**THE FREE-ENERGY APPROACH TO
COMPUTING DYNAMIC PHASE CHANGE IN MATERIALS**

Minao Kamegai

November 28, 1973

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THE FREE-ENERGY APPROACH TO COMPUTING DYNAMIC PHASE CHANGE IN MATERIALS

Abstract

The free energy approach to calculating dynamic phase change is described in this paper. It is assumed that the driving force for the transition is the difference

in the Gibbs free energy for the phases present in the material. To demonstrate the validity of the theory, the model is applied to δ -phase plutonium.

Introduction

The kinematics of the shock-induced phase change in a material is discussed in this paper. Although the theory is, in principle, applicable to any phase change, here we examine only the polymorphic transition.

The objective of this work is to formulate a model which adequately describes the transition process so that the physical parameters such as pressure, temperature, and volume can be calculated for a broad range of material. Although the computational procedure is quite cumbersome, the model itself is very simple. It assumes that the driving force for the transition is the difference in the Gibbs

free energy among all the phases present, and that the transition proceeds toward the phase with the lowest free energy. For good discussions on this subject see Refs. 1-3.

Since only two phases are present in polymorphic transitions, a two-phase equation of state is derived from the experimental data. The fundamental equations which govern the transition process are given in a finite difference form. The material strength and shear modulus are also included in the calculation. A comparison of the computation with the actual data is presented in order to demonstrate the validity of the theory.

Theory

The dynamic phase change is considered to be a two-step process. First, the shock compression brings the material to a metastable state in phase 1.

Then, after a finite time, the material relaxes to the final state in phase 2. However, often in polymorphic transitions there is no singular transition

pressure. Instead, the phase change takes place gradually at a rate increasing with pressure up to the transition point, where the process is suddenly completed at a rapid rate. Figure 1 shows a qualitative description of such transitions.

In developing the model for phase change, the following assumptions were made:

1. During the transition, the materials in the two phases are homogeneously

mixed so that equal pressure and temperature exist in both phases.

2. There is no surface energy associated with the phase interface.

From the first assumption, it is evident that the pressure and temperature should be taken as independent variables. Thus, the two-phase equation of state is expressed by

$$\frac{1}{V_1} - 1 = f(P) + g(P)(T - T_0) \quad (1)$$

Fig. 1. Dynamic phase change in a material may follow a two-step process or it may be a gradual transition.

and

$$\frac{1}{V_2} - 1 = F(P) + G(P)(T - T_0) \quad (2)$$

for phase 1 and phase 2, respectively, where V_1 and V_2 are normalized to the initial volume in phase 1. The functions f , F , g , G are usually polynomials in pressure. How these functions are determined from the Hugoniot data is explained in detail in Appendix A. A brief outline of the procedure is as follows:

First, a plot of the Hugoniot data, such as shown in Fig. 2, is reduced to the two separate Hugoniots for the individual phases after corrections are made on the data pressures. They are given by the dotted curves.

Next, the individual equations of state are plotted in their own coordinate systems. This means that the second Hugoniot must be transformed into the phase 2 coordinates. The transformation is easily done after the reference density of phase 2 is established.

The individual plot is now fitted by the Grüneisen type of equation of state, choosing the appropriate Grüneisen constants. Once the equation of state is derived in one form, we can readily generate a P-T equation of state. Figures 3 and 4 give the functions $G(P)$ and $F(P)$ for δ -Pu plotted in the phase 2 coordinate system.

Finally, the second Hugoniot is transformed back to the original coordinate system in the P-T form so that the pair of equations can constitute the two-phase equation of state. Appendix A describes each step of the procedure.

The material is transformed from phase 1 to phase 2 by a relaxation proc-

ess. That is to say, the relaxation equation describes the kinematics of the phase change.

A simple model was assumed for the relaxation process; namely, the driving

Fig. 2. Hugoniot plots for δ -phase plutonium.

Fig. 3. Plot of the function $G(P)$.

Fig. 4. Plot of the function $F(P)$.

force for the transition is the difference in the Gibbs free energy between the two phases. To be more specific, the system relaxes by changing the proportion of the two phases at a rate which is a function of the free energy difference; i.e., we write the relaxation equation as

$$\frac{d\alpha}{dt} = F(G_1 - G_2), \quad (3)$$

where α is the molar mass fraction of phase 2 material, and G_1 and G_2 are the Gibbs free energies for phases 1 and 2. Thus the mass fraction, α , changes from 0 to 1 as the material transforms into phase 2.

In some polymorphic transitions such as δ -Pu, the phase change seems to take place quite gradually at a rate increasing with pressure up to the transition point.

At the transition pressure, the phase change completes very rapidly. In contrast, the phase reversal in the unloading process is marked by a smooth exponential type of material behavior.

