LA-8833-M
Manual

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

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

Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

This work was supported by the US Department of Energy, Office of Office of Basic Energy Sciences.

Edited by Patricia Metropolis
Photocomposition by Kristine Mathieson

LA-8833-M
Manual

UC-32 and UC-34
Issued: November 1981

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Gerald I. Kerley

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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ACKNOWLEDGMENTS

Much of this research, especially those parts pertaining to the Sesame library and to statistical atom theories, is based upon work done by Jack Barnes. I am grateful to Jack and also to Walter Huebner for their support, encouragement, and guidance during the past 12 years. I thank Joe Abdallah, who has run the PANDA code and found a number of problems that had to be corrected, and Vickie Montoya, who typed the manuscript. Finally, I am grateful to the Department of Energy for financial support.

USER'S MANUAL FOR PANDA:
A COMPUTER CODE FOR CALCULATING
EQUATIONS OF STATE

by

Gerald I. Kerley

ABSTRACT

PANDA is an interactive computer code that constructs equations of state (EOS) for materials over a wide range of densities and temperatures. It provides several options for such contributions to the EOS as the cold curve, lattice vibrations, fluid degrees of freedom, electronic excitations, and intramolecular vibration and rotation. The user enters parameters that define the EOS and makes calculations to test and study the model. The code generates standard Sesame EOS tables that can be read in to other codes or added to a data library for applications.

I. INTRODUCTION

A. Equations of State: General Considerations

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 bulk properties of matter are needed for a variety of applications, particularly those that involve numerical simulation of dynamic processes (hydrodynamic flow). The PANDA code is one member in a family of computer programs developed at Los Alamos National Laboratory for computing tables of the EOS and related material properties. These tables are made available to users through the computer-based Sesame library.[1-3]

When an EOS is calculated over a wide range of densities and temperatures, many different physical phenomena are encountered. At low temperatures, atoms and molecules are in the ground electronic state, and the EOS is determined by the nuclear degrees of freedom: translation, vibration, and rotation. At high temperatures, thermal excitation and ionization of the electrons become important and may dominate the effects of nuclear motion. A rigorous treatment of the electronic contributions requires a quantum mechanical model for hot condensed matter. Heating and compression also induce phase transitions and chemical reactions, which are often accompanied by dramatic changes in the thermodynamic properties.

At present there is no single model or computer code that can treat all of these phenomena simultaneously and accurately. For this reason, a computational model that uses *several* computer codes linked together has been developed at Los Alamos. The total problem is broken down into parts, each of which can be handled by a separate code. The approach consists of the following steps.

(1) Begin with a single phase of a single molecular species. Separate the EOS into contributions from different degrees of freedom (see Appendix A).
(2) Assemble data for the ground electronic state (cold curve) and thermal electronic contributions from quantum mechanical calculations and experimental measurements.
(3) Combine cold curve, contributions from nuclear motion, and thermal electronic excitations into a total EOS table.
(4) If chemical reactions are important, construct the EOS for a mixture of several chemical species, using EOS tables for the pure species. Do 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 diagram and multiphase EOS, using EOS tables for each of the phases.

B. Functions of the PANDA Code

PANDA is a code for constructing an EOS table in the standard Sesame format for a single phase of a single molecular species. The phase may be either the fluid one (including the vapor, liquid, and supercritical regions) or one of the solid phases. With one exception, the dimer model, chemical reactions are not allowed. PANDA can also be used to construct a crude EOS for a more complex system, but other codes have been developed to deal with the problems of chemical reactions and phase transitions.

When constructing an EOS, the user can include the following contributions:

- cold curve
- solid lattice vibrations
- fluid nuclear motion (translational)
- vibration and rotation
- electronic excitation and ionization
- dimerization (fluids only).

The cold curve can be constructed from experimental static and shock wave measurements and from band theoretical calculations or other models. PANDA provides several options for analyzing, fitting, and extrapolating the data selected by a user. The cold curve can be put in as a table if desired.

For solids, the lattice vibration terms can be calculated using a Debye or Einstein model. The user must select one of several options for the Debye temperature and Grüneisen function and read in the required parameters. If he desires, these models can be made to extrapolate to the ideal gas limit at high temperatures and low densities, giving a crude description of melting and vaporization.

For fluids, contributions from center-of-mass motion of the molecules are computed using the CRIS model,[4-6] which is based upon hard-sphere perturbation theory. Unlike other fluid theories that use a pair potential, this model uses the solid cold curve to specify intermolecular forces. Hence the CRIS model requires no input but the cold curve.

Vibrational and rotational contributions are calculated using the harmonic oscillator-rigid rotator approximation.[7] The user must supply vibrational frequencies and rotational constants, quantities obtained from spectroscopic data.[7,8] As a first approximation, perturbations to the vibrational and rotational motion in fluids and solids can be included in the cold curve.[9]

Accurate calculations of the contributions from thermal electronic excitation require sophisticated models, which involve large amounts of labor and computing time. Therefore, computation of these terms is left to separate codes, and the results are read in to PANDA in one of several tabular formats.

An option is available that corrects the EOS of monoatomic fluids for effects of dimer formation, a useful feature in calculations of metallic vapors. The POGO code (Sec. I.D) has been designed to deal with problems where the chemistry is more complex.

In addition to the options listed above, all or part of the EOS may be read in to PANDA as a table in the standard Sesame format. This tabular option provides a link between other codes and the computing machinery provided by PANDA. For example, the user can write a separate program to compute part of the EOS as a table and read in the results to PANDA in place of the standard option.

After entering parameters that define the EOS, the user can choose from many options to analyze the predictions of his model and compare them with experiment. He can change parameters and study the results of these changes. Calculations can be sent to a plot file for graphing with a separate program. Finally, the user can construct an EOS table that can be either added to the Sesame library or read in to other codes.

C. Running the PANDA Code

PANDA is an interactive code. It has 42 commands that can be used to enter data for the models, make and display calculations, and send tables to external files. These commands are independent of one another; they can be entered in any order and repeated as often as desired. When PANDA receives an instruction, it asks the user for any data needed, executes the specified task, and prompts the user for the next option. The command END is used to terminate a run.

Table I-1 gives a list of the commands used to define an EOS model, their functions, and the sections of this manual in which they are discussed. The code can construct models for both a solid and a liquid. Both EOS models consist of up to five contributions, which the user selects by setting flags with the MOD SOL and MOD LIQ commands. These two instructions are the most general ones because they automatically call the other options if they are needed. (They do not call an option that has already been executed.) The INPUT, MOD SOL, and MOD LIQ commands are discussed in Sec. II.

The other instructions in Table I-1 are used to select options and enter data for certain parts of the EOS model. The options available under these commands are discussed in Secs. III-IX. Note that these instructions merely enter data; they do not turn that contribution "on." For example, the command COLD CURVE can be used to select an option and enter various parameters, but the user must set a flag

TABLE I-1. Commands Used to Define the EOS Model[a]

Command	Function	Section
INPUT	enter basic material data	II.A
MOD SOL	define solid model	II.B
MOD LIQ	define liquid model	II.C
COLD CURVE	define cold curve	III
LJ MATCH	revise cold curve at low densities	III.G
SOL NUC	define lattice vibration model for solid	IV
CRIS	enter parameters for liquid model	V
ELEC	define thermal electronic terms	VI
VIB ROT	enter vibrational and rotational parameters	VII
DIMER	enter parameters for dimerization model	VIII
SOL TAB	read in table for solid	IX.B
LIQ TAB	read in table for liquid	IX.B

[a] The INPUT command is automatically called at the start of each run. The MOD SOL and MOD LIQ commands automatically call any other options needed. The other commands must be called to change parameters already entered.

with the MOD SOL command to add the cold curve into the total EOS. This feature of the code makes it easy for a user to turn contributions to the EOS on and off without having to reenter data.

Table I-2 gives a list of the commands that make various calculations using the models (see Sec. X). The results are listed at the teletype (TTY). The PLOT command can be used to send the results to an external file for graphing. The instructions in Table I-2 should not be called until those in Table I-1 have been used to define a model, or part of it.

The instructions listed in Table I-3 are used to create EOS tables in the standard Sesame 2 format and send them to external files. These tables can be read in to display codes for evaluation, submitted to other physics programs for calculations of phase transitions and chemical equilibrium, or incorporated directly into a data library for use in applications.

Several examples of PANDA runs are given in Sec. XI.

D. Interface with Other Codes

As noted above, PANDA can accept input from and provide output to other codes. A brief description of these programs and their functions is given below.

- SES2D, SES3D, and DSPLX[1] display data from an EOS library in the Sesame 2 format. SES2D, written by J. D. Johnson, plots a variety of curves on a two-dimensional grid. SES3D, written by J. Abdallah, graphs EOS surfaces in three dimensions. DSPLX, written by G. I. Kerley, makes many kinds of calculations, including impedance matching of two materials, and prints the results at the TTY.
- CURVES,[10] written by J. Abdallah, makes graphs from plot files like those generated by PANDA.

TABLE I-2. Computational Options

Command	Function	Section
EOS SOL EOS LIQ	compute EOS and sound speed for solid or liquid	X. B
ISTH SOL ISTH LIQ	compute an isotherm for solid or liquid	X. C
ISCHR SOL ISCHR LIQ	compute an isochore for solid or liquid	X. C
ISB SOL ISB LIQ	compute an isobar for solid or liquid	X. D
ISEN SOL ISEN LIQ	compute an isentrope for solid or liquid	X. E
HUG SOL HUG LIQ	compute a shock Hugoniot for solid or liquid	X. F
VAP SOL VAP LIQ	compute vapor coexistence curve for solid or liquid	X. G
SPN SOL SPN LIQ	compute spinodal points for solid or liquid	X. H
CRIT SOL CRIT LIQ	compute critical point for solid or liquid	X. I
MELT	compute melting curve	X. J
RDF LIQ SFAC LIQ	compute radial distribution function or structure factor for liquid	X. K
XPT LIQ	compute transport properties for liquid	X. L
PLOT	set flag to generate PLOT file	X. A
NO PLOT	turn PLOT flag off	X. A

- SES2M, written by G. T. Rood and S. P. Lyon, is the data manager for the Sesame library. This code can be used to add tables produced by PANDA to the data file.
- INFERNO, written by D. A. Liberman,[11] calculates the electronic structure of condensed matter. ERMA, written by G. I. Kerley, processes the results, which can be used for the cold curve and the electronic excitations in PANDA. These codes are still under development. The thermal electronic terms can also be computed from statistical atom theory, [12] using a library created by J. D. Johnson.
- POGO, written by G. I. Kerley and S. P. Lyon, computes effects of chemical reactions on the EOS. It uses PANDA EOS tables for several chemical species to calculate the thermodynamic functions of the mixture and minimizes the free energy to determine the equilibrium composition. This code is still under development.

TABLE I-3. Commands Used to Generate Sesame Tables

Command	Function	Section
SHIP SOL SHIP LIQ	make Sesame 2 EOS table for solid or liquid	IX
MESH SOL MESH LIQ	make density-temperature mesh for Sesame table 301	IX. E
READ MESH	read mesh for 301 table from external file	IX. E
SAVE MESH	write mesh for 301 table to external file	IX. E

- TUTTI and SES2R, written by G. I. Kerley and G. T. Rood, are used for problems involving phase transitions. TUTTI computes the phase diagram and multiphase EOS from PANDA tables for several distinguishable phases. SES2R is used to analyze shock-wave data for porous materials and materials with phase transitions.

E. Conventions

1. **Energy Zero.** The zero of energy is determined by the solid cold curve for both the solid and fluid phases. The energy on the cold curve is chosen to be zero at zero pressure, solid density. In PANDA, the solid cold curve does not include contributions from zero-point motion, which are part of the lattice vibration model. The user can change the energy zero as desired, using the MOL SOL and MOL LIQ options.

2. **Thermodynamic Consistency.** The EOS models in PANDA provide pressure, internal energy, and Helmholtz free energy as functions of density and temperature. These three functions satisfy the usual thermodynamic relations.

3. **Symbols and Units.** A list of the most important symbols and units is given in Table I-4. Consistent units are used throughout the code, as well as for input and output. (One exception to this rule is in calculation of the thermal electronic contributions to the EOS from the library of statistical atom tables; in these tables, temperature is specified in electron volts. See Sec. VI.)

4. **Programming Features.** PANDA is written for use on the Los Alamos National Laboratory CDC 7600 computer, using the FTN/LTSS compiler. Standard Fortran is used throughout most of the code, but system-dependent features include input/output and the use of large-core memory (LCM). All numerical input from the TTY and packed ASCII files is done using field-free READ statements. For files in binary format, all input and output are isolated in two routines. Output files are made monitor-mode by use of the SETMON routine. Direct addressing is used for all arrays in LCM.

TABLE I-4. Symbols and Units

Symbol	Name	Units
ρ	density	gm/cm^3
T	temperature	K
P	pressure	GPa
E	internal energy	MJ/kg
A	Helmholtz free energy	MJ/kg
S	entropy	MJ/kg-K
D_0	dissociation energy (dimer molecule)	eV
ω	vibrational frequency	cm^{-1}
B	rotational constant	cm^{-1}

F. Program Availability

Los Alamos users can obtain the PANDA code from the Common File System, using the MASS utility.

```
MASS   GET   DIR = /PANDA/CODE   FPAN   APAN
```

FPAN is the Fortran source code, and APAN is the absolute binary. APAN can be executed as shown in the examples of Sec. XI.

Users outside Los Alamos can obtain PANDA by writing to

Sesame Library, MS 925
Los Alamos National Laboratory
P. O. Box 1663
Los Alamos, NM 87545

and providing a magnetic tape on which the Fortran source code will be written.

II. DEFINING AN EOS MODEL

A. The INPUT Command

The instruction INPUT enters seven basic material parameters that are used in several places throughout the code. This command is automatically called at the beginning of a PANDA run. The user is prompted as follows.

```
  ENTER NAME OF OPTION
? INPUT
  ENTER Z,AW,ECOH,RHOREF,TREF,GAMREF,DEBREF
?
```

Z	(total atomic number)
AW	(molecular weight)
ECOH	(solid cohesive energy)
RHOREF	(reference density)
TREF	(reference temperature)
GAMREF	(Grüneisen parameter)
DEBREF	(Debye temperature)

Use of these parameters varies slightly, and often some can be defaulted (set to 0), depending upon the EOS models specified by the user.

The atomic number Z is used in high-density extrapolations of the cold curve and the CRIS model, in thermal electronic contributions, and in creation of the Sesame 201 table. For molecules, Z is set equal to the *total* number of electrons in a molecule (sum of the atomic numbers for the atoms).

The cohesive energy ECOH is the experimental heat of vaporization of the solid at 0 K. (The code adds a correction for zero-point energy, when needed.) This quantity is used when the cold curve is computed from the Hugoniot or entered as a table and in the low-temperature extrapolation of the CRIS model.

The optional parameters RHOREF and TREF define a reference state for the solid under typical experimental conditions. 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 and in making guesses and setting bounds on variables used in searches.

GAMREF and DEBREF are the Grüneisen parameter and the Debye temperature at the reference state. These quantities are used for the solid lattice vibration model. In some cases the code will calculate estimates for these parameters if they are set to zero on input (see Sec. IV).

B. The Solid Model

The solid EOS consists of up to five contributions, which the user selects by setting flags. The Helmholtz free energy A_s, the internal energy E_s, and the pressure P_s are given by the following expressions.

$$A_s(\rho,T) = E_c(\rho) + A_L(\rho,T) + A_e(\rho,T) + A_{VR}(\rho,T) + A_{TS}(\rho,T) + \Delta E_s \quad , \qquad \text{(II-1)}$$

$$E_s(\rho,T) = E_c(\rho) + E_L(\rho,T) + E_e(\rho,T) + E_{VR}(\rho,T) + E_{TS}(\rho,T) + \Delta E_s \quad , \tag{II-2}$$

and

$$P_s(\rho,T) = P_c(\rho) + P_L(\rho,T) + P_e(\rho,T) + P_{VR}(\rho,T) + P_{TS}(\rho,T) \quad . \tag{II-3}$$

E_c,P_c are the energy and pressure on the cold curve (Sec. III).
A_L,E_L,P_L are the lattice vibration terms (Sec. IV).
A_e,E_e,P_e are the thermal electronic terms (Sec. VI).
A_{VR},E_{VR},P_{VR} are the vibration-rotation terms (Sec. VII).
A_{TS},E_{TS},P_{TS} are the tabular terms (Sec. IX).
ΔE_s is the shift in energy zero.

The command MOD SOL defines the solid model. The user is prompted as follows.

```
  ENTER NAME OF OPTION
? MOD SOL
  DEFINE SOLID MODEL - ENTER FLAGS FOR COLD
  CURVE, NUC MOD, ELEC MOD, VIBRO, TABLE
?
```

The user responds by entering five integer flags; a 1 includes the contribution and a 0 leaves it out. (The flag for the tabular term can be either 1 or 2; see Sec. II. D.) Next the code prompts the user for needed data that have not *already* been entered. For example, if PANDA needs data for the lattice vibration terms, the user will receive the same prompts as if he had entered the SOL NUC instruction (see Sec. IV). Hence the entire setup for a solid model can be accomplished with a single MOD SOL command, if desired.

When all data have been entered, one last prompt is issued.

```
  ENTER SHIFT IN ENERGY ZERO (SOLID)
?
```

The user then enters the energy shift, ΔE_s. This quantity is chosen to fix the zero of energy at the desired value.

Detailed discussions of the options available for the various contributions to the solid EOS are given in subsequent sections. Examples using the MOD SOL command are given in Sec. XI.

C. The Fluid Model

The fluid EOS can consist of up to five contributions selected by the user with the MOD LIQ command. The thermodynamic functions are given by the following expressions.

$$A_F(\rho,T) = A_{CR}(\rho,T) + A_e(\rho,T) + A_{VR}(\rho,T) + A_{TF}(\rho,T) + A_{DM}(\rho,T) + \Delta E_F \quad , \tag{II-4}$$

$$E_F(\rho,T) = E_{CR}(\rho,T) + E_e(\rho,T) + E_{VR}(\rho,T) + E_{TF}(\rho,T) + E_{DM}(\rho,T) + \Delta E_F \quad , \qquad \text{(II-5)}$$

and

$$P_F(\rho,T) = P_{CR}(\rho,T) + P_e(\rho,T) + P_{VR}(\rho,T) + P_{TF}(\rho,T) + P_{DM}(\rho,T) \quad . \qquad \text{(II-6)}$$

A_{CR}, E_{CR}, P_{CR} are the CRIS model terms (Sec. V).
A_e, E_e, P_e are the thermal electronic terms (Sec. VI).
A_{VR}, E_{VR}, P_{VR} are the vibration-rotation terms (Sec. VII).
A_{TF}, E_{TF}, P_{TF} are the tabular terms (Sec. IX).
A_{DM}, E_{DM}, P_{DM} are the dimer terms (Sec. VIII).
ΔE_F is the shift in energy zero.

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 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.

The MOD LIQ command is used like MOD SOL. The user is prompted as follows.

```
  ENTER NAME OF OPTION
? MOD LIQ
  DEFINE LIQUID MODEL - ENTER FLAGS FOR CRIS,
  ELEC MOD, VIBRO, TABLE, DIM MOD
?
```

The user enters five flags; a 1 includes a term and a 0 leaves it out. (The flag for the tabular term can be either 1 or 2; see Sec. II. D.) Next the code prompts the user for data that have not been entered previously. One last prompt is issued.

```
  ENTER SHIFT IN ENERGY ZERO (LIQUID)
?
```

The solid and fluid models in PANDA have the same zero of energy. Hence the user should normally enter the same energy shift for both models.

The options available for the fluid model are discussed further in subsequent sections, and examples are presented in Sec. XI.

D. 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,[13] is used to study problems in which the ions and 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 SHIP SOL and SHIP LIQ commands (Sec. IX. G).

