?

end

# Appendix G

## Output File for Test Problem 3

THE PANDA CODE, VAX VERSION 2.01, 12/06/89  
SANDIA NATIONAL LABORATORIES, ALBUQUERQUE, NM 87185

PROBLEM: TESTPROB\_3 DATE: 12/07/89

OPTION?

@tp3inp

```
!
! PANDA Test Problem 3 - Shocked nitrogen gas, with dissociation.
! Analytic EOS option is used for electrons and species N2, N2+, N2-,
! N, and N+. Higher states of ionization would be needed at higher
! temperatures. Values of ESHIFT are chosen so that the energy zero
! is relative to the N2 gas in its standard state at zero K.
!
```

mod mix

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! electron

e

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

name=electron stw=2.

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! nitrogen molecule

n[2]e[14]

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

moles=1. name=n2 nvib=1 irot=1 brot=2.010 sym=2 cvol=380.

ENTER WE, GE, AND NE FOR 1 VIBRATIONAL LEVELS

2359.5 1 33

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! nitrogen molecule-negative ion

n[2]e[15]

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

name=n2-1 eshift=5.533 nvib=1 irot=1 brot=1.691 &

sym=2 stw=4. cvol=380.

ENTER WE, GE, AND NE FOR 1 VIBRATIONAL LEVELS

1900. 1 30

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! nitrogen molecule-positive ion

n[2]e[13]

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

name=n2+1 eshift=53.66 nvib=1 irot=1 brot=1.9319 &

sym=2 stw=2. cvol=380.

ENTER WE, GE, AND NE FOR 1 VIBRATIONAL LEVELS

2207. 1 30

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! neutral nitrogen atom

n[1]e[7]

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

name=n eshift=33.602 stw=4. cvol=144.

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! nitrogen +1 ion

n[1]e[6]

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

name=n+1 eshift=133.72 stw=9. cvol=20.



ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! nitrogen +2 ion

n[1]e[5]

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

name=n+2 eshift=337.63 stw=6. cvol=6.

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

FOR MIXTURE - ZBAR = 1.4000E+01, ABAR = 2.8021E+01, WT = 2.8021E+01

NUMBER OF ELEMENTS (NC) = 2

FORMULA MATRIX

I = 1, ELEMENT E

1.0000E+00 1.4000E+01 1.5000E+01 1.3000E+01 7.0000E+00 6.0000E+00  
5.0000E+00

I = 2, ELEMENT N

0.0000E+00 2.0000E+00 2.0000E+00 2.0000E+00 1.0000E+00 1.0000E+00  
1.0000E+00

NUMBER OF SPECIES (NS) = 7

1 ELECTRON	FZ, FW, MOLES =	0.0000E+00	5.4858E-04	4.6724E-01
2 N2	FZ, FW, MOLES =	1.4000E+01	2.8021E+01	2.1608E-01
3 N2-1	FZ, FW, MOLES =	1.4000E+01	2.8022E+01	2.7444E-01
4 N2+1	FZ, FW, MOLES =	1.4000E+01	2.8021E+01	1.7013E-01
5 N	FZ, FW, MOLES =	7.0000E+00	1.4011E+01	2.8194E-01
6 N+1	FZ, FW, MOLES =	7.0000E+00	1.4010E+01	2.2199E-01
7 N+2	FZ, FW, MOLES =	7.0000E+00	1.4009E+01	1.7478E-01

NUMBER OF CONSTRAINTS (NQ) = 2

CONSTRAINT MATRIX

I = 1

1.0000E+00 1.4000E+01 1.5000E+01 1.3000E+01 7.0000E+00 6.0000E+00  
5.0000E+00

I = 2

0.0000E+00 2.0000E+00 2.0000E+00 2.0000E+00 1.0000E+00 1.0000E+00  
1.0000E+00

OPTION?

! Find initial state for gas - 2 psi and 300 K

eos mix

RHO(G/CC)	T(K)	P(GPA)	E(MJ/KG)	S(MJ/KGK)	CS(KM/S)
-----------	------	--------	----------	-----------	----------

ENTER DENSITY (G/CC) AND TEMPERATURE (K)

1.55e-04 300

1.5500E-04	3.0000E+02	1.3811E-05	2.2258E-01	7.4289E-03	3.5330E-01
------------	------------	------------	------------	------------	------------

OPTION?

! Compute Hugoniot and send to plot file

plot tp3plt

OPTION?