The following functions were found to be most appropriate for the relaxation equation (3):

Loading process

For $P < P_{\text{transition}}$

$$\frac{d\alpha}{dt} = a_0 \exp[a_1(G_1 - G_2)]. \quad (4)$$

For $P \geq P_{\text{transition}}$

$$\frac{d\alpha}{dt} = \frac{G_1 - G_2}{\phi_0}. \quad (5)$$

Unloading process

For $P \leq P_{\text{phase reversal}}$

$$\frac{d\alpha}{dt} = b_0 \exp[-b_1(G_1 - G_2)]. \quad (6)$$

In the above expressions a_0 , a_1 , ϕ_0 , b_0 , b_1 are all positive constants. It should be pointed out that the relaxation equation at the transition pressure, Eq. (5), indeed transforms the material into the phase with the lowest free energy.

Since the relaxation equation has been determined, the volume and energy can be expressed in terms of the two-phase equation of state and the mass fraction, α . The molar volume and the molar energy are, respectively,

$$V = (1 - \alpha)V_1 + \alpha V_2, \quad (7)$$

$$E = (1 - \alpha)E_1 + \alpha E_2. \quad (8)$$

Equations (7) and (8) allow calculation of the pressure and temperature. Since

P and T are implicit variables in these equations, in practice the equations have to be inverted so that P and T are expressed as explicit functions of V, E, and α . Differentiating Eqs. (7) and (8) by pressure and temperature, we have

$$\Delta V = \left[(1 - \alpha) \left(\frac{\partial V_1}{\partial P} \right)_T + \alpha \left(\frac{\partial V_2}{\partial P} \right)_T \right] \Delta P + \left[(1 - \alpha) \left(\frac{\partial V_1}{\partial T} \right)_P + \alpha \left(\frac{\partial V_2}{\partial T} \right)_P \right] \Delta T + (V_2 - V_1) \Delta \alpha, \quad (9)$$

$$\Delta E = \left[(1 - \alpha) \left(\frac{\partial E_1}{\partial P} \right)_T + \alpha \left(\frac{\partial E_2}{\partial P} \right)_T \right] \Delta P + \left[(1 - \alpha) \left(\frac{\partial E_1}{\partial T} \right)_P + \alpha \left(\frac{\partial E_2}{\partial T} \right)_P \right] \Delta T + (E_2 - E_1) \Delta \alpha. \quad (10)$$

Solving simultaneous equations (9) and (10) for ΔP and ΔT , we obtain the very cumbersome equations which allow the calculation of the incremental change in pressure and temperature. The results are given only in an abbreviated form here. For the exact expressions, the reader is referred to Appendix B. The pressure and temperature increments are, respectively,

$$\Delta P = \frac{1}{|A|} [\partial E_T \Delta V - \partial V_T \Delta E + |B| \Delta \alpha], \quad (11)$$

$$\Delta T = \frac{1}{|A|} [-\partial E_P \Delta V + \partial V_P \Delta E + |C| \Delta \alpha], \quad (12)$$

where the determinants $|A|$, $|B|$, $|C|$ and the derivatives ∂E_T , ∂V_T , ∂E_P , ∂V_P are explicitly shown in Appendix B.

The two-phase equation of state, (1) and (2), the relaxation equation (3)—or more specifically, Eqs. (4), (5), and (6)—and the pressure and temperature equations, (11) and (12), form the constitutive relations for hydrodynamic calculation. These three sets of constitutive relations and the three conservation equations for hydrodynamics are sufficient to calculate all the physical parameters.

However, at low pressures where the material strength becomes increasingly important, the hydrodynamic calculation is not quite adequate. Thus the material strength is included to the first order; i.e., the yield and shear modulus are given, respectively, by

$$Y = (1 - \alpha)Y_1 + \alpha Y_2,$$

$$G = (1 - \alpha)G_1 + \alpha G_2.$$

The art of computational physics enters in developing the line of logic by placing the conservation equations and all the constitutive relations in a proper order so that the physical parameters can be calculated with the minimal error. That is the subject of the next section.

Integration Scheme

A finite difference method is used for integration. The integration cycle starts with the boundary conditions on velocity and pressure. Then the incremental change in the physical parameters is calculated in the following order:

1. Momentum conservation:

$$\Delta U = -\frac{V}{\rho} \frac{\Delta P + \Delta q}{\Delta X} \Delta t,$$

where q is the artificial viscosity.

2. Continuity equation:

$$\Delta V = V \frac{\Delta U}{\Delta X} \Delta t.$$

3. Energy conservation:

$$\Delta E = -(P + q)\Delta V.$$

4. Relaxation equation:

$$\Delta \alpha = F(G_1 - G_2)\Delta t.$$

5. Pressure and temperature equations:

$$\Delta P = \frac{1}{|A|} (\partial E_T \Delta V - \partial V_T \Delta E + |B| \Delta \alpha),$$

$$\Delta T = \frac{1}{|A|} (-\partial E_P \Delta V + \partial V_P \Delta E + |C| \Delta \alpha).$$

All the derivatives and determinants in the above equations can be calculated from the two-phase equation of state,

$$\frac{1}{V_1} - 1 = f(P) + g(P)(T - T_0)$$

and

$$\frac{1}{V_2} - 1 = F(P) + G(P)(T - T_0).$$

This completes the cycle. The last step, the calculation of the pressure and temperature, requires iterations which were found to converge very rapidly.