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[14] 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 EOS quantities go to zero at $T = 0$.
- The thermal electronic terms, denoted by A_e, E_e, and P_e in Eqs. (II-1)-(II-6), are always included in the electron EOS.
- If a tabular term is included in the EOS, the MOD SOL and MOD LIQ commands must set the flag to specify whether it belongs to the ion or electron EOS. For the ion EOS, the flag is set equal to 1; for the electron EOS, the flag is set equal to 2.

Note that the solid curve is included in the ion EOS rather than in the electron EOS. One reason for this decision is that the cold curve is not an additive term in the liquid EOS model; it is strongly coupled to the nuclear motions. The liquid EOS does not extrapolate to the solid cold curve at $T = 0$ because the molecular arrangement is disordered and therefore different from the arrangement of the solid. Similar changes in the structure occur when phase changes and chemical reactions take place at high temperature. The definitions of the ion and electron EOS used in PANDA are preserved and consistent when the results are used in the TUTTI and POGO codes.

III. COLD CURVE OPTIONS

A. General

PANDA offers four options for constructing a cold curve for the solid from experimental or theoretical data obtained by the user. In addition, it provides features for extrapolating to high densities [the Thomas-Fermi-Dirac (TFD) match] and low densities (the LJ match).

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

```
  ENTER NAME OF OPTION
? COLD CURVE
  COLD CURVE - ENTER ICLD, RTFD, ZTFD, RLJ, FACLJ
?
```

ICLD	(cold curve option)
ICLD = 1	(compute from Hugoniot)
ICLD = 2	(analytic LJ formula)
ICLD = 3	(analytic EXP-N formula)
ICLD = 4	(tabular cold curve)
RTFD	(density for TFD match)
ZTFD	(atomic number for TFD match)
RLJ	(density for LJ match)
FACLJ	(exponent for LJ match).

B. Cold Curve from Shock Hugoniot

In many applications, a good estimate of the 0 K curve can be made from shock-wave data by direct calculation using the Mie-Grüneisen EOS.[15-16] In this case, the user must define a model for the solid lattice vibration terms. Details of the calculation are given in Appendix B.

In PANDA, the experimental curve of shock velocity U_s vs particle velocity U_p is represented by a polynomial,

$$U_s = C_0 + S_1 U_p + S_2 U_p^2 \quad , \tag{III-1}$$

where C_0 is the bulk sound speed. When the user specifies the 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 Sec. IV). 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. (III-1). The cold curve is computed and saved as a table, along with interpolation coefficients. As explained in Appendix B, this table covers a limited density range, and extrapolation procedures are used for low and high densities.

Note: The procedure described above is not always valid, and it should be used carefully. 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 analyzed carefully and recentered.

C. Analytic Lennard-Jones (LJ) Formula

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

$$E_c(\rho) = a_1\rho^{a_2} - a_3\rho^{a_4} + E_B \qquad \text{(III-2)}$$

and

$$P_c(\rho) = \rho\,(a_1a_2\rho^{a_2} - a_3a_4\rho^{a_4}) \quad . \qquad \text{(III-3)}$$

PANDA prompts the user as follows.

```
   ENTER L-J CONSTANTS, A1,A2,A3,A4
 ?
```

The user enters the four constants in Eqs. (III-2) and (III-3). The code computes E_B to adjust the zero of energy as required by the convention. Setting $P_c(\rho_0) = 0$, $E_c(\rho_0) = 0$ gives

$$\rho_0 = \left(\frac{a_3a_4}{a_1a_2}\right)^{1/(a_2-a_4)} \qquad \text{(III-4)}$$

and

$$E_B = a_3\rho_0^{a_4} - a_1\rho_0^{a_2} \quad . \qquad \text{(III-5)}$$

This form of the cold curve is of interest because it can be derived from simple pair potentials that have been studied with Monte Carlo and molecular dynamics techniques.[6] 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.

D. Analytic EXP-N Formula

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

$$E_c(\rho) = a_1 \; \exp\left(-a_2/\rho^{1/3}\right) \; - a_3\rho^{a_4} + E_B \qquad \text{(III-6)}$$

and

$$P_c(\rho) = \rho\left[\frac{a_2}{3\rho^{1/3}}\, a_1 \; \exp\;\left(-a_2/\rho^{1/3}\right) - a_3a_4\rho^{a_4}\right] \quad . \qquad \text{(III-7)}$$

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 $P_c(\rho_o) = 0$, $E_c(\rho_o) = 0$, constants a_1 and a_3 can be written as follows.

$$a_1 = \frac{3a_3a_4}{a_2} \rho_o^{a_4+1/3} \exp\,(a_2/\rho_o^{1/3}) \quad . \tag{III-8}$$

$$a_3 = \frac{E_B}{\rho_o^{a_4}(1 - 3a_4\rho_o^{1/3}/a_2)} \tag{III-9}$$

In this way, a_1 and a_3 are eliminated so that the more convenient and familiar quantities E_B and ρ_o can be used for input. PANDA prompts the user as follows.

```
      ENTER EXP-N CONSTANTS, EBZPE,RZRO,A2,A4
  ?
```

The user enters E_B, ρ_o, a_2, and a_4, as defined above.

The EXP-N form is much more realistic at high densities than the LJ form. However, it breaks down drastically at extremely high densities where both E_c and P_c become negative. The TFD match option should be used to correct this problem, especially when the CRIS model is used.

The EXP-N form is closely related to the Buckingham (exp-6) potential, for which $a_4 = 2$. Calculations using this form have been very successful for the rare gases[17] and for molecular liquids.[9,18] This option also works well for metals when a_4 is treated as an adjustable parameter in fitting data. The constant a_2 can be expressed in terms of the bulk modulus of the solid, as follows.

$$a_2 = \frac{1}{2}\,\rho_o^{1/3}\left(Q \pm \sqrt{Q^2 - 36\beta_o/\rho_o E_B}\right) \tag{III-10}$$

and

$$\beta_o = \left(\rho\,\frac{dP_c}{d\rho}\right)_{\rho_o} \quad , \tag{III-11}$$

where $Q = 1 + 3a_4 + 3\beta_o/a_4\rho_oE_B$. If E_B, ρ_o, and β_o are known, the cold curve can be determined by adjusting a_4 until a good fit to experimental or theoretical data is obtained.

E. Tabular Cold Curve

If ICLD = 4, the cold curve is entered as a table of pressure vs density. PANDA issues the following message.

```
      ENTER INPUT TAPE NUMBER OR ZERO FOR TTY
  ?
```

If the user enters an integer number n > 0, PANDA reads the cold curve from a file called TAPEn. (TAPES 1-5 can be used for this purpose.) TAPEn must be an ASCII file containing one value of the density ρ and the corresponding cold curve pressure P_c per card. A minimum of 4 and a maximum of 75 ρ, P_c points can be entered without sorting. The last point should be followed with a blank card.

If the user enters a value of n = 0, input is from the TTY. PANDA issues the following message.

```
    ENTER DENSITY AND PRESSURE, POINT BY POINT
 ?
```

The code reads from the TTY just as it does from the external file, except that it enters a prompt (?) for each line of input. Data input terminates when the user enters a density of zero.

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

$$P_c = \rho^2 \frac{dE_c}{d\rho} \quad . \tag{III-12}$$

The following interpolation formula is used. For $\rho_i \leqq \rho < \rho_{i+1}$,

$$E_c = E_c(i) + \rho_i^{-1} \left[P_c(i)x + A_1(i)x^2 + A_2(i)x^3 + A_3(i)x^4\right] \quad , \tag{III-13}$$

$$P_c = (\rho/\rho_i)^2 \left[P_c(i) + 2\,A_1(i)x + 3\,A_2(i)x^2 + 4\,A_3(i)x^3\right] \quad , \tag{III-14}$$

and

$$x = \frac{\rho - \rho_i}{\rho_i} \tag{III-15}$$

The coefficients $A_1(i)$, $A_2(i)$, and $A_3(i)$ are chosen by fitting Eq. (III-14) to the pressure table. Equation (III-13), together with the convention for the zero of energy, determines the quantities $E_c(i)$. Note that the procedure just described does not give continuous derivatives of the pressure.

For low densities, $\rho < \rho_1$, the code extrapolates. An LJ match can be used to guarantee that the cold curve has the correct behavior in this region. For high densities, the TFD match is done automatically. If the user sets RTFD = 0, the match is made at RMAX, the highest density entered. The user can specify another value for RTFD, but the code takes RTFD = RMAX as the upper limit for the match.

F. 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 of RTFD. The extrapolation procedure is automatically used for ICLD = 1 and ICLD = 4. The other parameter in the TFD match, ZTFD, is normally set = Z or defaulted = 0 (which the code resets to Z). It can be used to modify the formula slightly, a step that may be necessary for molecular systems.

The high-density formula is based upon the TFD statistical model of the atom. The TFD theory is believed to be accurate at pressures above 10^3 GPa. To interpolate from the cold curve at ρ = RTFD to the TFD formula at high densities, the following expressions are used.

$$E_c(\rho) = \left[E_T(\rho) - E_T(\mathrm{RTFD})\right] y(\rho) + \Delta E_c \quad , \tag{III-16}$$

$$P_c(\rho) = P_T(\rho)\, y(\rho) + \rho[E_T(\rho) - E_T(RTFD)]\, \frac{dy}{d\rho} \quad , \tag{III-17}$$

and

$$y(\rho) = 1 + \frac{b_1}{\rho} + \frac{b_2}{\rho^{4/3}} + \frac{b_3}{\rho^{5/3}} \quad , \tag{III-18}$$

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

In PANDA, the TFD energies and pressures are represented by the formulas

$$E_T(\rho) = \frac{1505.2125}{Wx^2}\, Z\, e^{-F(x)} \quad , \tag{III-19}$$

$$P_T(\rho) = \frac{1003.475}{x^5}\, e^{-F(x)} \left(1 + \frac{x}{2}\frac{dF}{dx} \right) \quad ,. \tag{III-20}$$

and

$$F(x) = C_1 x + C_2 x^2 + C_3 x^2 \ell n\, x \quad , \tag{III-21}$$

where $x = (W/Z\rho)^{1/3}$, Z is the atomic number, and W is the molecular weight. The quantities C_1, C_2, and C are

$$C_1 = 0.703473 + 1.130622\, (ZTFD)^{2/3} \quad , \tag{III-22}$$

$$C_2 = 0.3 - \frac{0.00245\, (ZTFD)^{5/2}}{1 + 0.0028\, (ZTFD)^2} \quad , \tag{III-23}$$

and

$$C_3 = 0.6 + 0.0386\, (ZTFD)^{4/3} \quad . \tag{III-24}$$

These formulas agree with numerical results* to better than 2% for pressures above 100 GPa. At lower pressures they are accurate enough for interpolation.

The parameter ZTFD in Eqs. (III-22)-(III-24) can be adjusted to change the numerical results. For molecules, a value of ZTFD < Z gives the best fit to results obtained by additive volume mixing of the TFD data for atoms.

G. The LJ Match

A low-density extrapolation formula** can be obtained by entering nonzero values for the parameters RLJ and FACLJ. These quantities can also be entered separately, using the command LJ MATCH. PANDA prompts the user as follows.

---

*Numerical data were generated using unpublished TFD codes of R. D. Cowan and D. A. Liberman, Los Alamos National Laboratory.

**The idea for the LJ match was furnished by B. I. Bennett, Los Alamos National laboratory.

```
   ENTER NAME OF OPTION
? LJ MATCH
   LJ MATCH - ENTER RLJ, FACLJ
?
```

For $\rho \leq$ RLJ, the following expressions are used.

$$E_c(\rho) = f_1\rho^{f_2} - f_3\rho^{\mathrm{FACLJ}} + E_B \tag{III-25}$$

and

$$P_c(\rho) = \rho\left(f_1 f_2 \rho^{f_2} - f_3 f_4 \rho^{\mathrm{FACLJ}}\right) \quad . \tag{III-26}$$

These formulas are similar to Eqs. (III-2) and (III-3), but 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 $\rho = \mathrm{RLJ}$. 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 line may be sensitive to these adjustments.

IV. SOLID LATTICE VIBRATION MODELS

A. General

PANDA offers five models for computing the contributions from lattice vibrations to the EOS. there are three options for the Grüneisen function and Debye temperature used in these models. In addition, the code provides an extrapolation formula, the virial match, which can be used for low densities.

Data are entered using the command SOL NUC. 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.

```
  ENTER NAME OF OPTION
? SOL NUC
  LATTICE MODEL - ENTER INPT,IGRN,FT, SPSN,RV
?
```

INPT	(lattice vibration option)
INPT = 1	(Debye model)
INPT = −1	(Debye model with cutoff)
INPT = 2	(solid-gas formula)
INPT = 3	(Einstein model)
INPT = −3	(Einstein model with cutoff)
IGRN	(Grüneisen parameter option)
IGRN = 1	(cold curve formula)
IGRN = 2	(Sesame formula)
IGRN = 3	(Thompson formula)
FT	(used in Grüneisen formula) (see Sec. IV.E)
SPSN	(Poisson's ratio) (see Sec. IV. E)
RV	(density for virial match).

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).

B. THE DEBYE MODEL

PANDA provides two versions of the Debye model. In the standard model (INPT = 1), the Helmholtz free energy, internal energy, and pressure are given by the following expressions.[19,20]

$$A_L(\rho,T)=\frac{R}{W}\left[\frac{9}{8}\,\theta+3\,T\,\ell n\,(1-e^{-\theta/T})-T\,D\,(\theta/T)\right] \quad , \tag{IV-1}$$

$$E_L(\rho,T)=\frac{R}{W}\left[\frac{9}{8}\,\theta+3\,T\,D\,(\theta/T)\right] \quad , \tag{IV-2}$$

$$P_L(\rho,T) = \frac{R}{W}\,\rho\gamma(\rho)\left[\frac{9}{8}\theta + 3\,T\,D(\theta/T)\right] \quad , \tag{IV-3}$$

and

$$D(x) = \frac{3}{x^3}\int_0^x \frac{y^3}{e^y - 1}\,dy \quad . \tag{IV-4}$$

θ is the Debye temperature, γ is the Grüneisen parameter, W is the molecular weight, and R is the gas constant (8.3144×10^{-3} MJ/kg-mole/K). 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 vibration 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 corrections overcome these problems.

Formulas for the cutoff model are discussed in Appendix C. Corrections to the standard model are very small over the entire range where the solid is thermodynamically stable (relative to the fluid phase). When the temperature is raised well above the melting curve, 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 generates separate EOS tables for the fluid and solid phases, and the TUTTI code constructs the multiphase EOS. For a crude treatment of melting, the solid-gas interpolation formula, discussed below, may give better results than the cutoff model.

C. 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. F.

The Helmholtz free energy is given by the following formula.

$$A_L = \frac{R}{W}\left\{\frac{9}{8}\theta + \frac{3}{2}\,T\,\ell n\left[\frac{f_0 + f_1(x)}{f_0 + f_1(x) + f_2(x)}\right]\right\} \quad , \tag{IV-5}$$

where $x = \theta/T$,

$$f_0 = 111.56(\rho/W)^{2/3}/(WT) \quad , \tag{IV-6}$$

$$f_1 = .513417x^2 + .010855x^3 + .052934x^4 \quad , \tag{IV-7}$$

and

$$f_2 = 1 + .687497x \quad . \tag{IV-8}$$

If $f_0 = 0$ is set in Eq. (IV-5), the result agrees very well with the Debye formula, Eq. (IV-1). When the f_0 term is included, Eq. (IV-5) goes to the ideal gas limit[19] as $T \to \infty$ or as $\theta \to 0$ (low densities).

The internal energy and pressure are found from thermodynamic relations.

$$E_L = A_L - T\left(\frac{\partial A_L}{\partial T}\right)_\rho = \frac{R}{W}\left\{\frac{9}{8}\,\theta + T\,\frac{(3/2)f_0 + 3f_3(x)}{[f_0 + f_1(x)]\;[f_0 + f_1(x) + f_2(x)]}\right\} \quad , \tag{IV-9}$$

$$P_L = \rho^2\left(\frac{\partial A_L}{\partial \rho}\right)_T = \frac{R\rho}{W}\left\{\frac{9}{8}\gamma\theta + T\,\frac{\gamma\left[3f_3(x) + \frac{3}{2}\,f_0\right] + \left(1 - \frac{3}{2}\gamma\right)\,f_0 f_2(x)}{[f_0 + f_1(x)]\,[f_0 + f_1(x) + f_2(x)]}\right\} \quad , \tag{IV-10}$$

and

$$f_3 = 0.513417x^2 + 0.192769x^3 + 0.113331x^4 + 0.054588x^5 \quad . \tag{IV-11}$$

This model can be used either with or without the virial match. The latter is preferred if IGRN = 1.

D. The Einstein Model

PANDA provides two versions of the Einstein model.[20] In the standard model (INPT = 3), the thermodynamic functions are given by

$$A_L = \frac{R}{W}\left[\frac{3}{2}\theta + 3\,T\,\ell n\,(1 - e^{-\theta/T})\right] \quad , \tag{IV-12}$$

$$E_L = \frac{R}{W}\left[\frac{3}{2}\,\theta + \frac{3\theta}{e^{\theta/T} - 1}\right] \quad , \tag{IV-13}$$

and

$$P_L = \frac{R}{W}\,\rho\gamma\left[\frac{3}{2}\,\theta + \frac{3\theta}{e^{\theta/T} - 1}\right] \tag{IV-14}$$

(The Einstein temperature θ is identical with the Debye temperature as discussed in Sec. E.)

In the modified Einstein model (INPT = −3), the sum over the lattice vibration 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.

E. Options for the Grüneisen Function

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

$$\gamma = -\frac{1}{6} + \frac{1}{2}\,\frac{\beta_c' - (FT)\;(2/3)\beta_c}{\beta_c - (FT)\;(2/3)\,P_c} \quad , \tag{IV-15}$$

where

$$\beta_c = \rho \frac{dP_c}{d\rho} \quad , \tag{IV-16}$$

and

$$\beta_c' = \rho \, \frac{d\beta_c}{d\rho} \tag{IV-17}$$

Here FT is specified by the user, as mentioned above. Equation (IV-15) represents three well-known relations.

FT = 0 is the Slater formula,[21]
FT = 1 is the Dugdale MacDonald formula,[22]
and
FT = 2 is the free volume formula.[23]

In PANDA, FT can have noninteger values in addition to the above. If the user enters a nonzero value of GAMREF on input, the code solves for FT from Eq. (IV-15) and ignores the value specified by the user. In this case, the code does not allow FT to exceed 2.5, a choice that gives poor results at high densities; it sets FT = 2.5 and resets GAMREF. If the user sets GAMREF = 0 on input, PANDA takes the specified value of FT in Eq. (IV-15), and any value can be entered.

The Grüneisen function and the Debye temperature are related by

$$\gamma = \frac{d \, \ell n \, \theta}{d \, \ell n \, \rho} \quad . \tag{IV-18}$$

For IGRN = 1, Eqs. (IV-15) and (IV-18) require the following relation.

$$\theta = C \, \frac{[\beta_c - (FT) \; (2/3) \, P_c]^{1/2}}{\rho^{1/6}} \tag{IV-19}$$

The constant C is determined from the values of RHOREF and DEBREF put in by the user.

Note: Equation (IV-15) fails when $\beta_c \leq (FT)\,(2/3)\,P_c$, which typically occurs in the tension region, below the normal solid density range. At these low densities, the code sets $\gamma = 2/3$ and $\theta = 0$, but the model should not be used in this region.