hug mix 1.55e-04 1.3811e-05 .22232 3.e3 3.e4 30

TYPE SKIP OR ENTER LABEL FOR PLOT FILE

Hugoniot for nitrogen gas, shocked from 2 psi and 300 K

RHO(G/CC)	T(K)	P(GPA)	E(MJ/KG)	UP(KM/S)	US(KM/S)
1.0045E-03	3.0000E+03	8.9665E-04	2.7061E+00	2.1947E+00	2.5952E+00
1.0067E-03	3.0321E+03	9.0820E-04	2.7386E+00	2.2095E+00	2.6116E+00
1.0129E-03	3.1284E+03	9.4282E-04	2.8360E+00	2.2531E+00	2.6602E+00
1.0226E-03	3.2889E+03	1.0007E-03	2.9988E+00	2.3242E+00	2.7394E+00
1.0350E-03	3.5137E+03	1.0820E-03	3.2278E+00	2.4206E+00	2.8470E+00
1.0495E-03	3.8026E+03	1.1874E-03	3.5249E+00	2.5404E+00	2.9806E+00
1.0662E-03	4.1558E+03	1.3187E-03	3.8959E+00	2.6823E+00	3.1386E+00
1.0874E-03	4.5731E+03	1.4814E-03	4.3579E+00	2.8493E+00	3.3230E+00
1.1191E-03	5.0547E+03	1.6904E-03	4.9582E+00	3.0526E+00	3.5434E+00
1.1736E-03	5.6005E+03	1.9810E-03	5.8073E+00	3.3190E+00	3.8240E+00
1.2673E-03	6.2105E+03	2.4204E-03	7.1141E+00	3.6915E+00	4.2059E+00
1.4109E-03	6.8847E+03	3.1079E-03	9.1861E+00	4.2153E+00	4.7356E+00
1.5948E-03	7.6231E+03	4.1565E-03	1.2368E+01	4.9122E+00	5.4410E+00
1.7857E-03	8.4257E+03	5.6530E-03	1.6915E+01	5.7640E+00	6.3119E+00
1.9399E-03	9.2925E+03	7.5908E-03	2.2794E+01	6.7065E+00	7.2889E+00
2.0261E-03	1.0224E+04	9.7948E-03	2.9442E+01	7.6338E+00	8.2662E+00
2.0410E-03	1.1219E+04	1.1940E-02	3.5853E+01	8.4319E+00	9.1249E+00
2.0067E-03	1.2278E+04	1.3780E-02	4.1281E+01	9.0529E+00	9.8107E+00
1.9536E-03	1.3402E+04	1.5361E-02	4.5884E+01	9.5476E+00	1.0370E+01

1.9041E-03	1.4590E+04	1.6930E-02	5.0431E+01	1.0013E+01	1.0900E+01
1.8688E-03	1.5842E+04	1.8746E-02	5.5718E+01	1.0528E+01	1.1480E+01
1.8492E-03	1.7158E+04	2.1002E-02	6.2333E+01	1.1138E+01	1.2157E+01
1.8413E-03	1.8539E+04	2.3821E-02	7.0636E+01	1.1860E+01	1.2950E+01
1.8391E-03	1.9983E+04	2.7254E-02	8.0769E+01	1.2686E+01	1.3853E+01
1.8363E-03	2.1492E+04	3.1276E-02	9.2635E+01	1.3589E+01	1.4842E+01
1.8280E-03	2.3065E+04	3.5775E-02	1.0588E+02	1.4531E+01	1.5878E+01
1.8115E-03	2.4703E+04	4.0568E-02	1.1993E+02	1.5468E+01	1.6915E+01
1.7858E-03	2.6404E+04	4.5409E-02	1.3403E+02	1.6354E+01	1.7908E+01
1.7522E-03	2.8170E+04	5.0070E-02	1.4749E+02	1.7157E+01	1.8822E+01
1.7129E-03	3.0000E+04	5.4389E-02	1.5984E+02	1.7862E+01	1.9639E+01

OPTION?

! Compute concentrations as functions of temperature

conc plot

ENTER SYMBOL FOR THERMODYNAMIC VARIABLE - R, T, P, E, OR S

t

TYPE SKIP OR ENTER LABEL FOR PLOT FILE

Concentrations along Hugoniot for nitrogen gas

T(K)	ELECTRON (G/CC) AND	N2 TEMPERATURE (K)	N2-1	N2+1	N
1.0044e-03	3.0000e+03				
3.0000E+03	6.9527E-16	1.0000E+00	6.5544E-16	5.3480E-06	4.7271E-06
1.0066e-03	3.0321e+03				
3.0321E+03	1.1728E-15	1.0000E+00	5.8948E-16	5.3478E-06	5.7652E-06
1.0128e-03	3.1284e+03				
3.1284E+03	1.2004E-16	9.9999E-01	4.8460E-17	5.3468E-06	1.0205E-05
1.0225e-03	3.2889e+03				
3.2889E+03	2.6393E-16	9.9999E-01	5.2709E-16	5.3440E-06	2.4528E-05
1.0349e-03	3.5137e+03				
3.5137E+03	6.6010E-16	9.9996E-01	1.0988E-15	5.3367E-06	7.3150E-05
1.0494e-03	3.8026e+03				
3.8026E+03	4.5401E-14	9.9988E-01	6.5700E-16	5.3164E-06	2.4607E-04
1.0662e-03	4.1558e+03				
4.1558E+03	2.9414E-12	9.9957E-01	3.2329E-15	5.2624E-06	8.6021E-04
1.0873e-03	4.5731e+03				
4.5731E+03	1.8131E-10	9.9853E-01	2.6636E-13	5.1285E-06	2.9292E-03
1.1190e-03	5.0547e+03				
5.0547E+03	9.3683E-09	9.9535E-01	1.8016E-11	4.8436E-06	9.2912E-03
1.1735e-03	5.6005e+03				
5.6005E+03	3.5658E-07	9.8669E-01	8.8021E-10	4.5916E-06	2.6618E-02
1.2673e-03	6.2105e+03				
6.2105E+03	5.6615E-06	9.6621E-01	1.7637E-08	7.3124E-06	6.7579E-02
1.4108e-03	6.8847e+03				
6.8847E+03	3.5098E-05	9.2451E-01	1.3450E-07	2.0514E-05	1.5094E-01
1.5948e-03	7.6231e+03				
7.6231E+03	1.5220E-04	8.5101E-01	6.7999E-07	5.7219E-05	2.9777E-01
1.7857e-03	8.4257e+03				
8.4257E+03	5.4933E-04	7.3783E-01	2.5979E-06	1.3680E-04	5.2364E-01
1.9399e-03	9.2925e+03				
9.2925E+03	1.7212E-03	5.8635E-01	7.4822E-06	2.7418E-04	8.2529E-01
2.0261e-03	1.0224e+04				
1.0224E+04	4.7506E-03	4.1494E-01	1.5920E-05	4.5791E-04	1.1649E+00
2.0410e-03	1.1219e+04				
1.1219E+04	1.1609E-02	2.5798E-01	2.4970E-05	6.3884E-04	1.4717E+00
2.0067e-03	1.2278e+04				
1.2278E+04	2.5332E-02	1.4395E-01	3.0182E-05	7.6452E-04	1.6859E+00
1.9536e-03	1.3402e+04				
1.3402E+04	5.0036E-02	7.5898E-02	3.0510E-05	8.2274E-04	1.7973E+00
1.9041e-03	1.4590e+04				
1.4590E+04	9.0654E-02	3.9758E-02	2.7841E-05	8.3207E-04	1.8289E+00
1.8688e-03	1.5842e+04				
1.5842E+04	1.5239E-01	2.1228E-02	2.3977E-05	8.1150E-04	1.8043E+00
1.8491e-03	1.7158e+04				
1.7158E+04	2.3980E-01	1.1597E-02	1.9787E-05	7.7015E-04	1.7362E+00
1.8413e-03	1.8539e+04				
1.8539E+04	3.5578E-01	6.4232E-03	1.5608E-05	7.1067E-04	1.6306E+00