When the material strength is significant, the plastic work is calculated separately and is added to the energy conservation equation.

Discussion

All the elements of the determinants and the derivatives in the calculation of pressure and temperature were found to be only the first derivatives of the two-phase equation of state, such as

$$\left(\frac{\partial V_1}{\partial P}\right)_T, \left(\frac{\partial V_1}{\partial T}\right)_P, \left(\frac{\partial V_2}{\partial P}\right)_T, \left(\frac{\partial V_2}{\partial T}\right)_P,$$

..., etc.

The exceptions to this are three terms, which require special attention:

$G_1 - G_2$ (difference in Gibbs free energy),

$S_1 - S_2$ (difference in entropy),

$E_1 - E_2$ (difference in internal energy).

The term $G_1 - G_2$ appears in the relaxation equation. Since the Gibbs free energy is calculated from entropy, the

calculation of $S_1 - S_2$ must precede $G_1 - G_2$. The term $E_1 - E_2$ appears in the determinants, $|B|$ and $|C|$, of the pressure and temperature calculation (see Appendix B). These terms are calculated in the following manner.

Since the equation of state is available only above room temperature at 1 atm pressure, this point (i.e., room temperature and 1 atm) is taken as the reference state, and the entropy, Gibbs free energy, and internal energy are calculated above the reference state. The values at the reference state, which are denoted by S_{00} , G_{00} , E_{00} , are determined before starting integration, and they are treated as the constants of integration throughout

the computation. How to calculate these three thermodynamic quantities is explained in Appendix C. Appendix D shows how the reference state values of these thermodynamic quantities are determined from the experimental data on the latent heat, the volume change at the transition point, the Clausius-Clapeyron constant, and the two-phase equation of state.

A careful examination of the computational results suggests some interesting implications. The thermodynamic quantities S_{00} , G_{00} , and E_{00} , which were calculated merely for the boundary conditions, are actually more significant than they appear to be at first glance.

Fig. 5. Pressure-temperature plot and the phase boundary.

Fig. 6. Comparison of computational results for $\delta\text{-Pu}$ with experimental measurements made with a Manganin gauge.

The reference-state values, S_{00} and G_{00} , determine a phase boundary which is a locus of points in a P - T diagram, where the free-energy difference vanishes; i.e., a P - T plot for

$$G_1 - G_2 = 0.$$

Since S_{00} and G_{00} set the boundary conditions for the calculation of $G_1 - G_2$, these

reference-state values fix the phase boundary. Furthermore, as is shown in Appendix D, S_{00} is calculated from the Clausius-Clapeyron constant, dP/dT , taken at (P_{tr}, T_0) , where P_{tr} is the transition pressure. Thus the Clausius-Clapeyron constant becomes the slope of the phase boundary at (P_{tr}, T_0) .

Figure 5 is a plot of the pressure versus temperature in a zone in δ -Pu that undergoes phase change and phase reversal. Superimposed over the P-T plot is a phase boundary. Where the P-T plot intersects the phase boundary, a phase change (or a phase reversal) takes place. Since dP/dT is an input variable, it can be used to adjust the slope of the phase boundary so that the profiles of the phase change and the phase reversal are made to coincide with the experimental results, as shown in Fig. 6.

As derived in Appendix D, E_{00} is calculated from the latent heat. E_{00} sets the reference state value for the energy difference, $E_2 - E_1$, in such a way that as the material is transformed to phase 2, the latent heat is pumped into the internal energy of the material. As a consequence,

the threshold pressure for phase reversal in the unloading process is very sensitive to the latent heat as well as to the Clausius-Clapeyron constant, dP/dT . Since the latent heat is an input variable, it can be adjusted to suit the measured phase reversal. Conversely, the measurement of the unloading process including the phase reversal will yield the latent heat for the transition.

Figure 6 shows the comparison of the computational results with an experimental measurement on δ -Pu. The schematic of the experiment is shown in the insert of the figure. The measurement was made with a Manganin gauge (a piezoresistive gauge) which directly measures the stress. The agreement is quite satisfactory.

Nomenclature for the computer input is given in Appendix E.

Conclusion

The free energy theory can be successfully applied to some dynamic phase changes. Although the theory may not explain all the subtleties of the polymorphic transition, the approach seems to be

basically sound. The careful analysis of many experimental data by this technique will indeed yield much information on the kinematics of the dynamic phase change.

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Appendix A

Deriving the Two-Phase Equation of State

The two-phase equation of state is derived in the following manner. First, separate Hugoniot are obtained for the individual phases from the experimental data. Figure 2 (earlier in the report) shows an experimental plot for δ -Pu, and the two Hugoniot which are given by the dotted curves.

The second phase must be treated as if it were a separate entity. The second Hugoniot is reduced from the data after the pressures are adjusted. The correction consists of subtracting the contribution of the material strength, $\frac{2}{3}Y_0$, the latent heat for the phase change, and the Hugoniot energy in excess of the internal energy of the phase 2 material. The second Hugoniot thus establishes the reference density, ρ_2^0 , of the phase 2 material. With the reference density, the Hugoniot is transformed to the phase 2 coordinate system. The transformation is quite simple.