PANDA also offers two simple analytic options for γ and θ. Setting IGRN = 2 specifies the so-called Sesame formula.

$$\gamma = \gamma_o \frac{\rho_o}{\rho} + \frac{2}{3} \left(1 - \frac{\rho_o}{\rho} \right) \quad , \tag{IV-20}$$

and

$$\theta = \theta_o \left(\frac{\rho}{\rho_o} \right)^{2/3} \exp \left[(\gamma_o - 2/3) \; (1 - \rho_o/\rho) \right] \quad . \tag{IV-21}$$

Setting IGRN = 3 specifies the following formulas, from Thompson.[19]

$$\gamma = \gamma_o \frac{\rho_o}{\rho} + \frac{2}{3} \left(1 - \frac{\rho_o}{\rho} \right)^2 \tag{IV-22}$$

and

$$\theta = \theta_o \left(\frac{\rho}{\rho_o}\right)^{2/3} \exp\left\{ \gamma_o \left(1 - \frac{\rho_o}{\rho}\right) - \frac{1}{3}\left[3 - 4\left(\frac{\rho_o}{\rho}\right) + \left(\frac{\rho_o}{\rho}\right)^2\right]\right\} \quad . \qquad \text{(IV-23)}$$

In both of the above cases, the quantities ρ_o, γ_o, and θ_o are equated to the parameters RHOREF, GAMREF, and DEBREF, respectively.

As noted in Appendix B, there is one case for which the user does not have to specify a value for DEBREF. If the cold curve is determined from the Hugoniot (ICLD = 1) and if the user sets DEBREF = 0, Eq. (B-14) is used. This option requires a value for Poisson's ratio, SPSN. (If the user sets SPSN = 0, the code automatically resets it to a default value of 1/3.)

F. The Virial Match

For densities $\rho <$ RV, PANDA provides a smooth interpolation formula between the solid model and the low-density ideal gas law (Ref. 24).* The user obtains this option by entering a nonzero value for RV when specifying the lattice vibration model.

Formulas for the thermodynamic functions are as follows.

$$A_L(\rho,T) = A_L(RV,T) + \frac{RT}{W} \ell n \left(\frac{\rho}{RV}\right) + C_1(T)\mu + C_2(T)\mu^2 + C_3(T)\mu^3 \quad , \qquad \text{(IV-24)}$$

$$E_L(\rho,T) = E_L(RV,T) + D_1(T)\mu + D_2(T)\mu^2 + D_3(T)\mu^3 \quad , \qquad \text{(IV-25)}$$

and

$$P_L(\rho,T) = \frac{RT\rho}{W} + \frac{\rho^2}{RV}\left[C_1(T) + 2\,C_2(T)\mu + 3\,C_3(T)\mu^2\right] \quad , \qquad \text{(IV-26)}$$

where $\mu = \rho/RV - 1$. Continuity of the pressure at ρ = RV requires

$$C_1(T) = \frac{P_L(RV,T)}{RV} - \frac{RT}{W} \quad . \qquad \text{(IV-27)}$$

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

$$A_L \rightarrow \frac{RT}{W}\left[7.0719 - \ell n\left(\frac{W}{\rho}\right) - \frac{3}{2}\,\ell n\ (WT)\right] \text{ as } \rho \rightarrow 0 \quad . \qquad \text{(IV-28)}$$

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

$$E_L \rightarrow \frac{3}{2}\,\frac{RT}{W} \text{ as } \rho \rightarrow 0 \quad . \qquad \text{(IV-29)}$$

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*The idea for using the ideal gas free energy to extend the two-parameter virial match of Ref. 24 to a three-parameter formula was taken from B. I. Bennett, Los Alamos National Laboratory.

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

$$D_k(T) = C_k(T) - T\frac{dC_k}{dT} \text{ , where } k = 1,2,3 \quad . \qquad \text{(IV-30)}$$

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. (IV-1) and (IV-12) give

$$A_L \rightarrow 3\,\frac{RT}{W}\,\ell n\left(\frac{\theta}{T}\right) \text{ as } T \rightarrow \infty \quad . \qquad \text{(IV-31)}$$

Matching Eq. (IV-24) 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 because the pressure and internal energy do not have continuous derivatives everywhere (see Appendix C).

V. THE CRIS MODEL

A. General

The CRIS model[4-6] describes the contributions to the EOS from translational degrees of freedom 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 with one of the solid models discussed in Sec. IV, the code can predict the melting curve. 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 fluid reference system, in which the hard-sphere diameter is chosen by a variational principle. The model uses the zero-temperature 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 Sec. III. 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 nine parameters, all of which can be defaulted (set = 0).

```
  ENTER NAME OF OPTION
? CRIS
  CRIS - ENTER NGS,NZI,EPS,DR,DT,XG,BEXP,EFAC,QFAC
?
```

NGS	[number of primary quadrature points (1000)]
NZI	[number of secondary quadrature intervals (1)]
EPS	[error criterion (1×10^{-5})]
DR	[step for density derivatives (0.01)]
DT	[step for temperature derivatives (0.01)]
XG	[initial guess for search (0.4)]
BEXP	(used in expression for number of free electrons)
EFAC	(energy shift)
QFAC	(quantum correction factor).

The first six parameters apply to numerical procedures and are usually defaulted, the default value being given in parentheses. Hence only NGS and NZI, which are used in the calculation of integrals, are discussed. Use of the parameters BEXP, EFAC, and QFAC is discussed in Sec. V. B.

The CRIS model requires computation of several integrals of a single variable, which can be done by either Gauss or adaptive quadrature. For NGS $\geqq 60$, the adaptive scheme* is used: the integrand is evaluated a maximum of NGS times or until the error check is satisfied. For $1 \leqq$ NGS $\leqq 59$, the range of

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*The adaptive quadrature option calls routine QNC7, written by D. Kahaner and L. Rathmann, Los Alamos National Laboratory.

integration is divided into subintervals and a 10-point Gauss quadrature formula is used. NGS = 10 gives enough accuracy for most work, 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.

B. The Equations

Equations for the CRIS model are discussed in detail in Ref. 5. The formulas in PANDA have been generalized slightly, 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. The solid density ρ_s, which corresponds to a radius R, is given by

$$\rho_s = \frac{W\sqrt{2}}{N_0 R^3} \tag{V-1}$$

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 ρ, the coordination number is

$$\bar{\nu} = \frac{12\rho}{\rho_s} \quad . \tag{V-2}$$

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

$$N_0\phi \cong \frac{\rho}{\rho_s}\, E_c(\rho_s) \quad . \tag{V-3}$$

Equation (V-3) is valid only if the bonds are nearly additive. This result breaks down at very high densities, where the electrons are completely delocalized and $E_c \propto \rho_s^{2/3}$. In PANDA, Eq. (V-3) is revised as follows.

$$N_0\phi = \left[(1-f)\frac{\rho}{\rho_s} + f\left(\frac{\rho}{\rho_s}\right)^{2/3} \right] \left[E_c(\rho_s) - \mathrm{EFAC} \right] \quad . \tag{V-4}$$

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

$$f = \exp\left(-\mathrm{BEXP}/\rho_s^{1/3}\right) \quad , \tag{V-5}$$

where BEXP is entered by the user. If the user sets BEXP = 0, the code resets it as follows.

$$\mathrm{BEXP} = (0.23 + 0.6544 Z^{2/3})\,(W/Z)^{1/3} \quad . \tag{V-6}$$

This result 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. (V-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. (V-4) gives

$$N_0\phi \rightarrow \left(\frac{\rho}{\rho_s}\right)^{2/3} E_c(\rho_s) \rightarrow E_c(\rho) \quad . \tag{V-7}$$

Hence Eq. (V-4) provides an extrapolation to the correct limit.

The parameter EFAC in Eq. (V-4) has been introduced for empirical reasons. It can adjust the free energy of the liquid so that the calculated melting point agrees with experiment. Liquid metals usually require EFAC to be ~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. (V-3) 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

$$A_{CR}(\rho,T) = A_0(\rho,T) + A_{HS} + \mathrm{QFAC} * A_{QM} + N_0 <\phi>_0 + \Delta A_1 + \Delta A_2 \quad , \tag{V-8}$$

where A_0 is the free energy for an ideal gas.

$$A_0 = \frac{RT}{W}\left[7.0719 - \ell n\left(\frac{W}{\rho}\right) - \frac{3}{2}\ell n\,(WT)\right] \quad . \tag{V-9}$$

A_{HS} is the excess free energy for a classical hard-sphere fluid, $N_0 <\phi>_0$ is the first order perturbation term, and ΔA_1 and ΔA_2 are higher order terms (Ref. 5). The additional term, A_{QM}, is a quantum correction to the hard-sphere free energy. (To obtain this correction, set QFAC = 1 on input.) The formula of Singh and Sinha[25] is used.

$$A_{QM} = \frac{RT}{W}\left(C_1\eta + C_2\eta^2\right) \quad , \tag{V-10}$$

where

$$C_1 = 4.24264(\lambda/\sigma_0) + 1.27324(\lambda/\sigma_0)^2 \tag{V-11}$$

and

$$C_2 = 3.21645\,(\lambda/\sigma_0)^2 \quad . \tag{V-12}$$

Here λ is the thermal wavelength.

$$\lambda = \left(\frac{h^2}{2\pi WkT}\right)^{1/2} \quad . \tag{V-13}$$

The packing fraction is $\eta = N_0\pi\sigma_0^3W/6\rho$, and σ_0 is the effective hard-sphere diameter. These quantities are determined from the variational principle,[5]

$$\frac{\partial}{\partial\eta}\left(A_{HS} + \mathrm{QFAC} * A_{QM} + N_0 <\phi>_0\right)_{\rho,T} = 0 \quad . \tag{V-14}$$

The corresponding energy and pressure formulas are

$$E_{CR}(\rho,T) = \frac{3}{2}\,\frac{RT}{W} + QFAC * E_{QM} + N_o <\phi>_o + \Delta E_1 + \Delta E_2 \tag{V-15}$$

and

$$P_{CR}(\rho,T) = \frac{RT\rho}{W} + P_{HS} + QFAC * P_{QM} + N_o\rho^2 \left(\frac{\partial <\phi>_o}{\partial \rho} \right)_{\eta,T} + \Delta P_1 + \Delta P_2 \quad , \tag{V-16}$$

where

$$E_{QM} = \frac{RT}{W} \left(C_3\eta + C_2\eta^2 \right) \quad , \tag{V-17}$$

$$P_{QM} = \frac{2}{3}\,\rho\, E_{QM} \quad , \tag{V-18}$$

and

$$C_3 = 2.12132(\lambda/\sigma_0) + 1.27324(\lambda/\sigma_0)^2 \quad . \tag{V-19}$$

The above treatment of quantum effects on the EOS gives good results when applied to H_2 and D_2. Rosenfeld[26,27] has developed another model for computing quantum corrections to the CRIS model, but his approach is not included in the code at present.

C. Low-Temperature Extrapolation

The CRIS model gives good results over the entire fluid range and most of the supercooled region as well. However, there is a region near normal solid density and very low temperatures where the model has numerical problems and gives absurd 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 $T < T_L$, it sets

$$A(\rho,T) = \frac{T}{T_L}\,[A(\rho,T_L) - E(\rho,T_L)] + E(\rho,T_L) \quad , \tag{V-20}$$

$$E(\rho,T) = E(\rho,T_L) \quad , \tag{V-21}$$

and

$$P(\rho,T) = P(\rho,T_L) + (T - T_L) \left(\frac{\partial P}{\partial T} \right)_{T_L} \quad , \tag{V-22}$$

where A, E, and P are the *excess* thermodynamic quantities (deviations from the ideal gas values). The extrapolation temperature T_L is chosen from the cohesive energy,

$$\frac{RT_L}{W} = 0.020786 \text{ ECOH} \quad . \tag{V-23}$$

Equation (V-23) should put the extrapolation region well below the melting point for all materials.

D. Radial Distribution Function and Structure Factor

The CRIS model can be used to calculate the first peak in g(R), the radial distribution function of the fluid.[5] The structure factor is defined by

$$S(K) = 1 + \frac{N_0 \rho}{W} \int [g(R) - 1]\, e^{i\vec{K}\cdot\vec{R}}\, d\vec{R} \quad . \tag{V-24}$$

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

$$S(K) = S_0(K) + \Delta S(K) \quad . \tag{V-25}$$

$$\Delta S(K) = \frac{N_0 \rho}{W} \int [g(R) - g_0(R)]\, e^{i\vec{K}\cdot\vec{R}}\, d\vec{R} \quad . \tag{V-26}$$

The hard-sphere structure factor $S_0(K)$ is given by the equations of Verlet and Weis,[28] using the hard-sphere diameter predicted by Eq. (V-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 $\Delta S(K)$ 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[5] for large R, Eq. (V-26) gives erroneous oscillations for small wavelengths. However, the results are satisfactory for the first peak in S(K) and for larger wavelengths. In general, the corrections $\Delta S(K)$ are small.

E. Viscosity and Diffusivity

Dymond and Alder[29] 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. Dymond and Alder estimated the hard-sphere diameter from the EOS,[29] 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. Dymond's fit[30] to the molecular dynamics results[31] is used for the shear viscosity v_s.

$$v_s = v_0 \, \frac{6.1525\eta}{1 - 1.869\eta} \quad , \tag{V-27}$$

where $v_0 = 1.237 \times 10^5 \, (WT)^{1/2} \, (\rho/W\eta)^{2/3}$ poise. Numerical results for the bulk viscosity v_b are not as accurate as those for v_s. Hence PANDA uses the Enskog formula,[31]

$$v_b = 16.2975 \; v_0 \eta^2 g_0(\sigma_0) \quad , \tag{V-28}$$

where $g_o(\sigma_o)$ is the hard-sphere radial distribution function at contact. Molecular dynamics results for hard spheres[31] and soft spheres[32] indicate that v_b is less than the Enskog value at high densities. The diffusivity d is also computed from Dymond's fit.[30]

$$d = d_o\, 1.271(1 - 1.869\eta) \quad , \tag{V-29}$$

where

$$d_o = 1.484 \times 10^{-5} \frac{(WT)^{1/2}}{\rho} \left(\frac{\rho}{W\eta}\right)^{2/3} \qquad (\mathrm{cm^2/s}) \quad . \tag{V-30}$$

VI. THERMAL ELECTRONIC CONTRIBUTIONS

A. General

There are many models for calculating contributions to the EOS from thermal electronic excitation and ionization. Some of these models are so complex and require so much numerical computation that it is impractical to include them as options in the PANDA code. Therefore, the thermal electronic terms are calculated by separate codes and put in to PANDA in tabular form.

Electronic tables can be read in to the code using the general-purpose tabular option (Sec. IX) or the special purpose instruction ELEC. If the code needs data, the ELEC command will be issued automatically under the commands MOD SOL and MOD LIQ. The user is prompted as follows.

```
  ENTER NAME OF OPTION
? ELEC
  ELECTRONIC TERM - ENTER TABLE ID, TL(EV), RL
?
```

ID	(material number of electronic table)
TL	(low-temperature extrapolation boundary)
RL	(low-density extrapolation boundary).

If the user specifies ID = 0, PANDA reads an ASCII file called EMMIN, containing entropy tables supplied by the user, and the parameters TL and RL are not used. This option is discussed in Sec. VI. B. If the user specifies a nonzero value for ID, PANDA reads a binary file called TFDELS, containing a library of scaled electronic tables. The parameters TL and RL are used in an optional extrapolation procedure. The TFDELS library is discussed in Sec. VI. C.

B. The EMMIN Entropy Tables

For the case ID = 0, PANDA computes the entire EOS surface from a table of the electronic entropy, $S_e(\rho,T)$. The Helmholtz free energy, internal energy, and pressure are given by the following relations.

$$A_e(\rho,T) = -\int_0^T S_e(\rho,T^*)\,dT^* \quad , \tag{VI-1}$$

$$E_e(\rho,T) = A_e(\rho,T) + T\,S_e(\rho,T) \quad , \tag{VI-2}$$

and

$$P_e(\rho,T) = \rho^2 \left(\frac{\partial A_e}{\partial \rho}\right)_T \quad . \tag{VI-3}$$

This method guarantees thermodynamic consistency in the use of tabular EOS data. The numerical procedure was developed for the ERMA code, which constructs the thermal electronic contributions to the EOS using data from the INFERNO code of Liberman[11] and other theoretical models. ERMA generates the EMMIN file that is put in to PANDA.

The entropy data are tabulated at discrete densities covering the range of interest. A minimum of four densities is required. The mesh is arbitrary, but best results are obtained if $\ell n\ \rho$ is spaced at approximately equal intervals. 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 is RHO, NT. RHO (real) is the density for the isochore, and NT (integer) is the number of temperatures that are tabulated. Field lengths are arbitrary.
- The following lines are T(I), S(I) for I = 1,2, ...NT. T(I) is the I^{th} temperature on the isochore and S(I) is the corresponding entropy. There are no designated fields, so that more than one pair of T,S points can be entered on a single line.

The EMMIN 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 appear in any order. An example of the file EMMIN is displayed in Table VI-1. This file was generated by ERMA from INFERNO calculations for aluminum. (The original file had 27 isochores, of which only 4 are shown.)

The following procedure defines a continuous EOS surface from the discrete entropy data points. First, a rational function method[33] interpolates for the entropy as a function of temperature along each isochore. Using Eqs. (VI-1) and (VI-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, functions F and G are defined by

$$A_e(\rho,T) = T\{\alpha - \exp[F(x,T)]\} \qquad \text{(VI-4)}$$

and

$$E_e(\rho,T) = [\alpha T - A_e(\rho,T)]\, G(x,T) \quad , \qquad \text{(VI-5)}$$

where $x = \ell n\ \rho$. An arbitrary constant α has been introduced so that F and G are well behaved functions as $T \rightarrow 0$. (In the present version of PANDA, $\alpha = 10^{-20}$.) From Eq. (VI-3), the pressure is given by

$$P_e = -\rho T \exp[F(x,T)] \left(\frac{\partial F}{\partial x}\right)_T \quad . \qquad \text{(VI-6)}$$

Thermodynamic consistency also requires

$$E_e = A_e - T \left(\frac{\partial A_e}{\partial T}\right)_\rho \qquad \text{(VI-7)}$$

and

$$G(x,T) = T \left(\frac{\partial F}{\partial T}\right)_x \quad . \qquad \text{(VI-8)}$$

The functions F and G are defined as piecewise cubic polynomials in x, with continuous derivatives. In the interval $x_i \leqq x < x_{i+1}$, 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, $dP_e/d\rho$ is not continuous.) Furthermore, it can be shown that Eq. (VI-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. (VI-7) is satisfied at the tabulated values of x.