1.8391e-03	1.9983e+04				
1.9983E+04	5.0032E-01	3.5576E-03	1.1643E-05	6.3412E-04	1.4919E+00
1.8363e-03	2.1492e+04				
2.1492E+04	6.7027E-01	1.9377E-03	8.0965E-06	5.4306E-04	1.3253E+00
1.8280e-03	2.3065e+04				
2.3065E+04	8.5833E-01	1.0229E-03	5.1811E-06	4.4317E-04	1.1393E+00
1.8114e-03	2.4703e+04				
2.4703E+04	1.0539E+00	5.1712E-04	3.0210E-06	3.4268E-04	9.4506E-01
1.7858e-03	2.6404e+04				
2.6404E+04	1.2440E+00	2.4904E-04	1.6011E-06	2.5063E-04	7.5607E-01
1.7522e-03	2.8170e+04				
2.8170E+04	1.4172E+00	1.1427E-04	7.7501E-07	1.7377E-04	5.8441E-01
1.7130e-03	3.0000e+04				
3.0000E+04	1.5657E+00	5.0424E-05	3.4806E-07	1.1514E-04	4.3889E-01

OPTION?

end

# Appendix H

## Output File for Test Problem 4

THE PANDA CODE, SUN VERSION 2.01, 04/23/91  
SANDIA NATIONAL LABORATORIES, ALBUQUERQUE, NM 87185

PROBLEM: TESTPROB\_4 DATE: 04/30/91

OPTION?

@tp4inp

\$

\$ PANDA Test Problem 4 - PETN explosive. Requires EOS file HESPS.  
\$ Energy zero for EOS tables is gas phase, zero temperature and  
\$ density. Values of ESHIFT change energy zero relative to elements  
\$ in standard states.  
\$ PETN has formula c[5]h[8]n[4]o[12], formula weight = 316.138.  
\$ Heat of formation at 298k: -110.34 kcal/mole = -1.4608 mj/kg (Gibbs  
\$ & Popolato), -128.7 kcal/mole = -1.7039 mj/kg (Hardesty & Kennedy).  
\$ The energy of the explosive at 298k, relative to the elements in  
\$ their standard states at 0k, ranges from -1.358 to -1.115 mj/kg.  
\$

! First make and list file hesps

asc2bin aesps hesps 042391

OPTION?

list hesps

ID	FZ	FW	RHOREF	TREF	TABLE TYPES
102	7.000E+00	1.401E+01	2.942E+00	6.315E+01	201. 301.
107	1.000E+00	1.008E+00	5.375E-01	1.400E+01	201. 301.
108	8.000E+00	1.600E+01	3.231E+00	5.438E+01	201. 301.
201	2.200E+01	4.401E+01	1.177E+00	2.166E+02	201. 301.
202	1.400E+01	2.801E+01	8.739E-01	6.315E+01	201. 301.
203	1.000E+01	1.802E+01	9.980E-01	2.950E+02	201. 301.
204	1.400E+01	2.801E+01	8.484E-01	6.815E+01	201. 301.
205	1.000E+01	1.604E+01	4.515E-01	9.069E+01	201. 301.
206	1.000E+01	1.703E+01	7.221E-01	1.954E+02	201. 301.
207	2.000E+00	2.016E+00	9.889E-02	1.400E+01	201. 301.
208	1.600E+01	3.200E+01	1.267E+00	5.438E+01	201. 301.
209	1.500E+01	3.001E+01	1.328E+00	1.096E+02	201. 301.
210	6.000E+00	1.201E+01	3.126E+00	4.000E+03	201. 301.
213	6.000E+00	1.201E+01	2.280E+00	2.980E+02	201. 301.
214	6.000E+00	1.201E+01	3.515E+00	2.980E+02	201. 301.
301	2.400E+01	4.603E+01	1.383E+00	2.930E+02	201. 301.