Let V denote the volume of the second Hugoniot, then the volume in the phase 2 coordinate system is:

$$V' = V \frac{\rho_2^0}{\rho_1^0}$$

where ρ_1^0 is the original density of phase 1. It must be remembered that the volume is a dimensionless quantity normalized to the reference density of the coordinate system. In terms of $\mu = \frac{1}{V} - 1$, and $\mu' = \frac{1}{V'} - 1$, the relation is

$$\mu' = \frac{\rho_1^0}{\rho_2^0} \left[\mu - \left(\frac{\rho_2^0}{\rho_1^0} - 1 \right) \right]$$

Contrary to the phase 2 Hugoniot, only one adjustment is made on phase 1; that is, the contribution of the material strength is subtracted from the pressures. Phase 1 does not require any transformation.

With the data plotted in the individual coordinate system, the equation of state can be immediately derived in the Grüneisen form if the Grüneisen coefficient is known. The Grüneisen coefficient is empirically determined from the Manganin gauge data. The Manganin gauge measures the release wave as well as the shock pressure. Since the velocity of the release wave is determined by the slope of the adiabat, the velocity is a function of the Grüneisen coefficient; but since it is not a very sensitive function of the Grüneisen coefficient, the choice of the coefficient is not very critical. Thus we have the equation of state expressed by

$$P = \sum_n A_n \mu^n + \gamma E,$$

where

$$\mu = \frac{1}{V} - 1,$$

and γ is the Grüneisen coefficient.

Using the Hugoniot jump condition,

$$E = \frac{P}{2}(1 - V) = \frac{P}{2} \cdot \frac{\mu}{1 + \mu},$$

we can rewrite the equation as

$$P = \sum_n A_n \mu^n / \left(1 - \frac{\gamma}{2} \cdot \frac{\mu}{1 + \mu} \right). \quad (A-1)$$

Once the equation of state is established in one form, it must be transformed into a P-T form,

$$\frac{1}{V} - 1 = F(P) + G(P) \cdot (T - T_0). \quad (A-2)$$

The transformation is done in three steps:

1. Calculate the Hugoniot temperature, $(T - T_0)$.
2. Calculate the function $G(P)$.
3. Determine $F(P)$.

Step 1: Hugoniot Temperature, $(T - T_0)$

From the second law of thermodynamics, we have

$$T dS = dE + P dV + dZ,$$

where dZ is a dissipative energy. Substituting the Hugoniot energy in dE , the second law in an integral form is

$$\int_{S_0}^S T ds = \frac{P + P_0}{2} (V_0 - V) + \int_{V_0}^V P dV + \int_0^Z dZ.$$

Differentiating by volume, the equation reduces to

$$\frac{d}{dV} \left[\int_{S_0}^S T ds \right] = \frac{dP}{dV} \frac{V_0 - V}{2} + \frac{P}{2} + \frac{d}{dV} \left[\int_0^Z dZ \right], \quad (A-3)$$

where $P_0 = 0$.

The second law can be expressed differently by substituting a thermodynamic relation,

$$dE = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV,$$

in place of dE . Then the integral form becomes

$$\int_{S_0}^S T ds = C_V (T - T_0) + \int_{V_0}^V \left(\frac{\partial P}{\partial T} \right)_V T dV + \int_0^Z dZ,$$

which reduces to

$$\frac{d}{dV} \left[\int_{S_0}^S T ds \right] = C_V \frac{dT}{dV} + \left(\frac{\partial P}{\partial T} \right)_V T + \frac{d}{dV} \left[\int_0^Z dZ \right]. \quad (A-4)$$

Equating (A-3) and (A-4), we have a differential equation

$$C_V \frac{dT}{dV} + \left(\frac{\partial P}{\partial T} \right)_V T = \frac{dP}{dV} \frac{V_0 - V}{2} + \frac{P}{2}.$$

Since

$$\left(\frac{\partial P}{\partial T} \right)_V / C_V = -V \left(\frac{\partial P}{\partial V} \right)_T / V C_V \left(\frac{\partial T}{\partial V} \right)_P = \gamma,$$

the differential equation can be rewritten as

$$\frac{dT}{dV} + \frac{\gamma T}{V} = \frac{1}{C_V} \left(\frac{dP}{dV} \frac{V_0 - V}{2} + \frac{P}{2} \right). \quad (A-5)$$

The Hugoniot temperature is calculated by simply integrating (A-5) along the Hugoniot expressed by Eq. (A-1).