TABLE VI-1. Example of File EMMIN

```
 1   .64044127E+00        24
 2  0.               .62879125E-03       .23092955E+04  .69579789E-03
 3   .32144465E+04   .71149175E-03       .44677325E+04  .72918883E-03
 4   .61968030E+04   .75292616E-03       .85989345E+04  .80272827E-03
 5   .11929426E+05   .92797646E-03       .16559622E+05  .11672581E-02
 6   .22988515E+05   .15001124E-02       .31889166E+05  .18922361E-02
 7   .44259563E+05   .23266906E-02       .61422619E+05  .27942770E-02
 8   .85223448E+05   .32861402E-02       .11826146E+06  .38740920E-02
 9   .16411084E+06   .48632975E-02       .22771510E+06  .64125419E-02
10   .31599054E+06   .84087455E-02       .43846443E+06  .10789187E-01
11   .60842394E+06   .13521574E-01       .84426219E+06  .16471897E-01
12   .11715091E+07   .19342109E-01       .16256048E+07  .21860790E-01
13   .22557175E+07   .24006620E-01       .31300702E+07  .26519658E-01
14   .85412384E+00        24
15  0.               .11836121E-03       .23092955E+04  .49087980E-03
16   .32144465E+04   .55578832E-03       .44677325E+04  .61471744E-03
17   .61968030E+04   .67180221E-03       .85989345E+04  .74564473E-03
18   .11929426E+05   .87716083E-03       .16559622E+05  .11008011E-02
19   .22988515E+05   .14066120E-02       .31889166E+05  .17673767E-02
20   .44259563E+05   .21662898E-02       .61422619E+05  .25983316E-02
21   .85223448E+05   .30631685E-02       .11826146E+06  .36281374E-02
22   .16411084E+06   .45642911E-02       .22771510E+06  .60283956E-02
23   .31599054E+06   .79306658E-02       .43846443E+06  .10186734E-01
24   .60842394E+06   .12762359E-01       .84426219E+06  .15558303E-01
25   .11715091E+07   .18344717E-01       .16256048E+07  .20832340E-01
26   .22557175E+07   .22982026E-01       .31300702E+07  .25399190E-01
27   .11394855E+01        24
28  0.              0.                   .23092955E+04  .27998983E-03
29   .32144465E+04   .36070573E-03       .44677325E+04  .44955936E-03
30   .61968030E+04   .54383383E-03       .85989345E+04  .65182003E-03
31   .11929426E+05   .79915029E-03       .16559622E+05  .10137782E-02
32   .22988515E+05   .12975776E-02       .31889166E+05  .16330583E-02
33   .44259563E+05   .20039983E-02       .61422619E+05  .24048576E-02
34   .85223448E+05   .28418753E-02       .11826146E+06  .33816479E-02
35   .16411084E+06   .42666781E-02       .22771510E+06  .56517956E-02
36   .31599054E+06   .74570419E-02       .43846443E+06  .96053355E-02
37   .60842394E+06   .12034669E-01       .84426219E+06  .14686315E-01
38   .11715091E+07   .17355546E-01       .16256048E+07  .19810746E-01
39   .22557175E+07   .21958631E-01       .31300702E+07  .24294347E-01
40   .15199704E+01        24
41  0.              0.                   .23092955E+04  .16953261E-03
42   .32144465E+04   .23175948E-03       .44677325E+04  .31207391E-03
43   .61968030E+04   .41160072E-03       .85989345E+04  .53456376E-03
44   .11929426E+05   .69215445E-03       .16559622E+05  .90095993E-03
45   .22988515E+05   .11677605E-02       .31889166E+05  .14837275E-02
46   .44259563E+05   .18349136E-02       .61422619E+05  .22123815E-02
47   .85223448E+05   .26237903E-02       .11826146E+06  .31361870E-02
48   .16411084E+06   .39701738E-02       .22771510E+06  .52784003E-02
49   .31599054E+06   .69921079E-02       .43846443E+06  .90329999E-02
50   .60842394E+06   .11336443E-01       .84426219E+06  .13838614E-01
51   .11715091E+07   .16401759E-01       .16256048E+07  .18801941E-01
52   .22557175E+07   .20949310E-01       .31300702E+07  .23214720E-01
```

C. The TFDELS Library

The binary file TFDELS is a library of thermal electronic EOS tables for one or more materials.* Each EOS on this file is identified by a material number ID, which the user specifies as noted above. The scaling procedure for these data was developed for use with TFD tables, but the method does not depend on the source of the data.

---

*The TFDELS library and methods for scaling the data were developed by J. D. Johnson, Los Alamos National Laboratory.

The TFDELS file consists of one logical record, containing 1882 words, for each material. The structure of a material record is given in Table VI-2. Note that the atomic number given on the file is not used in PANDA; the value of Z appearing in the following equations is obtained from the INPUT command (Sec. II). The atomic weight from the file is used only to scale ρ_0 when interpolations are made on the tables. The value of W appearing in Eqs. (VI-12) through (VI-15) is obtained from the INPUT command. PANDA obtains the data record for material ID from file TFDELS and interpolates for the scaling functions, $P_x(\eta,T)$, $E_x(\eta,T)$, and $A_x(\eta,T)$, using methods discussed elsewhere.[1,2,33]

The free energy, internal energy, and pressure are computed from the scaling functions as follows.

$$A_e(\rho,T) = A_e^o(\rho,T) \exp\left[A_x(\eta,T)\right] \quad , \tag{VI-9}$$

$$E_e(\rho,T) = E_e^o(\rho,T) \exp\left[E_x(\eta,T)\right] \quad , \tag{VI-10}$$

and

$$P_e(\rho,T) = P_e^o(\rho,T) \exp\left[P_x(\eta,T)\right] \quad , \tag{VI-11}$$

where A_e^o, E_e^o, and P_e^o are the thermal contributions to the EOS of a homogeneous electron gas. These functions have been fit to the following formulas.[34]

$$A_e^o = -\frac{3}{4} Z \frac{RT}{W} \ell n \left[\frac{1 + by + cy^2}{cy^2}\right] \quad , \tag{VI-12}$$

$$E_e^o = \frac{3}{2} Z \frac{RT}{W} \frac{1 + by/2}{1 + by + cy^2} \quad , \tag{VI-13}$$

$$P_e^o = \left(\frac{2}{3}\right) \rho E_e^o \quad , \tag{VI-14}$$

TABLE VI-2. Structure of a Record on File TFDELS

Words	Symbol	Description
1	ID	material number
2	NR	No. of compressions
3	NT	No. of temperatures
4	Z	atomic number (not used)
5	ρ_o	normal density
6	W	atomic weight
7 - 32	-	not used
33 - 62	$\eta(30)$	compressions (ρ/ρ_o)
63 - 82	T(20)	temperatures (in eV)
83 - 682	$P_x(30,20)$[a]	pressure scaling function
683 - 1282	$E_x(30,20)$[a]	energy scaling function
1283 - 1882	$A_x(30,20)$[a]	free energy scaling function

[a] First index of arrays P_x, E_x and A_x corresponds to compression, second index to temperature.

and

$$y = \frac{21.5086}{T} \left(\frac{Z\rho}{W} \right)^{2/3} , \qquad \text{(VI-15)}$$

where b = 0.71729, c = 0.2636, and T is in electron volts. The scaling functions P_x, E_x, and A_x all approach zero at high densities or high temperatures.

Equations (VI-9)-(VI-11) sometimes give unsatisfactory results when extrapolating off the table at low densities or temperatures. PANDA provides an optional extrapolation procedure for T < TL and ρ < RL. (Defaults for these parameters are 1 eV = 11604.5 K and 10^{-6} gm/cm^3, respectively.)

For ρ < RL, the following formulas are used.

$$A_e(\rho,T) = A_e(RL,T) + \frac{1}{RL} P_e(RL,T) \ \ell n \left(\frac{\rho}{RL} \right) , \qquad \text{(VI-16)}$$

$$E_e(\rho,T) = E_e(RL,T) + \ell n \left(\frac{\rho}{RL} \right) \ RL \left(\frac{\partial E}{\partial \rho} \right)_{RL} , \qquad \text{(VI-17)}$$

and

$$P_e(\rho,T) = \frac{\rho}{RL} P_e(RL,T) . \qquad \text{(VI-18)}$$

For T < TL, the following formulas are used.

$$A_e(\rho,T) = C_1 \left(\frac{T}{T_L} \right)^2 - C_2 \left(\frac{T}{T_L} \right)^3 , \qquad \text{(VI-19)}$$

$$E_e(\rho,T) = - C_1 \left(\frac{T}{T_L} \right)^2 + 2C_2 \left(\frac{T}{T_L} \right)^3 , \qquad \text{(VI-20)}$$

and

$$P_e(\rho,T) = \left(\frac{T}{T_L} \right)^2 \left[P_e(\rho,T_L) + C_3 \left(1 - \frac{T}{T_L} \right) \right] , \qquad \text{(VI-21)}$$

where

$$C_1 = E_e(\rho,T_L) + 2\, A_e(\rho,T_L) , \qquad \text{(VI-22)}$$

$$C_2 = E_e(\rho,T_L) + A_e(\rho,T_L) , \qquad \text{(VI-23)}$$

and

$$C_3 = P_e(\rho,T_L) + \rho^2 \left(\frac{\partial E_e}{\partial \rho} \right)_{T_L} . \qquad \text{(VI-24)}$$

It can be shown that Eqs. (VI-16)-(VI-24) are thermodynamically consistent.

VII. VIBRATIONAL AND ROTATIONAL TERMS

A. General

In PANDA, contributions to the EOS from rotational and vibrational degrees of freedom are calculated from the rigid-rotator, harmonic oscillator approximation.[7] Data for the model are entered using the command VIB ROT. If the code needs data, this instruction will be issued automatically under the commands MOD SOL and MOD LIQ. The user is prompted as follows.

```
  ENTER NAME OF OPTION
? VIB ROT
  VIBRATION/ROTATION - ENTER IROT,BROT,SYM,NVIB
?
```

IROT	(type of molecular rotation)
IROT = 0	(no rotation)
IROT = 1	(linear molecule)
IROT = 2	(nonlinear molecule)
BROT	[rotational constant B (cm^{-1})]
SYM	(molecular symmetry number σ)
NVIB	(number of vibrational frequencies).

B. Rotational Terms

The rotational contribution to the Helmholtz free energy is

$$A_R(T) = -\frac{RT}{W} \ln Q_R \quad , \qquad \text{(VII-1)}$$

where Q_R is the rotational partition function. In PANDA, the formulas for Q_R are taken from high-temperature expansions[7] with minor modifications to insure reasonable behavior at low temperatures.

For *linear molecules* (IROT = 1) the formula is

$$Q_R = \sigma^{-1}(x^3 + x^2 + 1)^{1/3} \quad , \qquad \text{(VII-2)}$$

where

$$x = \frac{kT}{hcB} = \frac{0.69519T}{B} \quad . \qquad \text{(VII-3)}$$

Equation (VII-2) agrees with the high-temperature expansion[7] for large x. At low temperatures it is well behaved and is approximately correct, although not exact. The internal energy for a linear molecule is

$$E_R(T) = \frac{1}{3}\,\frac{RT}{W}\,\frac{3x^3 + 2x^2}{1 + x^2 + x^3} \quad . \tag{VII-4}$$

There is no contribution to the pressure in the rigid rotator approximation.

Nonlinear molecules have three rotational degrees of freedom, each of which can have a different rotational constant. For this case (IROT = 2), B is defined to be the geometric mean of the three constants,

$$B = (B_1B_2B_3)^{1/3} \quad . \tag{VII-5}$$

At high temperatures all nonlinear molecules have the same partition function as the spherical top ($B_1 = B_2 = B_3 = B$), provided B is defined as above.[7] In PANDA, the formulas are

$$Q_R = \frac{1}{\sigma}\left(\pi x^3 + \frac{1}{2}\pi x^2 + 1\right)^{1/2} \tag{VII-6}$$

and

$$E_R(T) = \frac{3}{2}\,\frac{RT}{W}\,\frac{x^3 + x^2/3}{x^3 + x^2/2 + 1/\pi} \quad , \tag{VII-7}$$

where x is defined by Eq. (VII-3). Equation (VII-6) agrees with the high-temperature result for $x \gg 1$ and is well behaved, although not exact, at low temperatures.

The above expressions, for 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 (see Ref. 9).

C. Vibrational Terms

In PANDA, the standard harmonic oscillator formulas[7] have been modified to include a cutoff in the sum over vibrational states. This cutoff excludes excited states with energies far in excess of the molecular dissociation energy. If a cutoff is not used, the harmonic oscillator 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 partition function for a harmonic oscillator (with a cutoff) is given by

$$q_\omega = \sum_{k<n} \exp\left[-\beta(k + 1/2)hc\omega\right] = \exp\left(-\beta hc\omega/2\right)\frac{1 - \exp(-n\beta hc\omega)}{1 - \exp(-\beta hc\omega)} \quad , \tag{VII-8}$$

where ω is the vibrational frequency. Note that q_ω contains a contribution from zero-point motion. This term is ignored in PANDA because it affects only the energy zero of the EOS.

The vibration contributions to the free energy and internal energy are

$$A_v(\rho,T) = \frac{RT}{W}\sum_l g_l\,\ell n\left[\frac{1 - \exp(-\beta hc\omega_l)}{1 - \exp(-n_l\beta hc\omega_l)}\right] \tag{VII-9}$$

and

$$E_v(\rho,T) = \frac{RT}{W}\sum_i g_i \ \beta hc\omega_i \ F_i \quad , \tag{VII-10}$$

where

$$F_i = \frac{1}{\exp(\beta hc\omega_i) - 1} - \frac{n_i}{\exp(n_i\beta hc\omega_i) - 1} \quad . \tag{VII-11}$$

The sum is taken over the NVIB vibrational levels with frequencies ω_i, degeneracies g_i, and cutoff values n_i. PANDA allows the frequencies to be density dependent.

$$\omega_i = \omega_i^o + a_i\rho \quad , \qquad i = 1, \ ...\text{NVIB}, \tag{VII-12}$$

where ω_i^o are the frequencies for an isolated molecule and a_i are constants specified by the user. The constants a_i define the pressure dependence of the vibrational terms.

$$P_v(\rho,T) = \frac{RT}{W} \ \rho\sum_i \gamma_i \ g_i\beta hc\omega_i \ F_i \quad , \tag{VII-13}$$

where

$$\gamma_i = \frac{d \ \ell n \ \omega_i}{d \ \ell n \ \rho} = \frac{a_i\rho}{\omega_i} \quad . \tag{VII-14}$$

The user must enter four parameters for each of the NVIB frequencies specified using the VIB ROT instruction. PANDA issues the following message.

```
  FOR LEVEL 1, ENTER W,G,FN,AG
?
```

The user responds by entering ω_1^o, g_1, n_1 (real), and a_1 for the first frequency. The code issues additional prompts until data for all NVIB levels have been entered.

For many molecules, the vibrational frequencies and degeneracies can be obtained from spectroscopic data.[7,8] An estimate of the cutoff n_i can be made from the dissociation energy. In the absence of experimental data, the user should set $a_i = 0$ except to perform sensitivity studies.

VIII. DIMERIZATION MODEL

A. General

The PANDA dimerization model is used for fluids that are monoatomic in the condensed phase but form some diatomic molecules in the vapor. A simple approximation is used to calculate the thermodynamic functions for a mixture of the dimer and monomer components, 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 POGO code can be used for problems where a more sophisticated theory is needed.

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

```
  ENTER NAME OF OPTION
? DIMER
  DIMER - ENTER RZRO,DZRO,WVIB,BROT,S,QE,FACN
?
```

RZRO	(hard-sphere density for dimer)
DZRO	[dissociation of energy of dimer (eV)]
WVIB	(vibrational frequency of dimer)
BROT	(rotational constant for dimer)
S	(symmetry factor for dimer)
S = 1	(for heteronuclear molecules)
S = 2	(for homonuclear molecules)
QE	(electron factor for monomer)
FACN	(cutoff factor for vibrational states).

With the exception of QE, all of the above parameters are used to calculate the EOS of a fluid of dimer molecules, as described in Sec. B. The factor QE (normally set = 1) is used in the chemical equilibrium calculation, described in Sec. C.

B. EOS for Dimer Molecules

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

$$A_D(\rho,T) = A_0(\rho,T) + A_{HS}(\rho,T) + A_{VR}(T) + \Delta E_D \quad , \tag{VIII-1}$$

$$E_D(\rho,T) = \frac{3}{2}\,\frac{RT}{W_D} + E_{VR}(T) + \Delta E_D \quad , \tag{VIII-2}$$

and

$$P_D(\rho,T) = \frac{RT\rho}{W_D} + P_{HS}(\rho,T) \quad , \tag{VIII-3}$$

where W_D is the *molecular* weight (twice the atomic weight W, specified using the INPUT command). A_0 is the free energy for an ideal gas, as given in Eq. (V-9). A_{HS} and P_{HS} are the excess free energy and pressure for a hard-sphere fluid (Ref. 5). The packing fraction is defined by

$$\eta = \frac{\pi \sigma_0^3 \rho}{6W_D} = \frac{0.645\ \rho}{\mathrm{RZRO}} \quad , \tag{VIII-4}$$

where σ_0 is the hard-sphere diameter and RZRO is specified by the user. In this simple model, A_D and P_D are infinite at $\rho = \mathrm{RZRO}$, and no dimer molecules can form for $\rho \geq \mathrm{RZRO}$. 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 RZRO. As a rough approximation, σ_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 Sec. VII for a linear rigid rotator with one vibrational degree of freedom. (The vibrational frequency is independent of density.) The symmetry factor should be S = 2 in normal use of the model, because dimer molecules are homonuclear. The cutoff in the sum over the vibrational levels is given by

$$n = 8067 * \mathrm{FACN} * \frac{\mathrm{DZRO}}{\mathrm{WVIB}} \quad , \tag{VIII-5}$$

where DZRO is in electron volts and WVIB is in centimeters^{-1}. With FACN = 1, Eq. (VIII-5) excludes all vibrational states with energies exceeding the dissociation energy. The parameter FACN can be varied to study the sensitivity of the EOS to the vibrational model.

The constant term ΔE_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

$$\Delta E_D = E_B - R * \frac{\mathrm{DZRO}}{W_D} \quad , \tag{VIII-6}$$

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 DZRO in electron volts.)

C. 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 a monomer and dimer components is given by

$$A(\rho,T) = f A_M(\rho,T) + (1-f)\left[A_D(\rho,T) + \frac{RT}{W}\ell n\ (QE)\right] + \frac{RT}{W}\left[f\,\ell n\, f + \frac{1}{2}(1-f)\,\ell n\,(1-f)\right] \quad . \tag{VIII-7}$$

The monomer fraction f is given by

$$f = \frac{1}{2}\left[\sqrt{x^2 + 4x} - x\right] \quad , \tag{VIII-8}$$

where

$$x = \exp\left[\frac{2W}{RT}(A_D - A_M) + 2\,\ell n\,(QE) - 1\right] \quad . \tag{VIII-9}$$

The internal energy and pressure are

$$E(\rho,T) = f\, E_M(\rho,T) + (1 - f)\, E_D(\rho,T) \qquad \text{(VIII-10)}$$

and

$$P(\rho,T) = f\, P_M(\rho,T) + (1 - f)\, P_D(\rho,T) \quad . \qquad \text{(VIII-11)}$$

The thermodynamic quantities for the monomer component, A_M, E_M, and P_M, are constructed from the *first four* contributions specified by the user with the MOD LIQ command. The EOS for a monoatomic fluid must include a translational term (CRIS model), and it may include an 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 QE is the electron spin degeneracy for the ground state of the atom. In principle, the effects of spin degeneracy should be included in the electronic contributions to the EOS. Therefore, the user should set QE = 1 when the electronic terms are specified for the monomer component. If an electronic term is not included in the monomer EOS, the value of QE for an isolated atom should be entered so that the model predicts the correct amount of dissociation.

IX. SESAME TABULAR OPTIONS

A. Structure of Sesame Files

The Sesame library[1-3] is a general-purpose system for storing, accessing, and using EOS and other material properties. The PANDA code can access data from external files having the standard Sesame format, and it can construct tables and send them to external files. A brief discussion of Sesame files is given in this section and a more complete description in Refs. 1-3.

A *data record* is the fundamental unit of information in the Sesame library. A *catalog number* identifies the type of data and the table format. PANDA works with five types of records, which are described in Table IX-1. The most important data type (catalog number 301) contains tables of pressure, internal energy, and Helmholtz free energy at discrete points on a rectangular grid of densities and temperatures. 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.

A *material file* consists of one or more data records for a specific material, together with an index. Each material is assigned a *material number*. Finally, a *library file* consists of one or more material files and a directory. Binary-formatted files are used for the Sesame library.*

---

*The structure of a binary file depends upon both the computer and the operating system. References 1 and 2 describe a method for sending Sesame data from one computing system to another, using a system-independent format (BCD or ASCII representation).

TABLE IX-1. Format of Sesame Data Records

Table No.	Word No.	Symbol	Description
201: Basic data	1	Z	av atomic number
	2	W	av atomic weight
	3	ρ_0	normal density
	4	β_0	bulk modulus
	5	T_0	std temperature
301: Total EOS 303: Ion EOS 304: Electron EOS	1	NR	no. of densities
	2	NT	no. of temperatures
	3	ρ(I),I=1,NR	density mesh
	3+NR	T(J),J=1,NT	temperature mesh
	3+NR+NT	(P(I,J),I=1,NR),J=1,NT	pressure
	3+NR+NT+NR*NT	(E(I,J),I=1,NR),J=1,NT	internal energy
	3+NR+NT+2*NR*NT	(A(I,J),I=1,NR),J=1,NT	Helmholtz free energy
401: Vaporization	1	NT	no. of temperatures
	2	P(I),I=1,NT	pressure
	2+NT	T(I),I=1,NT	temperature
	2+2*NT	RV(I),I=1,NT	vapor density
	2+3*NT	RL(I),I=1,NT	liquid density
	2+4*NT	EV(I),I=1,NT	vapor internal energy
	2+5*NT	EL(I),I=1,NT	liquid internal energy

In PANDA, the commands SOL TAB and LIQ TAB access a 301 table for constructing an EOS model. These options are discussed in Sec. IX. B. The rest of this section discusses the methods and options for building Sesame tables and sending them to external files.