OPTION?

! Next enter data for mixture

mod mix ezro=1.36

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! carbon dioxide (tabular eos)

c[1]o[2]

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

moles=5. name=co2 eshift=-8.9363 matid=201 file=hesps

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

! molecular nitrogen (tabular eos)

n[2]

ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES

moles=2. name=n2 matid=202

```

ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED
!   water (tabular eos)
    h[2]o[1]
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES
    name=h2o   eshift=-13.2662   matid=203
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED
!   carbon monoxide (tabular eos)
    c[1]o[1]
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES
    name=co   eshift=-4.0644   matid=204
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED
!   methane (tabular eos)
    c[1]h[4]
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES
    name=ch4   eshift=-4.1717   matid=205
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED
!   ammonia (tabular eos)
    n[1]h[3]
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES
    name=nh3   eshift=-2.2856   matid=206
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED
!   molecular hydrogen (tabular eos)
    h[2]
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES
    moles=4.   name=h2   matid=207
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED
!   molecular oxygen (tabular eos)
    o[2]
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES
    moles=1.   name=o2   matid=208
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED
!   nitric oxide (tabular eos)
    n[1]o[1]
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES
    name=no   eshift=2.9934   matid=209
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED
!   formic acid (tabular eos)
    h[2]c[1]o[2]
ENTER (NAMELIST) EOS PARAMETERS FOR THIS SPECIES
    name=hcooh   eshift=-8.062   matid=301
ENTER CHEMICAL FORMULA, OR HIT RETURN IF FINISHED

FOR MIXTURE - ZBAR = 1.3500E+01, ABAR = 2.6345E+01, WT = 3.1614E+02
NUMBER OF ELEMENTS (NC) = 4
FORMULA MATRIX
I = 1, ELEMENT C
1.0000E+00 0.0000E+00 0.0000E+00 1.0000E+00 1.0000E+00 0.0000E+00
0.0000E+00 0.0000E+00 0.0000E+00 1.0000E+00
I = 2, ELEMENT O
2.0000E+00 0.0000E+00 1.0000E+00 1.0000E+00 0.0000E+00 0.0000E+00
0.0000E+00 2.0000E+00 1.0000E+00 2.0000E+00
I = 3, ELEMENT N
0.0000E+00 2.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00 1.0000E+00
0.0000E+00 0.0000E+00 1.0000E+00 0.0000E+00
I = 4, ELEMENT H
0.0000E+00 0.0000E+00 2.0000E+00 0.0000E+00 4.0000E+00 3.0000E+00
2.0000E+00 0.0000E+00 0.0000E+00 2.0000E+00
NUMBER OF SPECIES (NS) = 10
1 CO2      FZ, FW, MOLES = 2.2000E+01 4.4010E+01 1.9093E+00
2 N2      FZ, FW, MOLES = 1.4000E+01 2.8013E+01 1.1772E+00
3 H2O     FZ, FW, MOLES = 1.0000E+01 1.8015E+01 5.3162E-01
4 CO      FZ, FW, MOLES = 1.4000E+01 2.8010E+01 1.0905E+00
5 CH4     FZ, FW, MOLES = 1.0000E+01 1.6043E+01 4.2432E-01
6 NH3     FZ, FW, MOLES = 1.0000E+01 1.7031E+01 4.9346E-01
7 H2      FZ, FW, MOLES = 2.0000E+00 2.0159E+00 3.0364E-01