Step 2: Calculation of G(P)

The G(P) function in the two-phase equation of state is calculated from the Grüneisen equation which has been empirically derived to fit the experimental data. Let us write, for clarity, the Grüneisen equation and the two-phase equation of state in juxtaposition:

$$P = A(\mu) + \gamma(\mu)E, \quad (A-6)$$

$$\mu = F(P) + (T - T_0) G(P), \quad (A-7)$$

where

$$\mu = \frac{1}{V} - 1.$$

Then, from Eq. (A-7),

$$G(P) = \left(\frac{\partial \mu}{\partial T} \right)_P,$$

which can be calculated from the Grüneisen equation (A-6) as follows: Differentiating (A-6) with respect to T, we have

$$0 = \left(\frac{\partial A}{\partial \mu} \right)_P \left(\frac{\partial \mu}{\partial T} \right)_P + \left(\frac{\partial \gamma}{\partial \mu} \right)_P \left(\frac{\partial \mu}{\partial T} \right)_P E + \gamma \left(\frac{\partial E}{\partial T} \right)_P. \quad (A-8)$$

Now we introduce some thermodynamic relationships,

$$\begin{aligned} \left(\frac{\partial E}{\partial T} \right)_P &= C_P - P \left(\frac{\partial V}{\partial T} \right)_P \\ &= C_V - \left(\frac{\partial V}{\partial T} \right)_P^2 T / \left(\frac{\partial P}{\partial T} \right)_T - P \left(\frac{\partial V}{\partial T} \right)_P \end{aligned}$$

$$= C_V + \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P T - P \left(\frac{\partial V}{\partial T} \right)_P$$

$$= C_V - P \left(\frac{\partial V}{\partial T} \right)_P.$$

Also,

$$\begin{aligned} \left(\frac{\partial V}{\partial T} \right)_P &= \left(\frac{\partial V}{\partial \mu} \right)_P \left(\frac{\partial \mu}{\partial T} \right)_P \\ &= \left(\frac{-1}{\rho^0 (1 + \mu)^2} \right) \left(\frac{\partial \mu}{\partial T} \right)_P. \end{aligned}$$

Substituting these into Eq. (A-8), we can solve it for $(\partial \mu / \partial T)_P$, i.e.,

$$\begin{aligned} \left(\frac{\partial \mu}{\partial T} \right)_P &= \frac{-\gamma C_V}{\left[\left(\frac{\partial A}{\partial \mu} \right)_P + \left(\frac{\partial \gamma}{\partial \mu} \right)_P E + \frac{\gamma P}{\rho^0 (1 + \mu)^2} \right]} \\ &= G(P). \quad (A-9) \end{aligned}$$

An example of G(P) is shown in Fig. 3 (earlier in this report).

Step 3: Calculation of F(P)

The calculation of F(P) is a simple matter. F(P) is the difference between the Hugoniot and $(T - T_0) \cdot G(P)$. An example of F(P) is shown in Fig. 4, earlier in this report.

After F(P) and G(P) are calculated at several pressures, smooth curves are drawn through the points. Then these curves are fitted by polynomials in P.

Finally, the phase 2 equation is transformed back to the original coordinate in the P-T form so that the pair of equations can constitute the two-phase equation of state.

Appendix B

Deriving the Difference Equations for ΔP and ΔT

In this section, we derive the difference equations for ΔP and ΔT from Eqs. (7) and (8) in the main text:

$$V = (1 - \alpha)V_1 + \alpha V_2, \quad (7)$$

$$E = (1 - \alpha)E_1 + \alpha E_2. \quad (8)$$

Taking the derivatives, we have

$$\Delta V = (1 - \alpha)\Delta V_1 + \alpha\Delta V_2 + (V_2 - V_1)\Delta\alpha,$$

$$\Delta E = (1 - \alpha)\Delta E_1 + \alpha\Delta E_2 + (E_2 - E_1)\Delta\alpha.$$

Since P and T are independent variables, all the thermodynamic parameters and the equations of state, V_2 and V_1 , must be expressed in terms of P and T .

Therefore

$$\begin{aligned} \Delta V = (1 - \alpha) & \left[\left(\frac{\partial V_1}{\partial P} \right)_T \Delta P + \left(\frac{\partial V_1}{\partial T} \right)_P \Delta T \right] \\ & + \alpha \left[\left(\frac{\partial V_2}{\partial P} \right)_T \Delta P + \left(\frac{\partial V_2}{\partial T} \right)_P \Delta T \right] \\ & + (V_2 - V_1)\Delta\alpha, \end{aligned}$$

$$\begin{aligned} \Delta E = (1 - \alpha) & \left[\left(\frac{\partial E_1}{\partial P} \right)_T \Delta P + \left(\frac{\partial E_1}{\partial T} \right)_P \Delta T \right] \\ & + \alpha \left[\left(\frac{\partial E_2}{\partial P} \right)_T \Delta P + \left(\frac{\partial E_2}{\partial T} \right)_P \Delta T \right] \\ & + (E_2 - E_1)\Delta\alpha. \end{aligned}$$

Putting this in a better form, we write

$$\Delta V = \partial V_P \Delta P + \partial V_T \Delta T + (V_2 - V_1)\Delta\alpha, \quad (B-1)$$

$$\Delta E = \partial E_P \Delta P + \partial E_T \Delta T + (E_2 - E_1)\Delta\alpha, \quad (B-2)$$

where

$$\partial V_P = (1 - \alpha) \left(\frac{\partial V_1}{\partial P} \right)_T + \alpha \left(\frac{\partial V_2}{\partial P} \right)_T,$$

$$\partial V_T = (1 - \alpha) \left(\frac{\partial V_1}{\partial T} \right)_P + \alpha \left(\frac{\partial V_2}{\partial T} \right)_P,$$

$$\partial E_P = (1 - \alpha) \left(\frac{\partial E_1}{\partial P} \right)_T + \alpha \left(\frac{\partial E_2}{\partial P} \right)_T,$$

$$\partial E_T = (1 - \alpha) \left(\frac{\partial E_1}{\partial T} \right)_P + \alpha \left(\frac{\partial E_2}{\partial T} \right)_P.$$