B. Reading in a 301 Table

The command SOL TAB instructs the code to read an external Sesame file and load a 301 table for the solid EOS model, and LIQ TAB causes PANDA to load a 301 table for the liquid EOS. Different tables can be specified for the two cases. If the code needs data, these two instructions will be issued automatically under the MOD SOL and MOD LIQ commands. The user is prompted as follows.

```
  ENTER NAME OF OPTION
? SOL TAB
  ENTER MATERIAL ID AND INPUT TAPE NUMBER
?
```

The user enters the material number (integer) defined above and an integer number n that specifies external file TAPEn. (TAPES 1-5 can be used for this purpose.) For a two-temperature EOS, the commands MOD SOL and MOD LIQ should be used to label the tabular term; the flag is set to 1 if the term belongs with the ion table and to 2 if it belongs with the electron table.

C. Constructing Sesame Tables

The instructions SHIP SOL and SHIP LIQ are used to make Sesame tables for the solid and liquid, respectively. Each SHIP command generates a file having the standard Sesame format, containing one material file and a directory. Hence the user should specify a different tape unit each time a SHIP command is used.

The user is prompted as follows.

```
  ENTER NAME OF OPTION
? SHIP SOL
  ENTER TABLE ID NUMBER
?
```

The user responds by entering the catalog number (integer) 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 send the data to an external file. 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 SHIP 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 TABLE ID NUMBER
? 0
  ENTER MATERIAL ID, DATE, OUTPUT TAPE NUMBER
?
```

The user enters three parameters (all integers).

ID	(material number to be assigned to the EOS)
DATE	[a 6-digit number (for example, 021281 represents Feb. 12, 1981)]
n	(number of external file)

The code writes out the EOS tables to a file called TAPEn. (TAPES 1-5 can be used for this purpose.)

D. The 201 Table

The structure of a 201 data record is given in Table IX-1. The atomic number Z and atomic weight W are taken from the values specified with the INPUT command.

The normal density ρ_o, bulk modulus β_o, and temperature T_o refer to a standard state having a pressure and temperature specified by the user. The code issues the following prompt.

```
  ENTER TABLE ID NUMBER
? 201
  STANDARD STATE - ENTER P, T, AND GUESS OF RHO
?
```

The user enters the pressure and temperature of the standard state and a guess of the density ρ_o. The code makes an iterative computation to find ρ_o and β_o and prints out the results at the TTY.

The standard state is used most frequently as a default for the initial state in hydrodynamic calculations. At Los Alamos the following conventions have been adopted.

(1) If the substance is a solid or a liquid at room temperature (defined as 298 K), the standard state is $P = 0, T = 298$ K.

(2) If the substance is a vapor at room temperature, the standard state is the liquid at the triple point.

(3) The internal energy is set to zero at the standard state, using the energy shift discussed in Sec. II.

E. 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 four commands for this purpose: MESH SOL, MESH LIQ, READ MESH, and SAVE MESH. When the user instructs the code to make a 301 or 300 table with a SHIP command, the mesh entered previously is used. If no mesh has been entered, PANDA requests one by issuing the same prompts as if the user had entered MESH SOL or MESH LIQ.

The commands MESH SOL and MESH LIQ instruct 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. There are four options.

MTYPE = 1 is linear. Values of the density or temperature are equally spaced on the specified interval.

MTYPE = 2 is logarithmic. The logarithms of the density or temperature are equally spaced on the specified interval. (This option cannot be used if the interval includes zero or negative values.)

MTYPE = 3 is a special mesh for density only. Densities on the specified interval are chosen so that the corresponding values of the pressure are equally spaced in the logarithm. The pressures are evaluated along the $T =$ TREF isotherm, using the solid model (MESH SOL) or the liquid model (MESH LIQ). (This option should be used only in the compression region, where pressure is a monotonically increasing function of density.)

MTYPE = 4 is a special mesh for temperature only. Temperatures on the specified interval are chosen so that the corresponding values of the pressure are equally spaced in the logarithm. The pressures are evaluated along the $\rho =$ RHOREF isochore, using the solid model (MESH SOL) or the liquid model (MESH LIQ).

Options 3 and 4 are particularly useful when the EOS table covers a wide density and temperature range. They give an accurate representation of the EOS using fewer points than the linear or logarithmic meshes.[33]

PANDA prompts the user as follows.

```
  ENTER NAME OF OPTION
? MESH SOL
  DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE
?
```

The user enters the lower and upper limits of the density interval, the number of points on the interval, and the type of mesh to be used. 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.

```
  DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE
?0  0  0  0
  TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE
?
```

As before, the user enters the lower and upper limits, the number of points, and the type of mesh for the interval. Several sections can be entered and the process terminates if MTYPE = 0.

The command READ MESH instructs PANDA to read the mesh from an external ASCII file called MSHDAT. The format of this file is as follows.

- The first line gives NR (number of densities) and NT (number of temperatures). Both parameters are integers, and field lengths are arbitrary.
- The next lines give NR real values of the density, in monotonically increasing order. Field lengths are arbitrary, and there can be several values on one line.
- The next lines give NT real values of the temperature, in monotonically increasing order. Field lengths are arbitrary, and there can be several values on one line.

An example of the file MSHDAT is shown in Table IX-2. In this case, the mesh consists of 10 densities, spaced logarithmically on the interval $0.1 \leqq \rho \leqq 10$, and 6 temperatures, spaced equally on the interval $100 \leqq T \leqq 1000$.

TABLE IX-2. Example of File MSHDAT

```
1     10    6
2    .10000000E+00  .16681005E+00  .27825594E+00  .46415888E+00
3    .77426368E+00  .12915497E+01  .21544347E+01  .35938137E+01
4    .59948425E+01  .10000000E+02
5    .10000000E+03  .28000000E+03  .46000000E+03  .64000000E+03
6    .82000000E+03  .10000000E+04
```

The command SAVE MESH instructs PANDA to store the mesh in the file MSHDAT, using the same format described above. Hence the mesh can be saved for future use, either in PANDA or in another code. Note: This command writes over and destroys information already on the file.

F. The 301 Table: Maxwell Constructions

At 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.[35] However, the user can instruct the code to include the Maxwell constructions[36] 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.

Typical pressure isotherms are illustrated in Fig. IX-1. Consider first the highest temperature isotherm, denoted by T_1. Points C and D are called "spinodals." States between the spinodals, $\rho_C \leqq \rho \leqq \rho_D$, have $(\partial P/\partial \rho)_T \leqq 0$ and are mechanically unstable. Points A and B are states that have both the same pressure and the same Gibbs free energy. For densities $\rho_A \leqq \rho \leqq \rho_B$, 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

$$f_V = \frac{\rho_B/\rho - 1}{\rho_B/\rho_A - 1} \quad . \tag{IX-1}$$

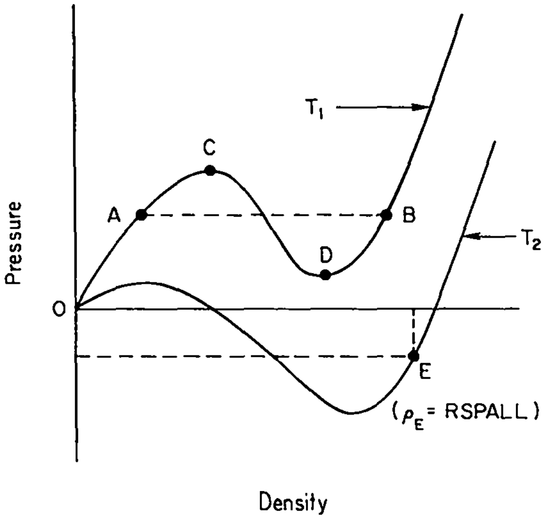

Fig. IX-1. Typical pressure isotherms, showing Van der Waals loops and Maxwell constructions.

The internal energy and Helmholtz free energy in the two-phase region are given by

$$E(\rho,T) = f_V\, E(\rho_A,T) + (1 - f_V)\, E(\rho_B,T) \qquad \text{(IX-2)}$$

and

$$A(\rho,T) = f_V\, A(\rho_A,T) + (1 - f_V)\, A(\rho_B,T) \quad . \qquad \text{(IX-3)}$$

In PANDA, the user can specify that the above Maxwell constructions be included only for temperatures above a value designated as TSPALL. For $T \leq$ TSPALL, the isotherms have the form shown by curve T_2 in Fig. IX-1. In this case, the isotherm is permitted to go into tension until it reaches point E, where ρ = RSPALL; RSPALL is defined as the liquid density at T = TSPALL and P = 0. For $\rho \leq$ RSPALL, the pressure, internal energy, and Helmholtz free energy are taken to be constant. (The EOS is fictitious for states having $\rho \leq$ RSPALL and $T \leq$ TSPALL, but this region is included to make a rectangular table.)

After constructing the nonequilibrium table, PANDA prompts the user as follows.

```
   ENTER 1 TO OBTAIN MAXWELL CONSTRUCTIONS
?
```

If the user enters 1, the code issues the following message.

```
   MAXWELL CONSTRUCTION - ENTER TSPALL,TCRIT
?
```

Here TSPALL is the lower limit of the equilibrium coexistence region, as defined above, and TCRIT is the critical temperature, which should be determined before making the table. (TCRIT must be specified so that the code will not search for coexistence boundaries at temperatures above the two-phase region.)

Next the user is prompted to enter a guess for the liquid density at T = TSPALL. The code iterates to obtain the exact value for RSPALL. Finally, PANDA prompts the user to enter guesses for the vapor and liquid densities at *each* temperature in the mesh for which TSPALL < T < TCRIT. The code iterates to obtain the exact densities and the vapor pressure. Guesses of the vapor and liquid densities should be obtained before making the table, by using the VAP LIQ or VAP SOL options or by constructing a 401 table (see Sec. IX. H).

If PANDA cannot find the vapor pressure using the guesses provided, it prompts the user for new guesses. The attempt to make the Maxwell constructions is aborted if zero is entered for either the vapor or liquid density. In this case, the user is given the chance to save the nonequilibrium table.

```
   ERROR IN MAXWELL CONSTRUCTION
   - ENTER 1 TO SAVE NONEQUILIBRIUM TABLE
?
```

Examples of making a 301 table, with and without Maxwell constructions, are discussed in Sec. XI.

G. The 303 and 304 Tables

The user can generate a two-temperature table 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 that for a 301 table.

If Maxwell constructions are selected, the total EOS table is treated as described above. The vapor density ρ_A and liquid density ρ_B are determined on the boundaries of the coexistence curve, and the fraction of vapor, f_V, is defined by Eq. (IX-1). Inside the coexistence region, the ion EOS is defined by

$$P_{ion}(\rho,T) = f_V\, P_{ion}(\rho_A,T) + (1 - f_V)\, P_{ion}(\rho_B,T) \quad , \tag{IX-4}$$

$$E_{ion}(\rho,T) = f_V\, E_{ion}(\rho_A,T) + (1 - f_V)\, E_{ion}(\rho_B,T) \quad , \tag{IX-5}$$

and

$$A_{ion}(\rho,T) = f_V\, A_{ion}(\rho_A,T) + (1 - f_V)\, A_{ion}(\rho_B,T) \quad . \tag{IX-6}$$

The electron EOS is similarly partitioned inside the coexistence region. The user should be aware that Eqs. (IX-4)-(IX-6) do not guarantee thermodynamic consistency. According to this prescription, only the total EOS obeys the thermodynamic relations in the region of the Maxwell constructions.

H. 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 IX-1. If the user specifies a 401 table under a SHIP command, PANDA prompts the user to enter the temperature mesh for this table.

```
  ENTER TABLE ID NUMBER
? 401
  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 (logarithmic). Then the code prompts the user to enter a second section of mesh, a third section, and so on until MTYPE = 0 is entered. 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 criticial point.

```
  TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE
? 0  0  0  0
  ENTER TCRIT, RHOCRIT
?
```

The critical point should be determined before making the table, using other options in the code (see Sec. X. A). 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 at the TTY while it is making the 401 table. The vapor and liquid densities obtained from this run also provide the user with the guesses that are needed when making the Maxwell constructions for the 301 table.

X. COMPUTATIONAL OPTIONS

A. General

The PANDA code offers several options for making calculations using the solid and liquid EOS models defined by the user. A list of the commands is given in Table I-2, Sec. I.

Results of the calculations are listed at the TTY. In addition, the PLOT command can send the results to an ASCII file (PLTOUT) for plotting with J. Abdallah's program CURVES.[10] The file PLTOUT consists of one or more blocks of data. The first card in each block contains the word START in columns 1-5 and may contain comments in columns 11-80. This card is followed by a variable number of data cards. Each specifies a single data point for plotting, but it may have several numerical fields for different variables associated with that point. The CURVES utility can plot any column within a data block as a function of any other column in the block.

The PLOT command turns on a flag that instructs PANDA to send data to the plot file. The command NO PLOT turns this flag off. (The flag is off at the beginning of a run.) When the flag is on, PANDA prompts the user to enter comments for columns 11-80 of the START card. If the user enters the word SKIP, no plot is made, but the flag stays on for future commands.

An example of the file PLTOUT is given in Table X-1, which shows one block of data generated during the sample PANDA run for aluminum (Sec. XI). The columns of data on the plot file vary for the different commands. In Table X-1, the four columns correspond to the temperature, pressure, liquid density, and solid density on the melting curve.

TABLE X-1. Example of File PLTOUT

```
START          THEORETICAL MELTING CURVE FOR ALUMINUM
   .95000000E+03  .15440064E+00  .23931907E+01  .25646938E+01
   .10000000E+04  .63570132E+00  .24121588E+01  .25742465E+01
   .11000000E+04  .16845853E+01  .24522484E+01  .25966503E+01
   .12000000E+04  .28723631E+01  .24954757E+01  .26240661E+01
   .14000000E+04  .57941952E+01  .25935641E+01  .26963861E+01
   .16000000E+04  .98794112E+01  .27200779E+01  .28010275E+01
   .18000000E+04  .16071946E+02  .28888923E+01  .29531579E+01
   .20000000E+04  .25434181E+02  .30999541E+01  .31572200E+01
   .22000000E+04  .38750472E+02  .33484721E+01  .34032975E+01
   .24000000E+04  .55982389E+02  .36121820E+01  .36699255E+01
   .26000000E+04  .76683354E+02  .38791470E+01  .39406369E+01
   .28000000E+04  .10071803E+03  .41457692E+01  .42104677E+01
   .30000000E+04  .12863363E+03  .44168535E+01  .44834218E+01
   .32000000E+04  .16152479E+03  .47003651E+01  .47662753E+01
   .34000000E+04  .20193084E+03  .50118460E+01  .50736166E+01
```

B. EOS and Sound Speed

The commands EOS SOL and EOS LIQ display thermodynamic quantities for the solid and liquid models, respectively.

```
  ENTER NAME OF OPTION
? EOS SOL
  ENTER RHO (GM/CC) AND T(KELVIN)
  R       T       P       E       A       C
?
```

The user responds by entering values for the density and temperature. PANDA prints out the density, temperature, pressure, internal energy, Helmholtz free energy, and bulk sound speed of the specified state under the column headings given above. Next the code issues another prompt (?), and the user can enter a second density and temperature point, a third, and so on. The calculation terminates when a zero density is specified.

The sound speed is calculated from the formula

$$C = \sqrt{(\partial P/\partial \rho)_s} \quad , \tag{X-1}$$

where the derivative at constant entropy is computed numerically.

If the plot flag is on, five quantities (density, temperature, pressure, internal energy, and sound speed) are sent to the plot file.

C. Isotherms and Isochores

The commands ISTH SOL and ISTH LIQ display the EOS at several densities on an isotherm. Use is as follows.

```
  ENTER NAME OF OPTION
? ISTH SOL
  ENTER TEMP, R1,R2,NPTS,MTYPE
?
```

TEMP	(temperature of isotherm)
R1,R2	(lower and upper density limits)
NPTS	(number of points on interval)
MTYPE = 1	(linear spacing)
MTYPE = 2	(logarithmic spacing)

PANDA lists a table of density, temperature, pressure, internal energy, and Helmholtz free energy. If the plot flag is on, five quantities (density, pressure, internal energy, free energy, and entropy) are sent to the plot file.

The commands ISCHR SOL and ISCHR LIQ display the EOS at several temperatures on an isochore.

```
  ENTER NAME OF OPTION
? ISCHR LIQ
  ENTER RHO,T1,T2,NPTS,MTYPE
?
```

RHO	(density for isochore)
T1,T2	(lower and upper temperature limits)
NPTS	(number of points on interval)
MTYPE = 1	(linear spacing)
MTYPE = 2	(logarithmic spacing).

PANDA lists the density, temperature, pressure, internal energy, and free energy. If the plot flag is on, five quantities (temperature, pressure, internal energy, free energy, and entropy) are sent to the plot file.

D. Isobars

The commands ISB SOL and ISB LIQ display the EOS at several temperatures on an isobar (constant pressure curve). Use is as follows.

```
  ENTER NAME OF OPTION
? ISB SOL
  ENTER P1,T1,TN,NPTS,R1(GUESS)
?
```

P1	(pressure for isobar)
T1,TN	(lower and upper temperature limits)
NPTS	(number of points on interval)
R1	(a guess of the density at pressure P1 and temperature T1).

PANDA lists the density, temperature, internal energy, free energy, and pressure. (The pressure will agree with P1 to within certain numerical limits.) Points on the temperature interval are equally spaced. 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. If the plot flag is on, four quantities (density, temperature, internal energy, and enthalpy) are sent to the plot file.

E. Isentropes

The commands ISEN SOL and ISEN LIQ display the EOS at several densities on an isentrope (constant entropy curve).

```
  ENTER NAME OF OPTION
? ISEN SOL
  ENTER T1, R1, R2, NPTS, MTYPE
?
```

T1	(initial temperature on isentrope)
R1,R2	(lower and upper density limits)
NPTS	(number of points on interval)
MTYPE = 1	(linear spacing)
MTYPE = 2	(logarithmic spacing)

PANDA lists the density, temperature, pressure, internal energy, and free energy. If the plot flag is on, these same five quantities are sent to the plot file.

F. Hugoniots

The commands HUG SOL and HUG LIQ compute Hugoniots for the solid and liquid as a function of temperature for a specified initial state. Use is as follows.

```
  ENTER NAME OF OPTION
? HUG SOL
  ENTER RZRO,PZRO,EZRO,TMIN,TMAX,NPTS,UPO
?
```

RZRO	(density of initial state)
PZRO	(pressure of initial state)
EZRO	(internal energy of initial state)
TMIN,TMAX	(lower and upper temperature limits)
NPTS	(number of points on interval)
UPO	(initial particle velocity).

PANDA lists the density, pressure, internal energy, temperature, shock velocity, and particle velocity. If the plot flag is on, five quantities (particle velocity, shock velocity, density, pressure, and temperature) are sent to the plot file. The k^th point on the temperature interval is chosen by the following prescription.

$$T_k = \mathrm{TMIN} + (\mathrm{TMAX} - \mathrm{TMIN}) \left(\frac{k-1}{\mathrm{NPTS}-1} \right)^2 \quad . \qquad \text{(X-2)}$$

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 UPO is used in the calculation of reflected shocks. For a single shock Hugoniot, where the material is initially at rest, UPO is set to 0. For a reflected shock, UPO 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.)