```

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8 O2          FZ, FW, MOLES = 1.6000E+01 3.1999E+01 1.1277E+00
9 NO          FZ, FW, MOLES = 1.5000E+01 3.0006E+01 1.1522E+00
10 HCOOH      FZ, FW, MOLES = 2.4000E+01 4.6026E+01 1.5759E+00
NUMBER OF CONSTRAINTS (NQ) = 4
CONSTRAINT MATRIX
I = 1
1.0000E+00 0.0000E+00 0.0000E+00 1.0000E+00 1.0000E+00 0.0000E+00
0.0000E+00 0.0000E+00 0.0000E+00 1.0000E+00
I = 2
2.0000E+00 0.0000E+00 1.0000E+00 1.0000E+00 0.0000E+00 0.0000E+00
0.0000E+00 2.0000E+00 1.0000E+00 2.0000E+00
I = 3
0.0000E+00 2.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00 1.0000E+00
0.0000E+00 0.0000E+00 1.0000E+00 0.0000E+00
I = 4
0.0000E+00 0.0000E+00 2.0000E+00 0.0000E+00 4.0000E+00 3.0000E+00
2.0000E+00 0.0000E+00 0.0000E+00 2.0000E+00
OPTION?
! Compute CJ state as function of loading density
plot tp4plt
OPTION?
cj mix
TYPE SKIP OR ENTER LABEL FOR PLOT FILE
CJ state for PETN as function of loading density
      RHO(G/CC)      T(K)      P(GPA)      E(MJ/KG)      UP(KM/S)      D(KM/S)
ENTER RZRO, PZRO, AND EZRO FOR UNBURNED EXPLOSIVE
0.2 0
2.6969E-01 4.4905E+03 4.6438E-01 3.0000E-01 7.7459E-01 2.9976E+00
0.3 0
4.3019E-01 4.6335E+03 8.9217E-01 4.5000E-01 9.4869E-01 3.1347E+00
0.4 0
5.9181E-01 4.7507E+03 1.4810E+00 6.0000E-01 1.0954E+00 3.3798E+00
0.5 0
7.3917E-01 4.8261E+03 2.1893E+00 7.0839E-01 1.1903E+00 3.6787E+00
0.6 0
8.6588E-01 4.8531E+03 2.9493E+00 7.5469E-01 1.2286E+00 4.0011E+00
0.7 0
9.9083E-01 4.8691E+03 3.8736E+00 8.1210E-01 1.2745E+00 4.3420E+00
0.8 0
1.1136E+00 4.8713E+03 4.9800E+00 8.7659E-01 1.3240E+00 4.7015E+00
0.9 0
1.2362E+00 4.8603E+03 6.3120E+00 9.5358E-01 1.3810E+00 5.0784E+00
1.0 0
1.3583E+00 4.8340E+03 7.8936E+00 1.0412E+00 1.4430E+00 5.4701E+00
1.1 0
1.4833E+00 4.7957E+03 9.8013E+00 1.1512E+00 1.5173E+00 5.8723E+00
1.2 0
1.6123E+00 4.7466E+03 1.2094E+01 1.2886E+00 1.6054E+00 6.2780E+00
1.3 0
1.7448E+00 4.6858E+03 1.4767E+01 1.4478E+00 1.7017E+00 6.6754E+00
1.4 0
1.8839E+00 4.6198E+03 1.7880E+01 1.6403E+00 1.8112E+00 7.0512E+00
1.5 0
2.0237E+00 4.5440E+03 2.1286E+01 1.8362E+00 1.9164E+00 7.4049E+00
1.6 0
2.1510E+00 4.4430E+03 2.4575E+01 1.9674E+00 1.9836E+00 7.7433E+00
1.7 0
2.2665E+00 4.3207E+03 2.7807E+01 2.0442E+00 2.0220E+00 8.0894E+00
1.8 0
2.3745E+00 4.1825E+03 3.1164E+01 2.0945E+00 2.0467E+00 8.4593E+00
OPTION?

```



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! Make plot file of concentrations vs. CJ pressure
conc plot
ENTER SYMBOL FOR THERMODYNAMIC VARIABLE - R, T, P, E, OR S
P
TYPE SKIP OR ENTER LABEL FOR PLOT FILE
Moles of species in PETN as function of CJ pressure
P(GPA)      CO2      N2      H2O      CO      CH4
ENTER DENSITY (G/CC) AND TEMPERATURE (K)
2.6969e-01  4.4905e+03
4.6438E-01  2.6091E+00  1.9563E+00  3.6640E+00  2.3897E+00  2.3191E-07
4.3019e-01  4.6335e+03
8.9216E-01  2.7020E+00  1.9559E+00  3.6913E+00  2.2955E+00  6.2851E-07
5.9181e-01  4.7507e+03
1.4810E+00  2.7770E+00  1.9560E+00  3.7131E+00  2.2182E+00  1.3902E-06
7.3901e-01  4.8258e+03
2.1883E+00  2.8492E+00  1.9575E+00  3.7310E+00  2.1427E+00  2.6414E-06
8.6590e-01  4.8531e+03
2.9495E+00  2.9193E+00  1.9607E+00  3.7449E+00  2.0683E+00  4.4553E-06
9.9082e-01  4.8691e+03
3.8735E+00  2.9802E+00  1.9641E+00  3.7533E+00  2.0007E+00  7.5677E-06
1.1130e+00  4.8702e+03
4.9729E+00  3.0323E+00  1.9678E+00  3.7554E+00  1.9381E+00  1.3074E-05
1.2361e+00  4.8603e+03
6.3113E+00  3.0747E+00  1.9715E+00  3.7486E+00  1.8789E+00  2.3512E-05
1.3585e+00  4.8342e+03
7.8963E+00  3.1072E+00  1.9747E+00  3.7289E+00  1.8186E+00  4.3625E-05
1.4831e+00  4.7955e+03
9.7983E+00  3.1297E+00  1.9771E+00  3.6882E+00  1.7485E+00  8.3108E-05
1.6117e+00  4.7458e+03
1.2082E+01  3.1426E+00  1.9781E+00  3.6128E+00  1.6531E+00  1.5680E-04
1.7448e+00  4.6857e+03
1.4768E+01  3.1453E+00  1.9777E+00  3.4839E+00  1.5112E+00  2.7023E-04
1.8841e+00  4.6201e+03
1.7885E+01  3.1360E+00  1.9766E+00  3.2829E+00  1.3025E+00  3.7853E-04
2.0233e+00  4.5433e+03
2.1273E+01  3.1149E+00  1.9765E+00  3.0206E+00  1.0359E+00  3.8270E-04
2.1513e+00  4.4434e+03
2.4584E+01  3.0879E+00  1.9784E+00  2.7478E+00  7.6071E-01  2.7389E-04
2.2667e+00  4.3209e+03
2.7812E+01  3.0603E+00  1.9817E+00  2.5010E+00  5.1251E-01  1.4036E-04
2.3744e+00  4.1824e+03
3.1160E+01  3.0354E+00  1.9856E+00  2.2967E+00  3.0756E-01  4.9344E-05

OPTION?
end