By solving simultaneous equations (B-1) and (B-2) for ΔP and ΔT , we arrive at

$$\Delta P = \frac{1}{|A|} [\partial E_T \Delta V - \partial V_T \Delta E + |B| \Delta\alpha], \quad (B-3)$$

$$\Delta T = \frac{1}{|A|} [-\partial E_P \Delta V + \partial V_P \Delta E + |C| \Delta\alpha], \quad (B-4)$$

where the determinants $|A|$, $|B|$, and $|C|$ are

$$|A| = \begin{vmatrix} \partial V_P & \partial V_T \\ \partial E_P & \partial E_T \end{vmatrix},$$

$$|B| = \begin{vmatrix} \partial V_T & (V_2 - V_1) \\ \partial E_T & (E_2 - E_1) \end{vmatrix},$$

$$|C| = \begin{vmatrix} (V_2 - V_1) & \partial V_P \\ (E_2 - E_1) & \partial E_P \end{vmatrix}.$$

Appendix C:

Calculating the Internal Energy and Gibbs Free Energy

The internal energy and the Gibbs free energy of the i th phase are calculated from the equation of state by integrating the following thermodynamic relations with P and T as independent variables:

1. Internal energy

$$\Delta E_i = \left[C_{Pi} - P \left(\frac{\partial V_i}{\partial T} \right)_P \right] \Delta T - \left[T \left(\frac{\partial V_i}{\partial T} \right)_P + P \left(\frac{\partial V_i}{\partial P} \right)_T \right] \Delta P, \quad (C-1)$$

where the specific heat at constant pressure is given by

$$C_{Pi} = C_{Vi} - \frac{T \left(\frac{\partial V_i}{\partial T} \right)_P^2}{\left(\frac{\partial V_i}{\partial P} \right)_T},$$

C_{Vi} being a measured quantity.

2. Gibbs free energy

$$\Delta G_i = -S_i \Delta T + V_i \Delta P, \quad (C-2)$$

where the entropy is given by

$$\Delta S_i = \frac{C_{Pi}}{T} \Delta T - \left(\frac{\partial V_i}{\partial T} \right)_P \Delta P. \quad (C-3)$$

The useful thermodynamic relations that come out of (C-1) and (C-2) are

$$\left(\frac{\partial E_i}{\partial T} \right)_P = C_{Pi} - P \left(\frac{\partial V_i}{\partial T} \right)_P,$$

$$\left(\frac{\partial E_i}{\partial P} \right)_T = -T \left(\frac{\partial V_i}{\partial T} \right)_P - P \left(\frac{\partial V_i}{\partial P} \right)_T,$$

$$\left(\frac{\partial G_i}{\partial P} \right)_T = -S_i,$$

$$\left(\frac{\partial G_i}{\partial T} \right)_P = V_i.$$

Appendix D

Calculating the Reference State Values of $E_2 - E_1$, $G_1 - G_2$, and $S_2 - S_1$

In this section we calculate the values of $E_2 - E_1$, $G_1 - G_2$, and $S_2 - S_1$ at room temperature and 1 atm pressure, which is defined as the reference state. We let E_{00} , G_{00} , and S_{00} denote the reference state values, which are calculated using the thermodynamic relations given in Appendix C.

Integrating Eq. (C-1), we have

$$\begin{aligned} (E_2 - E_1)_{P_{tr}, T_0} &= \int_{P_0}^{P_{tr}} \left[T \left(\frac{\partial V_1}{\partial T} \right)_P + P \left(\frac{\partial V_1}{\partial P} \right)_T \right]_{T=T_0} dP \\ &\quad - \int_{P_0}^{P_{tr}} \left[T \left(\frac{\partial V_2}{\partial T} \right)_P + P \left(\frac{\partial V_2}{\partial P} \right)_T \right]_{T=T_0} dP \\ &\quad + (E_2 - E_1)_{P_0, T_0}, \quad (D-1) \end{aligned}$$

where P_{tr} is the transition pressure, and (P_0, T_0) is the reference state. The integrands are expressed at $T = T_0$ because the integration is done only over P at $T = T_0$. The left side of Eq. (D-1) is the energy difference between the two phases at (P_{tr}, T_0) . Since this energy difference consists of the latent heat and the work done to the material during the transition, we can write

$$\begin{aligned} (E_2 - E_1)_{P_{tr}, T_0} &= L - P_{tr} \cdot (V_2 - V_1)_{P_{tr}, T_0}, \quad (D-2) \end{aligned}$$

where L is the latent heat.