G. Vaporization Curve

The commands VAP SOL and VAP LIQ compute the vapor pressure and properties of the vapor and liquid on the coexistence curve 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.) Use is as follows.

```
  ENTER NAME OF OPTION
? VAP LIQ
  ENTER T(KELVIN) AND GUESSES FOR RVAP, RLIQ(GM/CC)
  T        R        P        E        A
?
```

The user enters the temperature and guesses of the vapor and liquid densities. PANDA prints out the temperature, density, pressure, internal energy, and free energy. The top line gives properties for the vapor, and the second line gives properties for the liquid. Next the code issues another prompt (?), and the user can enter another temperature and guesses of the densities. The vaporization calculation terminates when the user enters a negative value for the temperature.

If the plot flag is on, five quantities (temperature, density, pressure, internal energy, and enthalpy) are sent to the plot file. Two lines are sent, one for the vapor and one for the liquid.

The pressures of the two phases are equal to within certain numerical limits. The *liquid* pressure may not be accurate 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.

H. Spinodal Points

Spinodals are points on an isotherm where $(\partial P/\partial \rho)_T = 0$ (see Sec. IX. F). They give the extreme limits for metastability of the supercooled vapor and superheated liquid. In addition, the spinodals can be used to search for the critical point.

The commands SPN SOL and SPN LIQ find the spinodals. Use is as follows.

```
  ENTER NAME OF OPTION
? SPN LIQ
  ENTER T(KELVIN) AND GUESSES FOR SVAP, SLIQ(GM/CC)
  T          R          P          E          A
?
```

The user enters the temperature and guesses of the vapor and liquid spinodal densities. PANDA prints out the temperature, density, pressure, internal energy, and Helmholtz free energy. The first line gives vapor properties, and the second line gives liquid properties. The code continues to prompt the user for additional points until a negative temperature is introduced. (Nothing is sent to the plot file in this case.)

I. Critical Point

The *critical temperature* is the highest temperature at which the fluid can separate into distinguishable vapor and liquid phases. At the critical temperature the vapor density, liquid density, and spinodal densities all coincide at one point. This state is called the *critical point.*

The commands CRIT SOL and CRIT LIQ find the critical point by searching for the density and temperature at which both the first and second density derivatives of the pressure vanish. Use is as follows.

```
  ENTER NAME OF OPTION
? CRIT LIQ
  ENTER GUESSES OF RHOCRIT, TCRIT
?
```

The user enters guesses of the critical density and temperature. If PANDA finds the critical point, it prints out the density, temperature, pressure, internal energy, free energy, and isothermal bulk modulus (which should be close to zero).

The search for the critical point requires good guesses (accurate to about 5%) to be successful. The critical point can be estimated by using the vaporization or spinodal searches at several temperatures and extrapolating to the point at which the vapor and liquid coincide.

Equations for the CRIS model involve various integrals and derivatives that are computed numerically. As a result, the second derivative of the pressure contains numerical "noise," which interferes with the search for the critical point. Therefore, the CRIS model requires great accuracy when the CRIT LIQ command is used. Even then, the search may fail and the user may be forced to estimate the critical point by extrapolating the spinodals.

J. Melting Curve

When models for both the solid and liquid have been defined, the melting curve can be determined by finding the pressure at which the two phases have equal Gibbs free energies as a function of temperature. The command MELT is used for this purpose.

```
  ENTER NAME OF OPTION
? MELT
  ENTER T(KELVIN) AND GUESSES FOR RLIQ, RSOL(GM/CC)
    T         R         P         E         A
?
```

The user enters the temperature and guesses of the liquid and solid densities. PANDA prints out the temperature, density, pressure, internal energy, and free energy. The first line gives properties for the liquid, and the second line gives properties for the solid. Next the code issues another prompt (?), and the user can enter another temperature and guesses of the density. The melting calculation terminates when the user enters a negative value for the temperature. If the plot flag is on, four quantities (temperature, pressure, liquid density, and solid density) are sent to the plot file.

As explained in Sec. V, the empirical parameter EFAC in the CRIS model can be adjusted to force the melting curve to agree with experiment at one point.

K. Radial Distribution Function

The radial distribution function (RDF) and structure factor of the liquid are computed from the CRIS model as described in Sec. V. D.

The command RDF LIQ calculates the RDF.

```
  ENTER NAME OF OPTION
? RDF LIQ
  ENTER RHO,TEMP,R1,R2,NPTS
?
```

RHO	(density)
TEMP	(temperature)
R1,R2	[lower and upper limits of radius (angstroms)]
NPTS	(number of points on interval).

Points on the interval are equally spaced. PANDA prints out a table of three quantities (radius, RDF for the real fluid, and RDF for the hard-sphere reference system). If the plot flag is on, these three quantities are also sent to the plot file.

The command SFAC LIQ calculates the structure factor.

```
  ENTER NAME OF OPTION
? SFAC LIQ
  ENTER RHO,TEMP,Q1,Q2,NPTS
?
```

RHO	(density)
TEMP	(temperature)
Q1,Q2	[lower and upper limits of wavelength (reciprocal angstroms)]
NPTS	(number of points or interval).

Points on the interval are equally spaced. PANDA prints out a table of three quantities (wavelength, structure factor for the real fluid, and structure factor for the hard-sphere reference system). If the plot flag is on, these three quantities are also sent to the plot file.

The commands RDF LIQ and SFAC LIQ do not require the MOD LIQ instruction to define a complete liquid model. However, it is necessary that the instruction CRIS be called to enter parameters for the CRIS model.

L. Transport Properties

The command XPT LIQ computes transport properties for the liquid from the CRIS model, as described in Sec. V. E.

```
  ENTER NAME OF OPTION
? XPT LIQ
  ENTER RHO(GM/CC) AND T(KELVIN)
?
```

The user responds by entering values for the density and temperature. PANDA prints out the packing fraction, hard-sphere diameter, bulk viscosity, shear viscosity, and diffusivity. Next the code issues another prompt (?), and the user can enter a second density and temperature point, a third, and so on. The calculation terminates when either a zero density or a zero temperature is specified. (Nothing is sent to the plot file for this case.)

The command XPT LIQ does not require the MOD LIQ instruction to define a complete liquid model. However, it is necessary that the instruction CRIS be called to enter parameters for the CRIS model.

XI. EXAMPLES USING PANDA

A. Aluminum EOS

Calculations of the EOS for solid and liquid aluminum are shown in Fig. XI-1. In the first line of input, the cohesive energy was obtained from Brewer's tables.[37] Values for the solid density, Grüneisen parameter, and Debye temperature were obtained from Refs. 38 and 39.

The code is instructed by the command MOD SOL to form a solid model, which includes a cold curve, lattice vibration terms, and thermal electronic excitations. The cold curve is calculated from the Hugoniot data, and an LJ match is included to ensure realistic behavior in the tension region. Because aluminum is computed to begin melting at 82 GPa on the Hugoniot (see below), only the low-pressure shock data[40] were included in making the fit

$$U_s = 5.3 + 1.39\ U_p \quad . \tag{XI-1}$$

The Debye model and the Thompson formula for the Grüneisen parameter are used for the lattice vibration model. The electronic terms are read in from file EMMIN, which was constructed using the INFERNO and ERMA codes.

The command MOD LIQ constructs a liquid EOS using the CRIS model for the nuclear degrees of freedom and the EMMIN file for the electronic excitations. The empirical factor EFAC has been set to 0.535, so that the liquid and the solid free energy agree at the observed melting point. Commands ISB SOL and ISB LIQ make this comparison.

Next the command PLOT is used to begin generating the plot file, PLTOUT. (A portion of this file is shown in Table X-1.) Then the command MELT calculates 15 points on the melting curve, for temperatures ranging from 950 to 3400 K. Hugoniots for the solid and liquid are calculated using the commands HUG SOL and HUG LIQ, respectively.

Figure XI-2 shows the calculated melting curve and Hugoniot temperatures. This plot was made using Abdallah's program CURVES[10] from the plot file generated during the PANDA run described above. The calculated melting curve is in fair agreement with experimental data,[41] which cover the range 0-6 GPa. The solid Hugoniot crosses the melting curve at a temperature of 2650 K and a pressure of 82 GPa. The liquid Hugoniot crosses the melting curve at 2900 K and 115 GPa. At intermediate temperatures and pressures, aluminum is in a mixed solid-liquid state.

The calculated Hugoniot is shown in Fig. XI-3. As expected, the predictions agree with Eq. (XI-1) in the solid region, $U_p < 3.5$ km/s. The theory predicts a slight change in slope upon melting, and the high pressure data agree well with the experimental measurements.[40,42]

B. Methane EOS

Computation of an EOS for methane (CH_4) is described in Ref. 18. For the fluid phase, the CRIS model calculated the contributions from translational motion of the molecules, and the rigid rotator and harmonic oscillator approximations provided the rotation and vibration contributions. Reference 9 and Appendix A discuss the justification for treating these degrees of freedom separately. For the cold curve at low densities, the EXP-N form was chosen, and the parameters were obtained from the Buckingham potential. At high densities the TFD extrapolation formula was used, and the match density was chosen to fit shock-wave data.

A PANDA run to make a Sesame EOS table for fluid CH_4 is shown in Fig. XI-4. On the INPUT line, the average atomic weight is Z = 10. In the TFD match, however, ZTFD = 3 gives the best agreement

```
APAN
 THE PANDA CODE, LASL T-4, 07-07-81, VERSION 1
 ENTER Z,AW,ECOH,RHOREF,TREF,GAMREF,DEBREF
? 13 26.98154 12.12 2.7 298 2.15 395
 ENTER NAME OF OPTION
? MOD SOL
 DEFINE SOLID MODEL - ENTER FLAGS FOR COLD
 CURVE, NUC MOD, ELEC MOD, VIBRO, TABLE
? 1 1 1 0 0
 COLD CURVE - ENTER ICLD,RTFD,ZTFD,RLJ,FACLJ
? 1 0 0 2.3 .415
 LATTICE MODEL - ENTER INPT,IGRN,FT,SPSN,RV
? 1 3 0 0 0
 ENTER 3-PARAMETER FIT TO US-UP CURVE
? 5.3 1.39 0
 ELECTRONIC TERM - ENTER TABLE ID, TL(EV), RL
? 0 0 0
 ENTER SHIFT IN ENERGY ZERO (SOLID)
? 0
 ENTER NAME OF OPTION
? MOD LIQ
 DEFINE LIQUID MODEL - ENTER FLAGS FOR CRIS,
 ELEC MOD, VIBRO, TABLE, DIM MOD
? 1 1 0 0 0
 CRIS - ENTER NGS,NZI,EPS,DR,DT,XG,BEXP,EFAC,QFAC
? 10 0 0 0 0 0 0 .535 0
 ENTER SHIFT IN ENERGY ZERO (LIQUID)
? 0
 ENTER NAME OF OPTION
? ISB SOL
 ENTER P1,T1,TN,NPTS,R1(GUESS)
? 0 298 933.25 2 2.7
       R            T            E            A            P
  2.6999E+00  2.9800E+02  3.0847E-01  3.3646E-03 -4.9448E-13
  2.5618E+00  9.3325E+02  9.6467E-01 -1.0677E+00  3.2563E-10
 ENTER NAME OF OPTION
? ISB LIQ
 ENTER P1,T1,TN,NPTS,R1(GUESS)
? 0 933.25 0 1 2.5
       R            T            E            A            P
  2.3871E+00  9.3325E+02  1.2108E+00 -1.0677E+00  8.0718E-10
 ENTER NAME OF OPTION
? PLOT
 ENTER NAME OF OPTION
? MELT
 TYPE SKIP OR ENTER LABEL FOR PLOT FILE
? THEORETICAL MELTING CURVE FOR ALUMINUM
 ENTER T(KELVIN) AND GUESSES FOR RLIQ, RSOL(GM/CC)

       T            R            P            E            A
? 950 2.5 2.6
  9.5000E+02  2.3932E+00  1.5440E-01  1.2232E+00 -1.1086E+00
              2.5647E+00  1.5440E-01  9.7848E-01 -1.1043E+00
? 1000 2.5 2.6
  1.0000E+03  2.4122E+00  6.3570E-01  1.2609E+00 -1.2310E+00
              2.5742E+00  6.3570E-01  1.0194E+00 -1.2144E+00
? 1100 2.5 2.6
  1.1000E+03  2.4522E+00  1.6846E+00  1.3398E+00 -1.4758E+00
              2.5967E+00  1.6846E+00  1.1005E+00 -1.4376E+00
? 1200 2.5 2.6
  1.2000E+03  2.4955E+00  2.8724E+00  1.4230E+00 -1.7188E+00
              2.6241E+00  2.8724E+00  1.1812E+00 -1.6624E+00
? 1400 3 3
  1.4000E+03  2.5936E+00  5.7942E+00  1.6114E+00 -2.1873E+00
              2.6964E+00  5.7942E+00  1.3475E+00 -2.1021E+00
? 1600 3 3
  1.6000E+03  2.7201E+00  9.8794E+00  1.8521E+00 -2.5978E+00
              2.8010E+00  9.8794E+00  1.5377E+00 -2.4928E+00
? 1800 3 3
  1.8000E+03  2.8889E+00  1.6072E+01  2.1982E+00 -2.8830E+00
              2.9532E+00  1.6072E+01  1.7995E+00 -2.7619E+00
```

Fig. XI-1. A PANDA EOS calculation for aluminum.

```
? 2000 3.5 3.5
  2.0000E+03  3.1000E+00  2.5434E+01  2.7238E+00 -2.9670E+00
              3.1572E+00  2.5434E+01  2.2168E+00 -2.8181E+00
? 2200 3.5 3.5
  2.2000E+03  3.3485E+00  3.8750E+01  3.5042E+00 -2.7783E+00
              3.4033E+00  3.8750E+01  2.8738E+00 -2.5918E+00
? 2400 4 4
  2.4000E+03  3.6122E+00  5.5982E+01  4.5459E+00 -2.3280E+00
              3.6699E+00  5.5982E+01  3.7965E+00 -2.0841E+00
? 2600 4 4
  2.6000E+03  3.8791E+00  7.6683E+01  5.8190E+00 -1.6478E+00
              3.9406E+00  7.6683E+01  4.9591E+00 -1.3393E+00
? 2800 4 4
  2.8000E+03  4.1458E+00  1.0072E+02  7.3047E+00 -7.6160E-01
              4.2105E+00  1.0072E+02  6.3356E+00 -3.8812E-01
? 3000 4 4
  3.0000E+03  4.4169E+00  1.2863E+02  9.0209E+00  3.5030E-01
              4.4834E+00  1.2863E+02  7.9350E+00  7.8285E-01
? 3200 4.5 4.5
  3.2000E+03  4.7004E+00  1.6152E+02  1.1018E+01  1.7437E+00
              4.7663E+00  1.6152E+02  9.7967E+00  2.2190E+00
? 3400 5 5
  3.4000E+03  5.0118E+00  2.0193E+02  1.3423E+01  3.5558E+00
              5.0736E+00  2.0193E+02  1.2035E+01  4.0463E+00
? -1 0 0
 ENTER NAME OF OPTION
? HUG SOL
 ENTER RZRO;PZRO;EZRO;TMIN;TMAX;NPTS;UP0
? 2.7 0 .30847 305 2650 12 0
 TYPE SKIP OR ENTER LABEL FOR PLOT FILE
? THEORETICAL HUGONIOT FOR SOLID ALUMINUM

      R          P          E          T          US         UP
    GM/CC       GPA       MJ/KG      KELVIN     KM/SEC     KM/SEC
  2.730E+00  8.501E-01  3.102E-01  3.050E+02  5.393E+00  5.838E-02
  2.808E+00  3.251E+00  3.316E-01  3.244E+02  5.601E+00  2.150E-01
  2.981E+00  9.483E+00  4.742E-01  3.825E+02  6.101E+00  5.757E-01
  3.149E+00  1.681E+01  7.520E-01  4.794E+02  6.608E+00  9.419E-01
  3.293E+00  2.428E+01  1.118E+00  6.151E+02  7.067E+00  1.273E+00
  3.420E+00  3.189E+01  1.552E+00  7.895E+02  7.489E+00  1.577E+00
  3.535E+00  3.966E+01  2.044E+00  1.003E+03  7.885E+00  1.863E+00
  3.641E+00  4.766E+01  2.590E+00  1.255E+03  8.263E+00  2.136E+00
  3.740E+00  5.590E+01  3.187E+00  1.545E+03  8.627E+00  2.400E+00
  3.834E+00  6.440E+01  3.835E+00  1.875E+03  8.981E+00  2.656E+00
  3.922E+00  7.319E+01  4.532E+00  2.243E+03  9.327E+00  2.907E+00
  4.007E+00  8.229E+01  5.279E+00  2.650E+03  9.666E+00  3.153E+00
 ENTER NAME OF OPTION
? HUG LIQ
 ENTER RZRO;PZRO;EZRO;TMIN;TMAX;NPTS;UP0
? 2.7 0 .30847 2900 10000 12 0
 TYPE SKIP OR ENTER LABEL FOR PLOT FILE
? THEORETICAL HUGONIOT FOR LIQUID ALUMINUM

      R          P          E          T          US         UP
    GM/CC       GPA       MJ/KG      KELVIN     KM/SEC     KM/SEC
  4.285E+00  1.146E+02  8.157E+00  2.900E+03  1.071E+01  3.962E+00
  4.294E+00  1.158E+02  8.270E+00  2.959E+03  1.075E+01  3.990E+00
  4.323E+00  1.194E+02  8.608E+00  3.135E+03  1.085E+01  4.074E+00
  4.367E+00  1.251E+02  9.154E+00  3.428E+03  1.102E+01  4.206E+00
  4.426E+00  1.330E+02  9.912E+00  3.839E+03  1.124E+01  4.383E+00
  4.497E+00  1.427E+02  1.087E+01  4.367E+03  1.150E+01  4.596E+00
  4.576E+00  1.543E+02  1.202E+01  5.012E+03  1.180E+01  4.840E+00
  4.663E+00  1.674E+02  1.336E+01  5.775E+03  1.214E+01  5.109E+00
  4.754E+00  1.822E+02  1.488E+01  6.655E+03  1.250E+01  5.399E+00
  4.850E+00  1.984E+02  1.659E+01  7.653E+03  1.287E+01  5.707E+00
  4.948E+00  2.160E+02  1.848E+01  8.768E+03  1.327E+01  6.028E+00
  5.048E+00  2.350E+02  2.055E+01  1.000E+04  1.368E+01  6.362E+00
 ENTER NAME OF OPTION
? END
APAN        LTSS TIME    25.090 SECONDS
CPU=    15.196        I/O=     3.716        MEM=     6.178

 ALL DONE
```

Fig. XI-1. (cont)

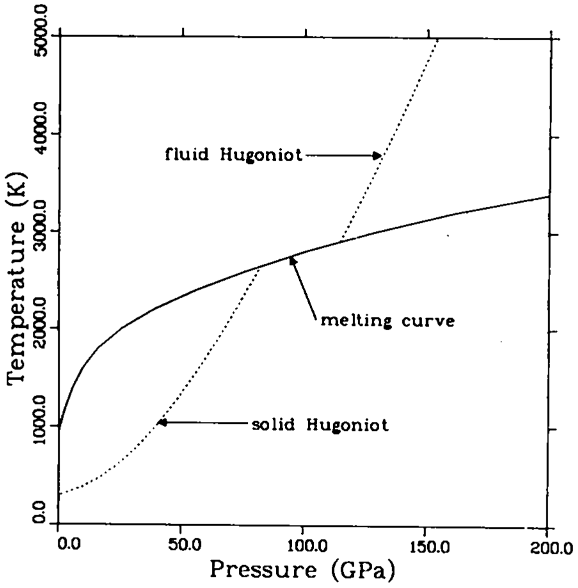

Fig. XI-2. Melting on the aluminum Hugoniot.