```



## References

- [1] G. E. Duvall and R. A. Graham, "Phase Transitions Under Shock Wave Loading," *Rev. Mod. Phys.* 49, 523-579 (1977).
- [2] L. Davison and R. A. Graham, "Shock Compression of Solids," *Phys. Reports* 55, 255-379 (1979).
- [3] R. M. More, "Atomic Physics in Inertial Confinement Fusion," Lawrence Livermore Laboratory report UCRL-84991, 1981.
- [4] B. K. Godwal, S. K. Sikka, and R. Chidambaram, "Equation of State Theories of Condensed Matter Up to About 10 TPa," *Phys. Rep.* 102, 121-197 (1983).
- [5] A. V. Bushman and V. E. Fortov, "Model Equations of State," *Sov. Phys. Usp.* 2, 465-496 (1983).
- [6] M. Ross, "Matter Under Extreme Conditions of Temperature and Pressure," *Rep. Prog. Phys.* 48, 1-51 (1985).
- [7] J. R. Asay and G. I. Kerley, "The Response of Materials to Dynamic Loading," *Int. J. Impact Engng.* 5, 69-99 (1987).
- [8] B. I. Bennett, J. D. Johnson, G. I. Kerley, and G. T. Rood, "Recent Developments in the Sesame Equation-of-State Library," Los Alamos Scientific Laboratory report LA-7130, 1978.
- [9] N. G. Cooper, "An Invitation to Participate in the LASL Equation of State Library," Los Alamos Scientific Laboratory report LASL-79-62, 1979.
- [10] K. S. Holian, "T-4 Handbook of Material Properties Data Bases," Los Alamos National Laboratory report LA-10160-MS, 1984.
- [11] J. Abdallah, Jr., G. I. Kerley, B. I. Bennett, J. D. Johnson, R. C. Albers, and W. F. Huebner, "HYDSES: A Subroutine Package for Using Sesame in Hydrodynamic Codes," Los Alamos Scientific Laboratory report LA-8209, 1980.
- [12] C. W. Cranfill, "EOSPAC: A Subroutine Package for Accessing the Los Alamos Sesame EOS Data Library," Los Alamos National Laboratory report LA-9728-M, 1983.
- [13] G. I. Kerley, "A Tabular Equation of State Option for the WONDY Code," Sandia National Laboratories report SAND88-0831, 1988.

- [14] G. I. Kerley, "CTH Reference Manual: The Equation of State Package," Sandia National Laboratories report SAND91-0344, 1991.
- [15] G. I. Kerley, "User's Manual for PANDA: A Computer Code for Calculating Equations of State," Los Alamos National Laboratory report LA-8833-M, 1981.
- [16] J. S. Rottler, C. M. Korbin, C. B. Selleck, G. I. Kerley, A. C. Robinson, and T. G. Trucano, "A Quality Assurance Policy for Computer Software and Computations in Department 1530," Sandia National Laboratories report SAND87-0187, 1987.
- [17] G. I. Kerley, "A Model for the Calculation of Thermodynamic Properties of a Fluid Using Hard-Sphere Perturbation Theory and the Zero-Kelvin Isotherm of the Solid," in *Molecular Based Study of Fluids*, edited by J. M. Haile and G. A. Mansoori (Am. Chem. Soc., Washington, DC., 1983) pp 107-138.
- [18] G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold Co., New York, 1945), Chap. 5.
- [19] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold Co., New York, 1950).
- [20] C. B. Selleck, "GRAPH III: A Digitizing and Graph Plotting Program," Sandia National Laboratories report SAND86-0525, 1986.
- [21] "Disk Operating System Version 3.20," Reference Manual, IBM Corp. and Microsoft, Inc., 1986.
- [22] "Microsoft FORTRAN Optimizing Compiler," User's Guide, Microsoft Corp., 1987.
- [23] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Co., New York, 1939), Ch. XIV.
- [24] G. I. Kerley, "Rational Function Method of Interpolation," Los Alamos Scientific Laboratory report LA-6903-M, 1977.
- [25] R. C. Albers, "An Introduction to Two-Temperature Equations of State," Los Alamos National Laboratory report LA-7934-MS, 1979.
- [26] R. W. Zwanzig, "Transition from Quantum to 'Classical' Partition Function," *Phys. Rev.* 106, 13-15 (1957).
- [27] M. H. Rice, R. G. McQueen, and J. M. Walsh, "Compression of Solids by Strong Shock Waves," in *Solid State Physics*, F. Seitz and D. Turnbull, Eds. (Academic Press, Inc., New York, 1956), Vol. 6, pp. 40-63.
- [28] R. Grover, R. N. Keeler, F. J. Rogers, and G. C. Kennedy, "On the Compressibility of the Alkali Metals," *J. Phys. Chem. Solids* 30, 2091-2103 (1969).