Substituting (D-2) into (D-1), we obtain

$$\begin{aligned} E_{00} &= (E_2 - E_1)_{P_0, T_0} \\ &= L - P_{tr} \cdot (V_2 - V_1)_{P_{tr}, T_0} \\ &\quad + \int_{P_0}^{P_{tr}} \left[T \left(\frac{\partial V_2}{\partial T} \right)_P + P \left(\frac{\partial V_2}{\partial P} \right)_T \right]_{T=T_0} dP \\ &\quad - \int_{P_0}^{P_{tr}} \left[T \left(\frac{\partial V_1}{\partial T} \right)_P + P \left(\frac{\partial V_1}{\partial P} \right)_T \right]_{T=T_0} dP. \quad (D-3) \end{aligned}$$

In calculating G_{00} , we apply a well-known thermodynamic rule which states that at the phase boundary, the Gibbs free energies of all the phases present are equal. Once again, we use Eq. (C-2) from Appendix C, and we set

$$\begin{aligned} (G_1 - G_2)_{P_{tr}, T_0} &= \int_{P_0}^{P_{tr}} (V_1 - V_2)_{T=T_0} dP \\ &\quad + (G_1 - G_2)_{P_0, T_0} = 0. \end{aligned}$$

It is needless to repeat that the integration is done at $T = T_0$. We obtain

$$\begin{aligned} G_{00} &= (G_1 - G_2)_{P_0, T_0} \\ &= \int_{P_0}^{P_{tr}} (V_2 - V_1)_{T_0} dP. \quad (D-4) \end{aligned}$$

The calculation of S_{00} follows the same procedure. First, from the Clausius-Clapeyron rule, we write

$$\frac{dP}{dT} = \frac{(S_2 - S_1)_{P_{tr}, T_0}}{(V_2 - V_1)_{P_{tr}, T_0}} \quad (D-5)$$

Integrating equation (C-3), we have

$$\begin{aligned} & (S_2 - S_1)_{P_{tr}, T_0} \\ &= - \int_{P_0}^{P_{tr}} \left[\left(\frac{\partial V_2}{\partial T} \right)_P - \left(\frac{\partial V_1}{\partial T} \right)_P \right]_{T_0} dP \\ & \quad + (S_2 - S_1)_{P_0, T_0} \quad (D-6) \end{aligned}$$

Combining (D-5) and (D-6), we derive S_{00} :

$$\begin{aligned} S_{00} &= (S_2 - S_1)_{P_0, T_0} \\ &= \frac{dP}{dT} (V_2 - V_1)_{P_{tr}, T_0} \\ & \quad + \int_{P_0}^{P_{tr}} \left[\left(\frac{\partial V_2}{\partial T} \right)_P - \left(\frac{\partial V_1}{\partial T} \right)_P \right]_{T_0} dP. \quad (D-7) \end{aligned}$$

Thus E_{00} , G_{00} , and S_{00} are calculated from the following inputs:

T_0 = reference temperature,

P_{tr} = transition pressure,

L = latent heat,

$(V_2 - V_1)_{P_{tr}, T_0}$ = volume change at (P_{tr}, T_0) ,

and the Clausius-Clapeyron rule gives

$$\frac{dP}{dT} = \frac{L}{T_0 \cdot (V_2 - V_1)_{P_{tr}, T_0}}.$$

Appendix E

Nomenclature for the Computer Input

Computation is done with a standard B-Division code, KO. Equation of state 61 is assigned to the phase change. The two-phase equation of state, the relaxation equation, the pressure and temperature calculation, the two-phase material strength, and the calculation of sound velocity constitute equation 61. The following is a description of the input quantities necessary to operate the equation.

TWO-PHASE EQUATION OF STATE

The phase 1 coefficients are:

A0PC1, A1PC1, ..., A10PC1.

Since the phase 1 Hugoniot can never be measured above the transition pressure, the phase 1 equation is quite ambiguous in this pressure range. However, this is compensated by the fact that the importance of the phase 1 equation rapidly diminishes above the transition pressure as the phase change is completed. Thus, the phase 1 equation is made to exponentially approach phase 2 above $P = P_{CUT}$. The rate is given by $\exp(TAOPC \cdot (P - P_{CUT}))$, where TAOPC and PCCUT are the input quantities.

The phase 2 coefficients are:

- (1) B0PC1, B1PC1, ..., B10PC1,
- (2) B0PC2, B1PC2, ..., B10PC2,
- (3) B0PC3, B1PC3, ..., B10PC3,
- (4) B0PC4, B1PC4, ..., B10PC4.

Four equations can be joined smoothly for phase 2 covering a wide range in pressure. The upper limits on the individual equations are respectively given by P1MAX, P2MAX, P3MAX, and P4MAX

Fig. E-1. Two-phase equation of state used in computer code allows phase 2 to be represented by four smoothly joined equations covering a wide range of pressure.

(see Fig. E-1). The equations are expressed by

$$\frac{1}{V} - 1 = \sum_{N=0}^5 ANPC1 \cdot P^N + (T - T_0) \cdot \sum_{N=6}^{10} ANPC1 \cdot P^{N-6},$$

$$\frac{1}{V} - 1 = \sum_{N=0}^5 BNPC1 \cdot P^N + (T - T_0) \cdot \sum_{N=6}^{10} BNPC1 \cdot P^{N-6},$$

..., etc.