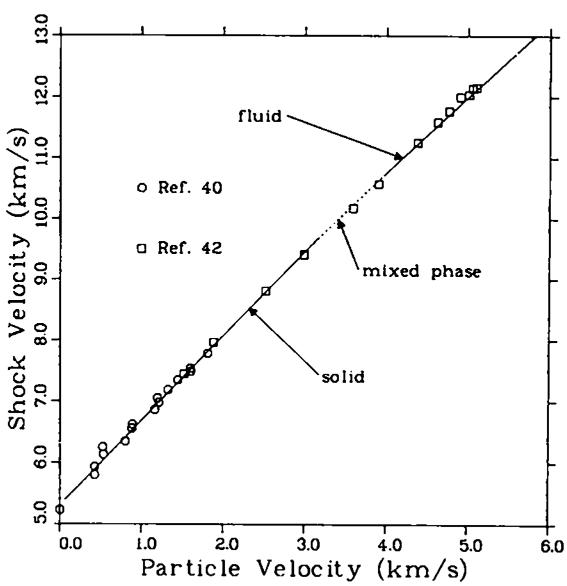

Fig. XI-3. Shock-wave data for aluminum.

with an average atom TFD calculation.* Note that CH_4 has nine vibration degrees of freedom with four unique frequencies. The cutoffs in the sum over the vibration levels were chosen by taking the C-H bond energy to be 100 kcal/mole.[43] The chosen energy shift gives an energy of zero at the triple point, $T = 90.688$ K.

The SHIP LIQ command generates Sesame tables 201, 301, and 401. No Maxwell constructions are included in the 301 table. The EOS is assigned material number 5501 and sent to file TAPE1. The command SAVE MESH is used to save the density-temperature grid that was generated for the 301 table.

Figure XI-5 plots the pressure vs volume and energy vs volume for the 301 table. The results display Van der Waals loops below the critical temperature, 200 K. These plots were made with J. D. Johnson's display code SES2D.

A second PANDA run, to make an equilibrium 301 table for fluid CH_4, is shown in Fig. XI-6. Note that the command READ MESH enters the density-temperature grid generated in the previous run. In this example, the parameter TSPALL is set to include a nonequilibrium region for $T \leq 75$ K. This EOS is assigned material number 5500 and sent to TAPE2.

Figure XI-7 plots the pressure vs volume and energy vs volume for the 301 table including Maxwell constructions. For temperatures below 75 K, the pressure is allowed to go into tension. For temperatures between 75 K and the critical point, 200 K, the coexistence region is treated according to the equilibrium model discussed in Sec. IX. F.

---

*Numerical data were generated using unpublished TFD codes of R. D. Cowan and D. A. Liberman, Los Alamos National Laboratory.

```
APAN
 THE PANDA CODE, LASL T-4, 07-07-81, VERSION 1
 ENTER Z,AW,ECOH,RHOREF,TREF,GAMREF,DEBREF
? 10 16.0426 .65 .488 90.688 2.97 112
 ENTER NAME OF OPTION
? MOD LIQ
 DEFINE LIQUID MODEL - ENTER FLAGS FOR CRIS,
 ELEC MOD, VIBRO, TABLE, DIM MOD
? 1 0 1 0 0
 COLD CURVE - ENTER ICLD,RTFD,ZTFD,RLJ,FACLJ
? 3 .7 3 0 0
 ENTER EXP-N CONSTANTS, EBZPE,RZRO,A2,A4
? .65 .54951 11.158 2
 CRIS - ENTER NGS,NZI,EPS,DR,DT,XG,BEXP,EFAC,QFAC
? 0 0 0 0 0 0 100. 0 0
 VIBRATION/ROTATION - ENTER IROT,BROT,SYM,NVIB
? 2 5.252 12 4
 FOR LEVEL 1, ENTER W,G,FN,AG
? 2914.2 1 12 0
 FOR LEVEL 2, ENTER W,G,FN,AG
? 1526.0 2 25 0
 FOR LEVEL 3, ENTER W,G,FN,AG
? 3020.3 3 12 0
 FOR LEVEL 4, ENTER W,G,FN,AG
? 1306.2 3 25 0
 ENTER SHIFT IN ENERGY ZERO (LIQUID)
? -.29040
 ENTER NAME OF OPTION
? ISB LIQ
 ENTER P1,T1,TN,NPTS,R1(GUESS)
? 0 90.688 0 1 .5
       R            T             E             A             P
  4.5306E-01  9.0688E+01  1.2030E-06 -3.7565E-01  9.9017E-10
 ENTER NAME OF OPTION
? SHIP LIQ
 ENTER TABLE ID NUMBER
? 201
 STANDARD STATE - ENTER P, T, AND GUESS OF RHO
? 0 90.688 .45
 STANDARD STATE - RHO =  4.53060E-01       B =  8.27127E-01
 ENTER TABLE ID NUMBER
? 301
 DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE
? .1 .6 20 1
 DENSITY MESH - ENTER RMIN,RMAX,NPTS,MTYPE
? 0 0 0 0
 TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE
? 25 300 12 1
 TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE
? 0 0 0 0
 ENTER 1 TO OBTAIN MAXWELL CONSTRUCTIONS
? 0
 ENTER TABLE ID NUMBER
? 401
 TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE
? 65 185 13 1
 TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE
? 190 195 2 1
 TEMPERATURE MESH - ENTER TMIN,TMAX,NPTS,MTYPE
? 0 0 0 0
 ENTER TCRIT, RHOCRIT
? 200 .145
       T              R              P              E              A
 ENTER GUESSES OF RVAP, RLIQ AT T =  6.50000E+01
? 3.E-06 .5
  6.5000E+01  3.4635E-06  1.1667E-07  4.5971E-01 -3.1568E-01
              4.7565E-01  1.1437E-07 -7.9511E-02 -2.8200E-01
  7.5000E+01  2.8542E-05  1.1088E-06  4.7524E-01 -3.5415E-01
              4.6808E-01  1.0992E-06 -4.9793E-02 -3.1530E-01
  8.5000E+01  1.3731E-04  6.0334E-06  4.9069E-01 -3.9661E-01
              4.5894E-01  6.0283E-06 -1.8461E-02 -3.5269E-01
  9.5000E+01  4.5944E-04  2.2459E-05  5.0597E-01 -4.4267E-01
              4.4829E-01  2.2455E-05  1.4289E-02 -3.9385E-01
```

Fig. XI-4. PANDA run to generate Sesame EOS table for methane.

```
   1.0500E+02  1.1925E-03  6.3874E-05  5.2092E-01 -4.9196E-01
               4.3607E-01  6.3871E-05  4.8538E-02 -4.3854E-01
   1.1500E+02  2.5819E-03  1.4936E-04  5.3533E-01 -5.4406E-01
               4.2221E-01  1.4935E-04  8.4299E-02 -4.8658E-01
   1.2500E+02  4.8939E-03  3.0150E-04  5.4895E-01 -5.9867E-01
               4.0660E-01  3.0149E-04  1.2162E-01 -5.3780E-01
   1.3500E+02  8.4103E-03  5.4413E-04  5.6150E-01 -6.5541E-01
               3.8908E-01  5.4412E-04  1.6060E-01 -5.9211E-01
   1.4500E+02  1.3438E-02  8.9981E-04  5.7265E-01 -7.1396E-01
               3.6941E-01  8.9980E-04  2.0137E-01 -6.4943E-01
   1.5500E+02  2.0360E-02  1.3885E-03  5.8198E-01 -7.7394E-01
               3.4718E-01  1.3884E-03  2.4426E-01 -7.0975E-01
   1.6500E+02  2.9722E-02  2.0260E-03  5.8890E-01 -8.3498E-01
               3.2186E-01  2.0260E-03  2.8966E-01 -7.7311E-01
   1.7500E+02  4.2496E-02  2.8250E-03  5.9239E-01 -8.9655E-01
               2.9245E-01  2.8250E-03  3.3846E-01 -8.3974E-01
   1.8500E+02  6.0783E-02  3.7941E-03  5.9028E-01 -9.5781E-01
               2.5682E-01  3.7940E-03  3.9264E-01 -9.1017E-01
   1.9000E+02  7.3672E-02  4.3442E-03  5.8545E-01 -9.8775E-01
               2.3503E-01  4.3442E-03  4.2334E-01 -9.4727E-01
   1.9500E+02  9.1885E-02  4.9393E-03  5.7529E-01 -1.0164E+00
               2.0790E-01  4.9393E-03  4.5904E-01 -9.8641E-01
   2.0000E+02  1.4500E-01  5.5758E-03  5.3029E-01 -1.0354E+00
               1.4500E-01  5.5758E-03  5.3029E-01 -1.0354E+00
 ENTER TABLE ID NUMBER
? 0
 ENTER MATERIAL ID, DATE, OUTPUT TAPE NUMBER
? 5501 031681 1
 ENTER NAME OF OPTION
? SAVE MESH
 ENTER NAME OF OPTION
? END
APAN        LTSS TIME   146.143 SECONDS
CPU=  128.797        I/O=     2.417        MEM=   14.928

 ALL DONE
```

Fig. XI-4. (cont)

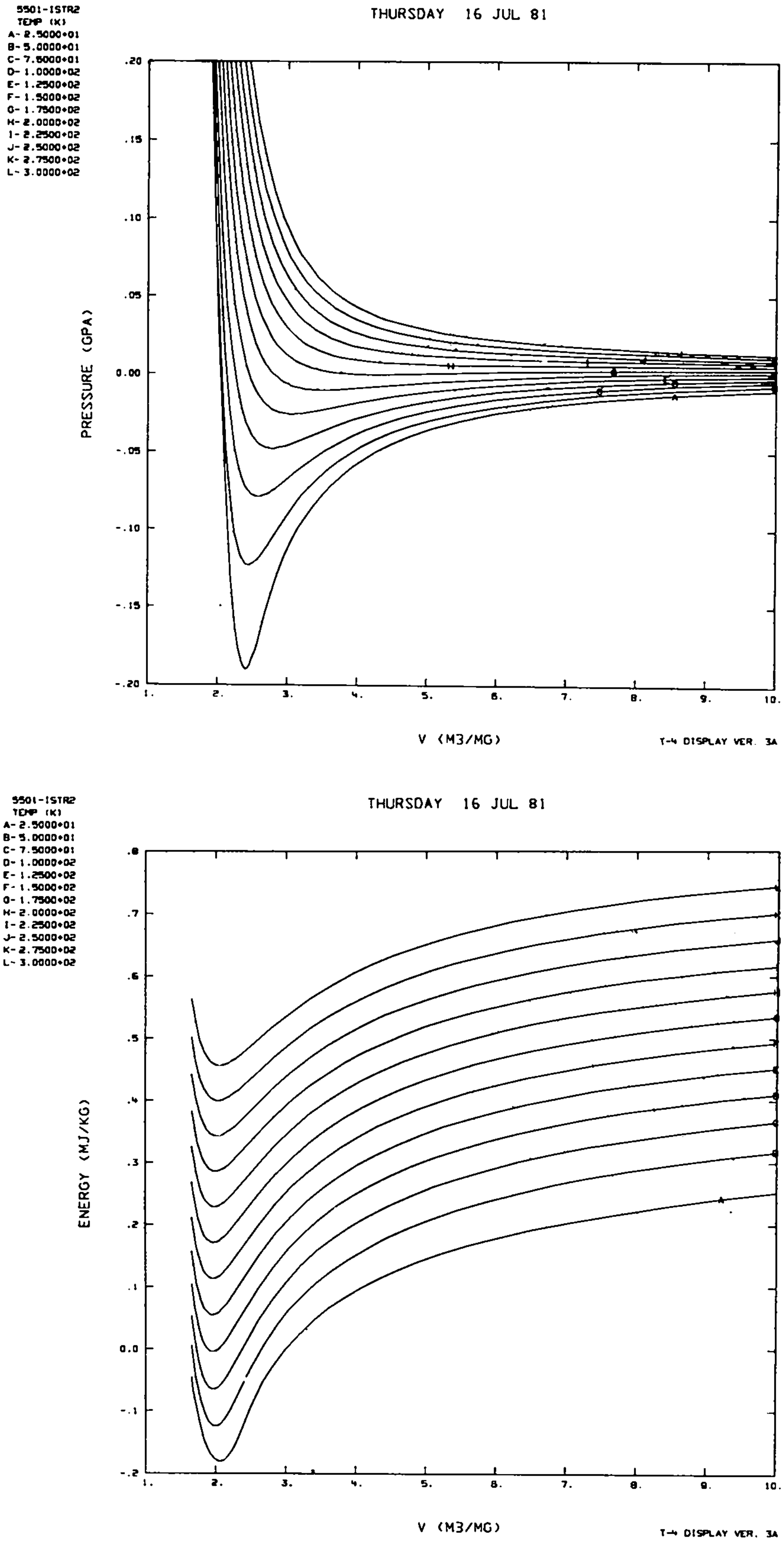

Fig. XI-5. Pressure and internal energy for nonequilibrium methane EOS table.

```
APAN
 THE PANDA CODE, LASL T-4, 07-07-81, VERSION 1
 ENTER Z,AW,ECOH,RHOREF,TREF,GAMREF,DEBREF
? 10 16.0426 .65 .488 90.688 2.97 112
 ENTER NAME OF OPTION
? MOD LIQ
 DEFINE LIQUID MODEL - ENTER FLAGS FOR CRIS,
 ELEC MOD, VIBRO, TABLE, DIM MOD
? 1 0 1 0 0
 COLD CURVE - ENTER ICLD,RTFD,ZTFD,RLJ,FACLJ
? 3 .7 3 0 0
 ENTER EXP-N CONSTANTS, EBZPE,RZRO,A2,A4
? .65 .54951 11.158 2
 CRIS - ENTER NGS,NZI,EPS,DR,DT,XG,BEXP,EFAC,QFAC
? 0 0 0 0 0 0 100. 0 0
 VIBRATION/ROTATION - ENTER IROT,BROT,SYM,NVIB
? 2 5.252 12 4
 FOR LEVEL 1, ENTER W,G,FN,AG
? 2914.2 1 12 0
 FOR LEVEL 2, ENTER W,G,FN,AG
? 1526.0 2 25 0
 FOR LEVEL 3, ENTER W,G,FN,AG
? 3020.3 3 12 0
 FOR LEVEL 4, ENTER W,G,FN,AG
? 1306.2 3 25 0
 ENTER SHIFT IN ENERGY ZERO (LIQUID)
? -.29040
 ENTER NAME OF OPTION
? READ MESH
 ENTER NAME OF OPTION
? SHIP LIQ
 ENTER TABLE ID NUMBER
? 201
 STANDARD STATE - ENTER P, T, AND GUESS OF RHO ,
? 0 90.688 .45
 STANDARD STATE - RHO =  4.53060E-01       B =  8.27127E-01
 ENTER TABLE ID NUMBER
? 301
 ENTER 1 TO OBTAIN MAXWELL CONSTRUCTIONS
? 1
 MAXWELL CONSTRUCTION - ENTER TSPALL,TCRIT
? 75 200
 ENTER GUESS OF RLIQ AT T =  7.50000E+01
? .5
 ENTER GUESSES OF RVAP, RLIQ AT T =  1.00000E+02
? 4.E-04 .45
 ENTER GUESSES OF RVAP, RLIQ AT T =  1.25000E+02
? 5.E-03 .4
 ENTER GUESSES OF RVAP, RLIQ AT T =  1.50000E+02
? 2.E-02 .35
 ENTER GUESSES OF RVAP, RLIQ AT T =  1.75000E+02
? 5.E-02 .3
 ENTER TABLE ID NUMBER
? 0
 ENTER MATERIAL ID, DATE, OUTPUT TAPE NUMBER
? 5500 031681 2
 ENTER NAME OF OPTION
? END
APAN         LTSS TIME   117.760 SECONDS
CPU=  102.893         I/O=     2.147         MEM=   12.721

 ALL DONE
```

Fig. XI-6. Methane EOS table with Maxwell constructions.

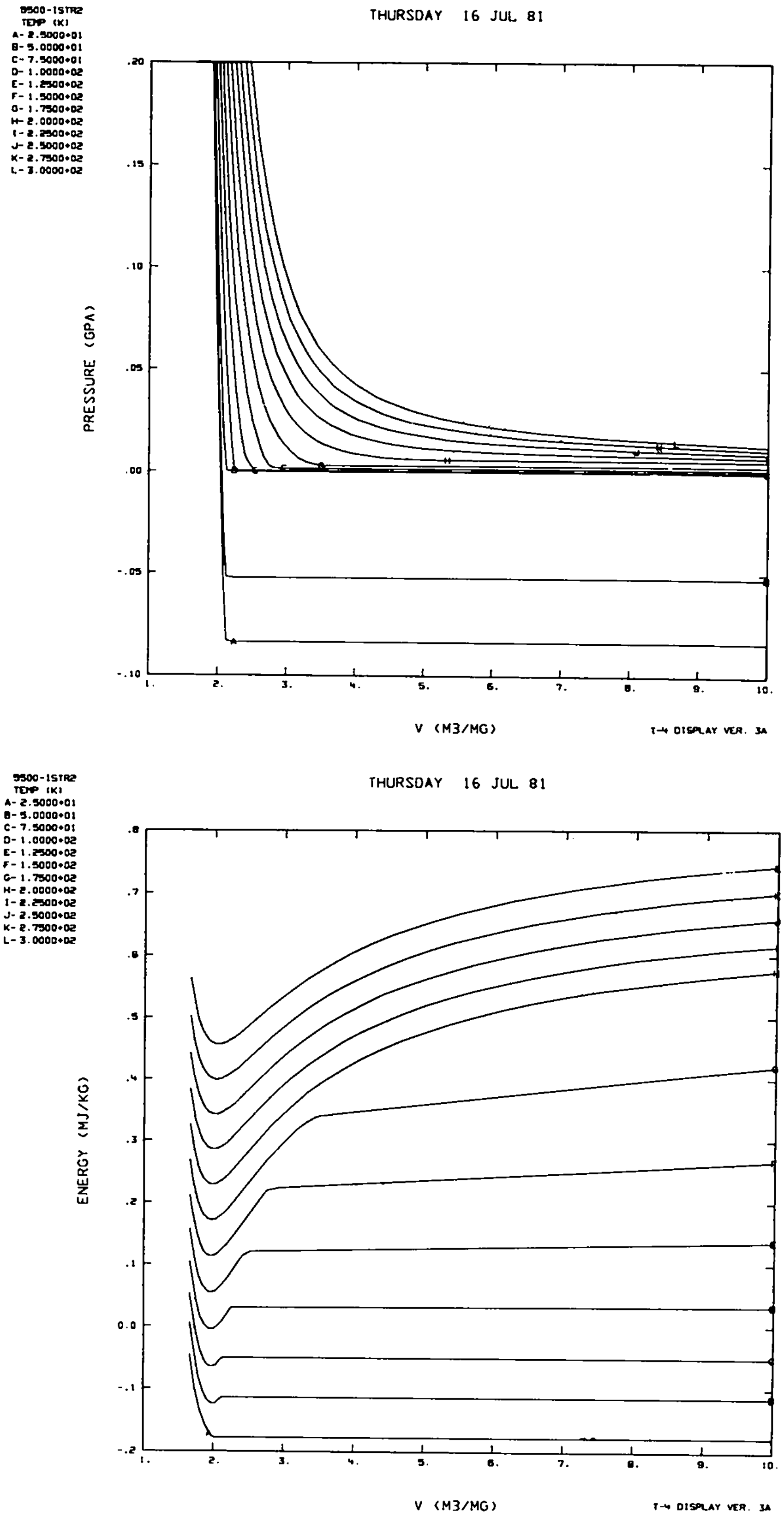

Fig. XI-7. Pressure and internal energy for methane, including Maxwell constructions.

APPENDIX A

SEPARATION OF DEGREES OF FREEDOM

The PANDA code assumes that various degrees of freedom can be decoupled from one another in computing thermodynamic properties. In this approximation, the EOS can be written as the sum of several terms, each computed separately from the others. 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[14] and to the separation between translational and vibrational-rotational degrees of freedom.[9] The problem for systems where chemical reactions can occur is also considered.

