MELTING BEHIND THE FRONT OF THE SHOCK WAVE

by

Evgeny I. KRAUS* and Ivan I. SHABALIN

Khristianovich Institute of Theoretical and Applied Mechanics SB RAS,
Novosibirsk, Russia

Original scientific paper
https://doi.org/10.2298/TSCI19S2519K

A simple caloric model of the equation of state is proposed to describe thermodynamic properties of solid materials with phase transitions with the minimum number of parameters as initial data. Thermodynamic characteristics are calculated in the wide range of densities and pressures.

The equation of state of the solid phase was modified by introducing configurational entropy, which made it possible to describe a liquid medium by the same functional dependence, but with its initial parameters. This allowed us not only to construct the equation of state for the liquid, but also to determine the dependence of the melting point on pressure as the boundary between the phases with the corresponding state. It is shown that the melting process is practically not noticeable on the shock adiabat in the pressure – volume plane; however, sharp adiabatic breaks are observed in the temperature – pressure plane. The calculated position of the melting curve agrees with the experimental data found; although this does not fully justify the conclusion about the accuracy of the calculation of the liquid phase adiabat, but fully confirms the qualitative picture.

Key word: equation of state, melting curve, height pressure, phase, equilibrium condition

Introduction

The modern wide-range equations of state, constructed to describe the behavior of metals in a wide range of compression parameters, contain dozens of free parameters and experimentally found constants [1-3]. Sometimes, these models are complemented by taking into account multiple solid phases, the number of constants in this case inexorably increases. The constants are calculated according to the shock-wave experiments, determined from isentropic curves of unloading of porous samples, or are found from the experimental data in a wide area of the phase diagram from thermodynamic relations. It is worth mentioning the modern models with fewer constants as the initial data, but still there are too many of them to solve real engineering problems [4-10]. With this approach, the search for constants for the equation of state becomes a separate, time-consuming research task. That is why the problem of a few-parameter equation of state has become an important issue.

The energy expenditure on melting leads to sharp breaks in the shock adiabat in the $T$-$P$ plane, and the neglect of melting during shock compression of the substance leads to significant errors in calculating temperatures (points 3 and 4, fig. 1). Previously [11], it was

* Corresponding author, e-mail:kraus@itam.nsc.ru
shown theoretically that melting does not strongly affect both the kinematic parameters of the shock wave and the form of the dynamic adiabat in the pressure-volume coordinates. This may explain the high accuracy of the calculations of the shock adiabats in most existing works on shock compression, despite the absence of melting in the equation of state.

Equation of solid state

The author’s model of the few-parameter equation of state was proposed in [12-14]. We consider the three-term Mie-Grüneisen equation of state with the solid-phase free energy being determined as:

\[ F(V,T) = E_{x}(V) + c_{v,l} T \ln \left( \frac{\theta(V)}{T} \right) - \frac{1}{2} c_{v,e0} T^2 \left( \frac{V}{V_0} \right)^{2/3} \]

where \( V \) is the specific volume, \( E_{x}(V) \) – the cold energy, \( T \) – the temperature, \( c_{v,l} = 3R/A \) – the specific heat of the lattice at constant volume, \( A \) – the mean atomic weight, \( R \) – the gas constant, \( \theta(V) \) – the Debye temperature, and \( c_{v,e0} \) – the experimental value of the electron heat capacity under standard conditions. The elastic (cold) component of energy \( E_{x}(V) \) is related exclusively to interaction forces between the body atoms and is equal (including the energy of zero vibrations) to the specific internal energy at the absolute zero temperature.

Kraus and Shabalin in [12] were demonstrated there that the set of semi-empirical relations (1) describes the behavior of thermodynamic properties of solids within 5% in a wide range of pressures and temperatures. For the equation of state to be applied, it is sufficient to know only six parameters \( V_0, \beta, K_c, \theta_0, \) and corresponding to the values of these quantities under standard conditions, which can be found in reference books on physical and mechanical properties of substances.