In addition to the coefficients of the equations, the following quantities must be supplied:

PTR = transition pressure,
 PZERO = reference pressure,
 TZERO = reference temperature,
 DVPTR = volume change at the transition point,
 DENTH = latent heat,
 DPDT = Clausius-Clapeyron constant,
 CV1 = specific heat, C_V , for phase 1,
 CV2 = specific heat, C_V , for phase 2.

Relaxation Equation

The relaxation equation consists of three parts, two equations for the loading process and one equation for the unloading process.

Loading Process

For $P < P_{tr}$,

$$\frac{\Delta\alpha}{\Delta t} = A_0 \exp [A_1(G_1 - G_2)/G_{00}].$$

For $P \geq P_{tr}$,

$$\frac{\Delta\alpha}{\Delta t} = \frac{G_1 - G_2}{\phi_0 + \phi_1 \cdot P}.$$

Unloading Process

$$\frac{\Delta\alpha}{\Delta t} = B_0 \exp [-B_1(G_1 - G_2)/G_{00}].$$

The input quantities are as follows:

SGF = A_0 .
 PCW = A_1 .
 SPH = Threshold value of $G_1 - G_2$ for phase change in the loading process. The first relaxation equation is turned on at $G_1 - G_2$

= SPH. If SPH = 0., the phase change starts at $P = 0$.

PHPC = ϕ_0 .

PHPC1 = ϕ_1 .

GFS = B_0 .

PCE = B_1 .

ALP = Threshold value of $G_1 - G_2$ for phase reversal in the unloading process. The third relaxation equation is turned on at $G_1 - G_2 = ALP$.

RAT61 = Oscillation dampener. In highly compressible materials, the large volume change sometimes causes oscillations in the computation of the unloading process. The oscillations can be dampened by reducing the rate of phase reversal. RAT61 puts a limit on the exponential function in the third relaxation equation.

Material Strength

TY(61) = 1, and TCMU(61) = 1, turn on the calculation of the material strength.

UY1 = Yield strength for phase 1.

UM1 = Shear modulus for phase 1.

UY2 = Yield strength for phase 2.

UM2 = Shear modulus for phase 2.

G139, RT39 = Multiplying factors for the yield strength and shear modulus, which are reduced in the unloading process if the Bauschinger effect is present.

PMEL = Pressure at which the material strength diminishes.

Sound Velocity

G239 = A multiplying factor for the sound velocity which determines the time step.

P-T Plot

NPTZPC = 1 turns on the P-T plot. The

input quantities are:

NPS1MU = zone,

FPS1MU = frequency in μsec ,

EPS1MU = final time for the plot.

Edit

NEDIT = 6 gives the following quantities:

ALPC = α ,

TZPC = temperature,

G1PC = $G_1 - G_2$,

S1PC = $S_2 - S_1$,

E1PC = $E_2 - E_1$.

NONTHERMODYNAMIC MODEL

The calculation of phase change requires much computer time. At very high pressures, where the contribution of the phase change is insignificant, such an effort is unwarranted. For this reason, a simple nonthermodynamic model is provided. It completely bypasses the thermodynamic phase change and thus greatly reduces the need for computer time. The nonthermodynamic model is turned on by setting NPOW = 1, PTR = 1., DVPTR = 1., and CV1 = 1..

The equation of state consists of several equations of a Grüneisen type joined smoothly to cover a wide range in pressure. The input coefficients are as follows:

A0PC1, A1PC1, A2PC1, A3PC1, A4PC1,
B0PC1, B1PC1, . . . , B7PC1, EPOW1,
B0PC2, B1PC2, . . . , B7PC2, EPOW2,
B0PC3, B1PC3, . . . , B7PC3, EPOW3,
B0PC4, B1PC4, . . . , B7PC4, EPOW4,
DENTH = latent heat.

Fig. E-2. Nonthermodynamic equation of state used for computations at very high pressures.

The equations are given in the following form:

$$(1) P = A1PC1 \cdot \mu + A2PC1 \cdot E,$$

$$(2) P = A0PC1 + A3PC1 \cdot \mu + A4PC1 \cdot E,$$

$$(3) P = \sum_{N=0}^5 BNPC1 \cdot \mu^N + E \left(\sum_{N=6}^7 BNPC1 \cdot \mu^{N-6} \right)^{EPOW1},$$

$$(4) P = \sum_{N=0}^5 BNPC2 \cdot \mu^N + E \left(\sum_{N=6}^7 BNPC2 \cdot \mu^{N-6} \right)^{EPOW2},$$

$$(5) P = \sum_{N=0}^5 BNPC3 \cdot \mu^N + E \left(\sum_{N=6}^7 BNPC3 \cdot \mu^{N-6} \right)^{EPOW3},$$

where

$$\mu = \frac{1}{V} - 1.$$

P1MAX, P2MAX, P3MAX, and
P4MAX are the joints for these equations.
See Fig. E-2.