I. 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.

$$H = K_1(\vec{x}) + K_2(\vec{y}) + U(\vec{x},\vec{y}) \quad , \tag{A-1}$$

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

$$Q = \mathrm{Tr}\,[\exp(-\beta H)] \quad , \tag{A-2}$$

where 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

$$Q = \sum_n \int \Psi_n^*(\vec{x}) \exp(-\beta Z)\, \Psi_n(\vec{x})\, d\vec{x} = \mathrm{Tr}_1[\exp(-\beta Z)] \quad , \tag{A-3}$$

where

$$\exp(-\beta Z) = \mathrm{Tr}_2\,[\exp(-\beta H)] \quad . \tag{A-4}$$

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.

$$H_2 = K_2(\vec{y}) + U(\vec{x},\vec{y}) \tag{A-5}$$

and

$$\exp(-\beta A_2) = \mathrm{Tr}_2[\exp(-\beta H_2)] \quad . \tag{A-6}$$

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 β and on the coordinates $\vec{x}$. The average value of an operator F on subspace 2 is defined as

$$<F> = \mathrm{Tr}_2[\exp(-\beta W_2)F] \tag{A-7}$$

and

$$W_2 = H_2 - A_2 \quad . \tag{A-8}$$

Now an expansion variable ξ is introduced so that

$$\exp[-\beta Z(\xi)] = <\exp(\beta\xi W_2)\exp(-\beta\xi H)> \quad . \tag{A-9}$$

$Z(\xi)$ is expanded as a power series

$$Z(\xi) = \sum_{k=0}^{\infty} \xi^k Z_k \quad , \tag{A-10}$$

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 ξ are equated. The leading term in Z is

$$Z_1 = K_1(\vec{x}) + A_2(\vec{x};\beta) \quad . \tag{A-11}$$

The remaining terms in the expansion involve the commutator of K_1 with U and A_2. For example, the second order term is

$$Z_2 = -\frac{\beta}{2} <K_1W_2 - W_2K_1> \quad . \tag{A-12}$$

Z_2 and higher order terms in Eq. (A-10) form a power series in βh^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.[14]

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 equation is solved for the energy levels, the partition function, and the free energy A_2 of subsystem 2. Then Z_1, 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,[44] which applies to a single quantum state of the system.

II. SEPARATION BETWEEN 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,[14] 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 the temperature dependence can be included by the methods of chemical equilibrium, using the POGO code. Each chemical species is treated separately, using PANDA to construct an EOS that describes the electronic and nuclear degrees of freedom correctly. Then the EOS for two or more species are combined into a mixture EOS, and the chemical composition is determined as a function of density and temperature by minimizing the free energy. The PANDA dimer model is a simple example of a chemical equilibrium model.

With the exception of the dimer model, PANDA considers only a *single chemical species*. In this case, it is useful to write the electronic free energy as

$$A_2 = \Phi(\vec{x}) + A_\theta(\vec{x};\beta) \quad , \tag{A-13}$$

where ϕ is the energy of the ground electronic state of the system and A_θ is the contribution from thermal electronic excitation and ionization. The thermal term A_θ is usually small for temperatures $<\sim 10^4$ 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 $\vec{x}_o$ that describe "average" positions of the nuclei. Then

$$A_\theta(\vec{x};\beta) = A_e(\rho,\beta) + \Delta A_\theta(\vec{x};\beta) \quad , \tag{A-14}$$

$$A_e(\rho,\beta) \equiv A_\theta(\vec{x}_o;\beta) \quad , \tag{A-15}$$

and

$$\Delta A_\theta(\vec{x};\beta) \equiv A_\theta(\vec{x};\beta) - A_e(\rho,\beta) \quad . \tag{A-16}$$

Here A_e is a "static" term, which does not affect the nuclear motion. This quantity can be computed using electronic structure models such as INFERNO.[11] However, there is no satisfactory model for calculating ΔA_θ, which depends upon displacements of the nuclei about their average positions. 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 ΔA_θ is ignored in PANDA.

Using the results derived above, the partition function for the system is given by

$$Q = \exp(-\beta A_e)\,\mathrm{Tr}_1[\exp(-\beta H_n)] = \exp[-\beta(A_n + A_e)] \tag{A-17}$$

and

$$H_n = K_1(\vec{x}) + \Phi(\vec{x}) + \Delta A_\theta(\vec{x};\beta) \cong K_1(\vec{x}) + \Phi(\vec{x}) \quad . \tag{A-18}$$

Here 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 Φ 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 terms in the fluid EOS model.

III. 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 an electronic term.

$$A(\rho,\beta) = A_n(\rho,\beta) + A_e(\rho,\beta) \quad . \tag{A-19}$$

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.[13]

$$A(\rho,\beta_n,\beta_e) = A_n(\rho,\beta_n) + A_e(\rho,\beta_e) \quad . \tag{A-20}$$

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 Φ, this term corresponds to a system where the nuclei can become excited but the electrons remain in the ground state.

These conclusions may not be valid in cases where chemical reactions occur. Such problems are beyond the scope of this report.

IV. SEPARATION BETWEEN TRANSLATIONAL AND VIBRATIONAL-ROTATIONAL MOTIONS

The preceding arguments can also be used to decouple translational degrees of freedom. This problem is discussed in Ref. 9, 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 particles. 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. These techniques are similar to those described by Rice et al.[15] and by Grover et al.[16] A Mie-Grüneisen EOS is assumed, which relates pressure, internal energy, and density as follows.

$$P(\rho,E) = P_c(\rho) + \rho\ \gamma(\rho)\,[E - E_c(\rho)] \quad . \tag{B-1}$$

The Grüneisen parameter γ depends only on density. It is related to the Debye temperature θ by

$$\gamma = \frac{d\ \ell n\ \theta}{d\ \ell n\ \rho} \tag{B-2}$$

The pressure and energy on the cold curve are related by

$$P_c = \rho^2 \frac{dE_c}{d\rho} \quad . \tag{B-3}$$

On the Hugoniot, the shock velocity U_S, particle velocity U_P, energy E_H, and density are related by the conservation laws of mass, momentum, and energy. These relations yield

$$U_S = \frac{\rho U_P}{\rho - \rho_o} \quad , \tag{B-4}$$

$$P_H = P_o + \rho_o U_S U_P \quad , \tag{B-5}$$

and

$$E_H = E_o + \frac{1}{2}\,(P_H + P_o)\left(\frac{1}{\rho_o} - \frac{1}{\rho}\right) \quad , \tag{B-6}$$

where ρ_o, P_o, and E_o are the initial conditions. In PANDA, ρ_o is taken to be the reference density RHOREF, $P_o = 0$, and E_o is computed from RHOREF and TREF using the solid lattice vibration model specified by the user. The Hugoniot curve is expressed as a polynomial,

$$U_S = C_o + S_1 U_P + S_2 U_P^2 \quad . \tag{B-7}$$

Equations (B-4)-(B-7) are solved to give P_H and E_H as functions of density. Note that physically meaningful solutions do not exist at high densities, because a single shock wave cannot compress matter above a certain density limit. The high-density portion of the curve must be constructed by some other technique such as the TFD match.

I. ANALYTIC FORMULA FOR γ AND θ

When γ and θ are specified by analytic expressions (IGRN = 2 or IGRN = 3 in Sec. IV), the zero-temperature isotherm is computed as follows. Equations (B-1)-(B-3) can be written

$$P_H - \rho\gamma E_H = P_C - \rho\gamma E_C = \rho^2\theta \frac{d}{d\rho}\left(\frac{E_c}{\theta}\right) \quad . \tag{B-8}$$

Integrating the above gives

$$E_C(\rho) = \theta(\rho)\left[\frac{E_c(\rho_o)}{\theta(\rho_o)} + \int_{\rho_o}^{\rho} \frac{P_H(x) - x\,\gamma(x)\,E_H(x)}{x^2\theta(x)}\,dx\right] \quad . \tag{B-9}$$

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-9) 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 γ and θ may 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.

II. COLD CURVE FORMULA FOR γ AND θ

If the user specifies the cold curve formula for γ and θ (IGRN = 1 in Sec. IV), a self-consistent solution for γ, θ, P_C, and E_C is required. Using Eqs. (IV-15) and (B-1),

$$\frac{P_H - P_C}{\rho(E_H - E_C)} = \gamma = -\frac{1}{6} + \frac{1}{2}\,\frac{\beta_c' - (FT)\,(2/3)\,\beta_C}{\beta_C - (FT)\,(2/3)\,P_C} \quad . \tag{B-10}$$

The energy, pressure, and derivatives are obtained at points on a standard density grid. The interpolation formula for the energy, in the interval $\rho_I \leqq \rho < \rho_{I+1}$, is

$$E_C = E_C(i) + \rho_I^{-1}\,[P_c(i)x + A_1(i)x^2 + A_2(i)x^3 + A_3(i)x^4] \tag{B-11}$$

and

$$x = \frac{\rho - \rho_I}{\rho_I} \quad . \tag{B-12}$$

The terms $P_c(i)$, $A_1(i)$, 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-10). In this way, Eq. (B-10) 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.

III. DEFAULTS FOR GAMREF AND DEBREF

If the user sets GAMREF = 0 or DEBREF = 0 using the INPUT option, these quantities will be calculated by the code. The default expression for GAMREF is

$$\text{GAMREF} = 2\,S_1 - \frac{2 + FT}{3} \quad , \tag{B-13}$$

where FT is specified by the SOL NUC command (see Sec. IV). Equation (B-13) can be derived from the cold curve formula. The default expression for DEBREF is

$$\mathrm{DEBREF} = 444.12 \sqrt{\frac{1-2\sigma}{1+\sigma}}\, C_o \left(\frac{\rho_o}{W\lambda}\right)^{1/3} , \tag{B-14}$$

where

$$\lambda = 2 + \left(\frac{0.5-\sigma}{1-\sigma}\right)^{3/2} , \tag{B-15}$$

$\rho_o \equiv$ RHOREF, W is the molecular weight, and σ, Poisson's ratio, is specified by the SOL NUC command (see Sec. IV). This result can be derived from the usual relation between θ and the longitudinal and transverse sound speeds.

IV. INTERPOLATION AND EXTRAPOLATION

To compute the cold curve from the calculated tables, the code interpolates, using Eq. (B-11). At low densities, it extrapolates off the tables. The LJ match can be used to guarantee that the cold curve has the correct behavior in this region. For high densities, the TFD match is done automatically. If the user sets RTFD = 0, the match is made at RMAX, the highest density obtained in the integration. The user can specify another value for RTFD, but the code takes RTFD = RMAX as the upper limit for the match.

APPENDIX C

CUTOFF CORRECTIONS TO THE EINSTEIN AND DEBYE MODELS

The standard Einstein and Debye models are derived using the harmonic approximation for the lattice vibration model.[20] This approximation breaks down for highly excited states, where the amplitudes of vibration are large and the lattice is unstable. Appendix C describes a model in which these unstable levels are excluded in calculating thermodynamic properties.

The energy levels of a harmonic oscillator are given by

$$E = \left(n + \frac{1}{2}\right) h\nu \quad . \tag{C-1}$$

The potential energy at the boundary of the Wigner-Seitz cell is

$$V = 2\pi^2 W \nu^2 r_s^2 \tag{C-2}$$

and

$$\frac{4\pi}{3} N_o r_s^3 = \frac{W}{\rho} \quad , \tag{C-3}$$

where N_0 is Avogadro's number, and W is the molecular weight; n_c is defined as the quantum number for which $E = V$. Hence

$$n_c \cong \frac{2\pi^2 k}{h^2} \theta W \left(\frac{3W}{4\pi N_o \rho}\right)^{2/3} = \frac{c\theta W^{5/3}}{\rho^{2/3}} \quad , \tag{C-4}$$

where $\theta = h\nu/k$ and $c = 5.5638 \times 10^{-3}$. For levels greater than n_c, the oscillator has sufficient energy to escape from its Wigner-Seitz cell. Hence n_c gives a rough estimate of where to cut off the sum over vibrational levels. Because the corrections to the solid properties are very small for temperatures below the melting curve, this estimate is sufficiently accurate.

I. THE EINSTEIN MODEL

In the Einstein model, the lattice consists of N_0 molecules ($3N_0$ oscillators), each of which has the same frequency. The partition function is

$$Q = q_\nu{}^{3N_0} \tag{C-5}$$

and

$$q_v = \sum_{n<n_c} \exp\left[-\beta\left(n + \frac{1}{2}\right) h\nu\right] = \exp(-\beta h\nu/2) \frac{1 - \exp(-n_c \beta h\nu)}{1 - \exp(-\beta h\nu)} \quad . \tag{C-6}$$

The Helmholtz free energy is

$$A = -\beta^{-1} \ell n\, Q = \frac{R}{W} \left[\frac{3}{2}\theta + 3\, \ell n \left(1 - e^{-\theta/T} \right) - 3\, \ell n \left(1 - e^{T_\lambda/T} \right) \right] \qquad \text{(C-7)}$$

and

$$T_\lambda = n_c\theta = \frac{c\,\theta^2 W^{5/3}}{\rho^{2/3}} \quad . \qquad \text{(C-8)}$$

The internal energy and pressure are found from thermodynamic relations.

$$E = A - T\left(\frac{\partial A}{\partial T}\right)_\rho = \frac{R}{W}\left(\frac{3}{2}\theta + \frac{3\theta}{e^{\theta/T} - 1} - \frac{3T_\lambda}{e^{T_\lambda/T} - 1}\right) \qquad \text{(C-9)}$$

and

$$P = \rho^2\left(\frac{\partial A}{\partial \rho}\right)_T = \frac{R}{W}\rho\left[\gamma\left(\frac{3}{2}\theta + \frac{3\theta}{e^{\theta/T} - 1}\right) - \left(2\gamma - \frac{2}{3}\right) \frac{3T_\lambda}{e^{T_\lambda/T} - 1}\right] \quad , \qquad \text{(C-10)}$$

where $\gamma = d\, \ell n\, \theta / d\, \ell n\, \rho$ is the Grüneisen function.

T_λ has the same density dependence as the Lindemann melting temperature,[45] but it is ~100-200 times higher. At high temperature ($T \cong T_\lambda$) 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 like those for an ideal gas.

$$A = \frac{RT}{W}\left[a_E - \ell n\left(\frac{W}{\rho}\right) - \frac{3}{2}\ell n\,(WT)\right] \quad , \qquad \text{(C-11)}$$

$$E = \frac{3}{2}\frac{RT}{W} \quad , \qquad \text{(C-12)}$$

and

$$P = \frac{RT\rho}{W} \quad . \qquad \text{(C-13)}$$

The switch to this gas formula is made at $T = 0.795905\ T_\lambda$, so that E and P are continuous. The free energy is made continuous by setting $a_E = 9.13465$, a value higher than that for an ideal gas. Note: Derivatives of the thermodynamic functions are not continuous at the switchover point.

II. THE DEBYE MODEL

In the Debye model, the $3N_0$ oscillators do not have the same frequency. The free energy becomes

$$A = -\beta^{-1} \int f_\nu\, \ell n\, q_\nu\, d\nu \quad , \qquad \text{(C-14)}$$

where f_ν is the degeneracy for frequency ν,

$$\int f_\nu \, d\nu = 3N_o \quad . \tag{C-15}$$

If the usual approximation[20] that $f_\nu \propto \nu^2$ for $\nu \leqq \nu_D$ is made and Eq. (C-6) is used for q_ν, then

$$A = \frac{R}{W}\left[\frac{9}{8}\theta + F(\theta/T) - F(T_\lambda/T)\right] \quad , \tag{C-16}$$

$$F(x) = \frac{9}{x^3}\int_o^x y^2 \ln(1 - e^{-y})dy = 3 \ln(1 - e^{-x}) - D(x) \quad , \tag{C-17}$$

and

$$D(x) = \frac{3}{x^3}\int_o^x \frac{y^3}{e^y - 1}dy \quad . \tag{C-18}$$

The internal energy and pressure are

$$E = \frac{R}{W}\left[\frac{9}{8}\theta + 3D(\theta/T) - 3D(T_\lambda/T)\right] \tag{C-19}$$

and

$$P = \frac{R\rho}{W}\left\{\gamma\left[\frac{9}{8}\theta + 3D(\theta/T)\right] - (6\gamma - 2)\, D(T_\lambda/T)\right\} \quad , \tag{C-20}$$

where T_λ is given by Eq. (C-8). The high-temperature behavior is similar to that for the Einstein model. PANDA switches over to the ideal gas expressions for $T \geqq 0.584597\ T_\lambda$. Continuity of the free energy gives

$$A = \frac{RT}{W}\left[a_D - \ln\left(\frac{W}{\rho}\right) - \frac{3}{2}\ln(WT)\right] \quad , \tag{C-21}$$

where $a_D = 8.69060$. The high-temperature formulas for E and P are Eqs. (C-12) and (C-13), respectively.

APPENDIX D

MONOMER-DIMER CHEMICAL EQUILIBRIUM MODEL

Appendix D considers 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[46]

$$Q = \frac{1}{N_1!N_2!}\left[V\left(\frac{2\pi W_1 kT}{h^2}\right)^{3/2} q_e\right]^{N_1}\left[V\left(\frac{2\pi W_2 kT}{h^2}\right)^{3/2} q_{VR}\right]^{N_2} \quad , \tag{D-1}$$

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

$$N = N_1 + 2N_2 \quad . \tag{D-2}$$

The monomer fraction is defined as the number of atomic nuclei in the monomer form.

$$f = \frac{N_1}{N} \quad . \tag{D-3}$$

For a fully dissociated gas, $f = 1$, Eq. (D-1) becomes

$$Q \rightarrow \left[\frac{eV}{N}\left(\frac{2\pi W_1 kT}{h^2}\right)^{3/2} q_e\right]^{N} \equiv \exp\left[-\beta A_M(\rho,T)\right] \quad , \tag{D-4}$$

where $A_M(\rho,T)$ is the Helmholtz free energy of a monomer gas. For $f = 0$, Eq. (D-1) becomes

$$Q \rightarrow \left[\frac{2eV}{N}\left(\frac{2\pi W_2 kT}{h^2}\right)^{3/2} q_{VR}\right]^{N/2} \equiv \exp\left[-\beta A_D(\rho,T)\right] \quad , \tag{D-5}$$

where $A_D(\rho T)$ is the Helmholtz free energy of a dimer gas. Hence Eq. (D-1) can be written

$$Q = \frac{1}{f^{fN}(1-f)^{(1-f)N/2}} \exp\left\{-\beta\left[fA_M + (1-f)A_D\right]\right\} \quad . \tag{D-6}$$

The free energy for the mixture is

$$A(\rho,T) = f\, A_M(\rho,T) + (1-f)\, A_D(\rho,T) + \frac{RT}{W_1}\left[f \ell n\, f + \frac{1}{2}(1-f)\, \ell n\, (1-f)\right] \quad . \tag{D-7}$$

The monomer fraction is obtained by minimizing the free energy.

$$\left(\frac{\partial A}{\partial f}\right)_{\rho,T} = 0 \quad . \tag{D-8}$$

The result is

$$f = \frac{1}{2}\left[\sqrt{x^2 + 4x} - x\right] \tag{D-9}$$

and

$$x = \exp\left[\frac{2W_1}{RT}(A_D - A_M) - 1\right] \quad . \tag{D-10}$$

The internal energy and pressure are

$$E(\rho,T) = A - T\left(\frac{\partial A}{\partial T}\right)_\rho = f\,E_M(\rho,T) + (1-f)\,E_D(\rho,T) \tag{D-11}$$

and

$$P(\rho,T) = \rho^2\left(\frac{\partial A}{\partial \rho}\right)_T = f\,P_m(\rho,T) + (1-f)\;P_D(\rho,T) \quad . \tag{D-12}$$

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 influence the formation of molecules. In PANDA, Eq. (D-7) is rewritten as

$$A(\rho,T) = f A_M(\rho,T) + (1-f)\left[A_D(\rho,T) + \frac{RT}{W_1}\ell n\, q_e\right] + \frac{RT}{W_1}\left[f\,\ell n f + \frac{1}{2}(1-f)\,\ell n\,(1-f)\right] \quad , \tag{D-13}$$

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

$$x = \exp\left[\frac{2W_1}{RT}(A_D - A_M) + 2\,\ell n\, q_e - 1\right] \quad . \tag{D-14}$$

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.[34] 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.

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