- [29] G. I. Kerley, "Perturbation Theory and the Thermodynamic Properties of Fluids. III. Inverse-Power and 6-12 Potentials," *J. Chem. Phys.* 73, 487-494 (1980).
- [30] J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, "Universal Features of the Equation of State of Metals," *Phys. Rev. B* 29, 2963-2969 (1984).
- [31] P. Vinet, J. R. Smith, J. Ferrante, and J. H. Rose, "Temperature Effects on the Universal Equation of State of Solids," *Phys. Rev. B* 35, 1945-1953 (1987).
- [32] R. P. Feynman, N. Metropolis, and E. Teller, "Equations of State of Elements Based on the Generalized Fermi-Thomas Theory," *Phys. Rev.* 75, 1561-1573 (1949).
- [33] R. D. Cowan and J. Ashkin, "Extension of the Thomas-Fermi-Dirac Statistical Theory of the Atom to Finite Temperatures," *Phys. Rev.* 105, 144-157 (1957).
- [34] R. D. Cowan and D. A. Liberman, Los Alamos National Laboratory, Los Alamos, NM, unpublished Thomas-Fermi-Dirac calculations.
- [35] B. I. Bennett, Los Alamos Scientific Laboratory, Los Alamos, NM, unpublished work.
- [36] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).
- [37] V. N. Zharkov and V. A. Kalinin, "Equations of State for Solids at High Pressures and Temperatures," English translation, A. Tybulewicz (Consultants Bureau, New York, 1971).
- [38] S. L. Thompson and H. S. Lauson, "Improvements in the Chart-D Radiation-Hydrodynamic Code III: Revised Analytic Equations of State," Sandia Laboratories report SC-RR-710714, 1972.
- [39] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), Chap. 6.
- [40] J. S. Dugdale and D. K. C. MacDonald, "The Thermal Expansion of Solids," *Phys. Rev.* 89, 832-834 (1953).
- [41] S. B. Kormer, A. I. Funtikov, V. D. Urlin, and A. N. Kolesnikova, "Dynamic Compression of Porous Metals and the Equation of State with Variable Specific Heat at High Temperatures," *Sov. Phys. JETP* 15, 477-488 (1962).
- [42] J. F. Barnes and W. Fickett, "Equation of State in the Mixed-Phase Region," *Bull. Am. Phys. Soc.* 18, 276 (1973).
- [43] G. I. Kerley, "Perturbation Theory and the Thermodynamic Properties of Fluids I. General Theory," *J. Chem. Phys.* 73, 469-477 (1980).
- [44] G. I. Kerley, "Perturbation Theory and the Thermodynamic Properties of Fluids II. The CRIS Model," *J. Chem. Phys.* 73, 478-486 (1980).

- [45] The adaptive quadrature option calls routine QNC7, written by D. Kahaner and L. Rathmann, Los Alamos National Laboratory.
- [46] B. P. Singh and S. K. Sinha, "Quantum Corrections to the Equilibrium Properties of Dense Fluids: Application to Hard Sphere Fluids," J. Chem. Phys. 67, 3645-3649 (1977).
- [47] Y. Rosenfeld, "On Equation of State Calculations from Experimental Zero-Temperature Isotherms," J. Chem. Phys. 73, 5753-5759 (1980).
- [48] Y. Rosenfeld, "Equations of State for Liquids from the Zero-Temperature Isotherm: Quantum Corrections for Hydrogen," J. Chem. Phys. 73, 5760-5765 (1980).
- [49] L. Verlet and J.-J. Weis, "Equilibrium Theory of Simple Liquids," Phys. Rev. A5, 939-952 (1972).
- [50] J. H. Dymond and B. J. Alder, "Van der Waals Theory of Transport in Dense Fluids," J. Chem. Phys. 45, 2061-2068 (1966).
- [51] J. H. Dymond, "Corrected Enskog Theory and the Transport Coefficients of Liquids," J. Chem. Phys. 60, 969-973 (1974).
- [52] B. J. Alder, D. M. Gass, and T. E. Wainwright, "Studies in Molecular Dynamics. VIII. The Transport Coefficients for a Hard-Sphere Fluid," J. Chem. Phys. 53, 3813-3826 (1970).
- [53] W. G. Hoover, A. J. C. Ladd, R. B. Hickman, and B. L. Holian, "Bulk Viscosity via Nonequilibrium and Equilibrium Molecular Dynamics," Phys. Rev. A 21, 1756-1760 (1980).
- [54] G. I. Kerley and J. Abdallah, Jr., "Theoretical Equations of State for Molecular Fluids: Nitrogen, Oxygen, and Carbon Monoxide," J. Chem. Phys. 73, 5337-5350 (1980).
- [55] J. O. Hirschfelder, C. F. Curtis, and R. B. Byrd, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), pp. 180-181, 364-367.
- [56] E. Salje and K. Viswanathan, "The Phase Diagram Calcite-Aragonite as Derived from the Crystallographic Properties," Contrib. Mineral. Petrol. 55, 55-67 (1976).
- [57] D. A. Liberman, "Self-Consistent Field Model for Condensed Matter," Phys. Rev. B 20, 4981-4989 (1979).
- [58] G. I. Kerley, "Theoretical Equation of State for Aluminum," Int. J. Impact Engng. 5, 441-449 (1987).
- [59] G. I. Kerley, "A Simple Approximation to the Temperature-Dependent Thomas-Fermi-Dirac Theory of the Atom," to be published.