Modification of the equation of state

Thermodynamic and kinetic properties of liquids usually cannot be predicted theoretically on the basis of the first principles only. The calculation of phase diagrams is additionally complicated by the fact that the most important characteristics of phase transitions (heat of transition, difference in phase densities, etc.) are small differences in quantities that have large values and cannot be calculated with sufficient accuracy. Because of thermodynamic non-equilibrium typical for polymorphic transformations in shock waves, the general thermodynamic relations for phase transitions (equality of chemical potential in the region of simultaneous existence of the phases and Clausius-Clapeyron equation) as applied to shock-wave processes can only be used as approximate estimates. Therefore, beginning from the famous van der Waals’ paper, numerous attempts have been made to construct the dynamics of a liquid substance by extrapolating the known thermodynamic functions from different areas of the phase diagram. The absence of a commonly accepted thermodynamic model for liquids, which would be equivalent to the Debye approximation for the crystalline state, is a severe obstacle for constructing the equation of state for liquids.
In studying particular models of thermodynamic states, it is clear that the usual classification of states in the region of high pressures and temperatures often loses its definiteness and becomes conventional, while the boundaries between the phases either disappear altogether or get fuzzy and actually correspond to continuous mutual transformation of states close to each other. The substance is both compressed and heated in the shock wave. In comparatively weak shock waves propagating over a cold substance, however, the pressure is mainly increased owing to compression. The pressure growth rate in relative units exceeds the temperature growth rate, and the increase in the cold compression energy is much greater than the increase in the thermal energy. As the shock wave intensity increases, the relative contribution of the thermal components of pressure and energy increases and becomes prevailing in strong shock waves.

To take into account melting, the equation for a solid body (1) is modified. Though the phonon spectrum in the liquid phase is obviously a non-Debye spectrum (as the liquid does not have the far order, its molecules do not have forbidden states; hence, the molecular motion is not discrete), such a modified model can provide positive results at sufficiently high densities of the liquid near the line of phase equilibrium between the liquid and solid phases, because the motion of a liquid molecule within the first coordination sphere at rather high densities can be conventionally considered as vibrational motion. Thus, the higher the pressure, the more precisely the model is satisfied.

The expression for the free energy \( F_L(V, T) \) of a monatomic liquid in the so-called rough classical model of the harmonic oscillator has the form:

\[
F_L(V, T) = E_{c,L}(V) + c_{v,L}T \ln \left( \frac{\theta_L(V)}{T} \right) - \frac{1}{2} c_{v,cd} T^2 \left( \frac{V}{V_{0,L}} \right)^{2/3} - \frac{R T}{A}
\]

where \( E_{c,L}(V) \) is the cold component of the internal energy of the liquid and \( \theta_L(V) \) – the characteristic Debye temperature of the liquid.

Formally, the expression for the free energy of the liquid (2) differs from the expression for the free energy of the solid (1) only by the presence of an additional entropy term \( F_c = -RT/A \). Nevertheless, the differences between the solid and liquid states are much more essential. Thus, different cold curves are used to describe the solid and liquid states.

First, the major part of the entropy jump is related to the change in the solid structure due to the transition to the liquid state, which is caused by the loss of the far order and leads to the formation of a collective or configuration entropy (equal to zero in an ideal crystal) in thermodynamic models of the liquid. The configuration part of the entropy \( S_c = -\partial F_c/\partial T \) characterizes the measure of liquid disordering and should remain a finite quantity (similar to the entropy of amorphous solids) as the temperature formally tends to zero \( T = 0 \) K.

Second, the zero isotherm of the liquid is shifted with respect to the zero isotherm of the solid toward lower densities. The primary reason is that the liquid-phase density extrapolated to the domain of low temperatures is somewhat lower than the density of the solid substance.

These principal differences between the thermodynamic descriptions of the liquid and solid states form the basis for the thermodynamic model modification considered in the present work. Thermodynamic functions of both solids and liquids are formally examined in the entire temperature range, including the domain close to \( T = 0 \) K. This is convenient for a unified description of both phases and allows functions typical for the solid state (such as the density at the temperature \( T = 0 \) K, zero isotherm, etc.) to be used to describe the liquid state thermodynamics. We assumed that the physically meaningful branches are those at \( T > T_m \) for the liquid state and at \( T < T_m \) for the solid state (\( T_m \) is the melting temperature).
Melting at high pressures behind the front of a strong shockwave

The phase transition of the first kind (melting) is understood as an equilibrium transition of the substance from one phase to another with jump-like changes in the first derivatives of the Gibbs energy, \(G\), with respect to temperature and pressure, \(i.e.,\) the entropy, \(S\), and specific volume, \(V\), experience jump-like changes during melting. The entropy of the liquid phase is always greater than the entropy of the solid; therefore, the entropy change during melting is always positive. The change in the volume during melting, however, can be either positive or negative. The inequalities \(\Delta S > 0\) and \(\Delta V > 0\), which mean greater orderliness and density of the crystalline phase as compared with the melt, seem to be natural. They are valid for most substances and ensure a positive slope of the melting curve \(dP/dT > 0\). At the same time, there are some substances (\(e.g.,\) gallium, bismuth, and water) with negative values of this derivative \(dP/dT < 0\).