- [60] G. I. Kerley, "Atomic Orbital Data for Elements with Atomic Numbers  $1 \leq Z \leq 103$ ," Sandia National Laboratories report SAND88-2594, 1988.
- [61] G. I. Kerley, "Theory of Ionization Equilibrium: An Approximation for the Single Element Case," J. Chem. Phys. 85, 5228-5231 (1986).
- [62] G. I. Kerley, "A Theoretical Equation of State for Deuterium," Los Alamos Scientific Laboratory report LA-4776, 1972.
- [63] W. F. Huebner, "Electron-Electron Interaction in Energy Level Determination," J. Quant. Spectrosc. Radiat. Transfer 10, 949-973 (1970).
- [64] T. A. Carlson, C. W. Nestor, Jr., N. Wasserman, and J. D. McDowell, "Calculated Ionization Potentials for Multiply Charged Ions," Atomic Data 2, 63-99 (1970).
- [65] D. A. Liberman, "The Use of Scaled Orbital Functions in Self-Consistent Field Calculations for Atoms," Int. J. Quantum Chem., Quantum Chem. Symp. 18, 359-368 (1984).
- [66] G. I. Kerley, "Equations of State and Gas-Gas Separation in Soft-Sphere Mixtures," J. Chem. Phys. 91, 1204-1210 (1989).
- [67] G. I. Kerley and A. C. Switendick, "Theory of Molecular Dissociation in Shocked Nitrogen and Oxygen," in Shock Waves in Condensed Matter, edited by Y. M. Gupta (Plenum Press, New York, 1986) pp. 95-100.
- [68] G. I. Kerley, "Theoretical Equations of State for the Detonation Properties of Explosives," in Proceedings of the Eighth Symposium (International) on Detonation, edited by J. M. Short, NSWC MP 86-194 (Naval Surface Weapons Center, White Oak, MD, 1986), pp. 540-547.
- [69] C. L. Mader, *Numerical Modeling of Detonations* (University of California, Berkeley, 1979).
- [70] G. I. Kerley and G. T. Rood, unpublished work.
- [71] G. I. Kerley, "A Theoretical Equation of State for Methane," J. Appl. Phys. 51, 5368-5374 (1980).
- [72] I. G. Dillon, P. A. Nelson, and B. S. Swanson, "Measurement of Densities and Estimation of Critical Properties of the Alkali Metals," J. Chem. Phys. 44, 4229-4237 (1966).
- [73] W. Fickett and W. C. Davis, *Detonation* (University of California, Berkeley, 1979).
- [74] L. Smith, "SIMMER-II: A Computer Program for LMFBR Disrupted Core Analysis," Los Alamos Scientific Laboratory report LA-7515-M (NUREG/CR-0453), Vol. I, 1979, pp.49-53.

- [75] J. M. McGlaun, F. J. Ziegler, S. L. Thompson, L. N. Kmetyk, and M. G. Elrick, "CTH - User's Manual and Input Instructions," Sandia National Laboratories report SAND88-0523, 1988.
- [76] S. P. Marsh, *LASL Shock Hugoniot Data* (University of California, Berkeley, 1980).
- [77] M. van Thiel, "Compendium of Shock Wave Data," Lawrence Livermore Laboratory report UCRL-50108, Vols. 1-3, Rev. 1, 1977.
- [78] M. S. Hoyt, "User's Manual for LASL Shock Hugoniot Data File," Los Alamos Scientific Laboratory report LA-7887-M, 1979.
- [79] M. E. Kipp, D. E. Grady, J. R. Asay, and R. A. Graham, "User Guide to the Sandia Shock Compression Database," Sandia National Laboratories report SAND88-2933, 1988.
- [80] D. J. Steinberg, S. G. Cochran, and M. W. Guinan, "A Constitutive Model for Metals Applicable at High-Strain Rate," J. Appl. Phys. 51, 1498-1504 (1980).
- [81] D. J. Steinberg, Lawrence Livermore National Laboratory, private communication.
- [82] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, "Equation of State Calculations by Fast Computing Machines," J. Chem. Phys. 21, 1087-1092 (1953).
- [83] J. A. Barker and D. Henderson, "What is 'Liquid'?", Rev. Mod. Phys. 48, 587-671 (1976).
- [84] The Monte Carlo routines in PANDA were adapted from a program obtained from P. A. Taylor, Sandia National Laboratories, Albuquerque, NM.
- [85] G. I. Kerley, "Equations of State and Gas-Gas Separation in Soft-Sphere Mixtures," J. Chem. Phys. 91, 1204-1210 (1989).
- [86] A. C. Mitchell and W. J. Nellis, "Shock Compression of Aluminum, Copper, and Tantalum," J. Appl. Phys. 52, 3363 (1981).
- [87] G. I. Kerley, "Equations of State for Calcite Minerals. I. Theoretical Model for Dry Calcium Carbonate," High Pressure Research 2, 29-47 (1989).
- [88] G. I. Kerley, "Theoretical Model of Explosive Detonation Products: Tests and Sensitivity Studies," to be published in Proceedings of the Ninth Symposium (International) on Detonation, Aug. 28 - Sep. 1, 1989, Portland, OR.
- [89] H. C. Hornig, E. L. Lee, M. Finger, and J. E. Kurrle, "Equation of State of Detonation Products," in Proceedings of the Fifth Symposium (International) on Detonation, edited by D. J. Edwards, ACR-184 (Office of Naval Research, Department of the Navy, 1970), pp. 503-511.

- [90] M. Born and J. R. Oppenheimer, "Zur Quantentheorie der Molekeln," *Ann. Physik* (Leipzig) 84, 457 (1927).
- [91] P. A. Urtiew and R. Grover, "The Melting Temperature of Magnesium Under Shock Loading," *J. Appl. Phys.* 48, 1122-1126 (1977). Eq. 4.
- [92] J. W. Bond, K. M. Watson, and J. A. Welch, Jr., *Atomic Theory of Gas Dynamics* (Addison-Wesley Publishing Co., Inc., Reading, Massachusetts, 1965). Chap. 5.



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