As the shock-wave pressure increases, the thermal energy imparted to the substance continuously increases and the transition of the initially solid substance to the liquid state is expected to start at a certain pressure level. The further behavior of the dependence \(T(P)\) along the dynamic adiabat can be understood by analogy with melting at atmospheric pressure, where an increase in the energy imparted to the substance starting to melt does not lead to an increase in temperature until the substance becomes completely melted. Further heating of the liquid is accompanied by an increase in temperature. A similar pattern should also be observed under shock compression, with the only difference that a certain increase in temperature can be expected in the domain of simultaneous existence of two phases (segment of the melting curve between the shock adiabats for the solid and liquid substances, in fig. 1), because \(dT/dP > 0\) for the melting curve of the majority of substances (so-called “standard” substances).

To construct the melting curve, we use the phase equilibrium condition \([1, 15]\):

\[
P_L = P_S, \quad T_L = T_S, \quad F_L = F_S + P \Delta V_m
\]  

(3)

The last equation is the equality of the chemical potentials of both phases per 1 mole of the substance. The subscripts refer to the solid state (\(S\)), liquid state (\(L\)), and values on the melting curve (\(m\)).

Calculation results of equation of state

Using the system of equations of state of the solid (1), liquid (2) phases and the phase equilibrium condition (3), we calculated by \([16]\) the dynamic adiabats and the melting curves for several metals. The calculated adiabats with the phase transition in the \(T-P\) co-ordinates are shown in fig. 2. The correctness of taking into account melting behind the shock-wave front in the equation of state derived is indirectly confirmed in the paper of Sakharov \([17]\) who measured the viscosity behind the shock-wave front in aluminum and concluded that it remains in the solid phase up to pressures of 100 GPa. The calculations show (see fig. 2.) that aluminum melting begins at the pressure \(P = 107\) GPa. The transition of Al to the liquid state is finalized at the pressure \(P = 120\) GPa. The calculation for lead shows that Pb melting begins at the pressure \(P = 36\) GPa. The transition of Pb to the liquid state ends at the pressure \(P = 41\) GPa. The result obtained is in reasonable agreement with the data \([18]\), where it was noted that melting in the shock wave begins when the mass velocity reaches \(~650-700\) m/s, which corresponds to pressures of 23-25 GPa. In \([19]\) experiment, lead behind the shock-wave front is already in the melted state at pressures of 40 GPa.
Now let us consider the melting curve found as the boundary between the phases with the corresponding equations of state. Figure 3 shows the melting curve calculated for aluminum, the experimental data and Simon’s melting curve (dashed line) [20]. The calculated melting curve lies somewhat lower than the optimal curve, and the error of calculating the temperature on the melting curve is smaller than 5% in the entire range of pressures considered. Figure 4 shows the lead melting curve and the experimental data; the results are seen to be in good agreement. As an estimate, the figure also contains Simon’s melting curve for lead (dashed line) extrapolated to the range of high pressures [21]. As the parameters were chosen on the basis of low-temperature experiments, Simon’s melting curve underestimates the melting temperatures in the high-pressure domain.

Conclusions

Considerations used to derive the expression for the Grüneisen parameter are not confined to the condensed phase. For this reason, all relations in contain only the general thermophysical properties of the material, which are defined and have an identical meaning both for the solid and form the liquid states. Therefore, repeating all transformations applied in solid, we can obtain equations for \( E_x(V) \), \( P_x(V) \), etc., whose functional form is similar to those for the solid state. The differences are only in the parameters determined by particular initial conditions. Therefore, the use of the modified equation of state requires only six constants, as the equation for the solid phase. The constants for liquid metals can be found by literature. Moreover, the liquid model requires the jumps of the volume \( \Delta V \) and entropy \( \Delta S \) due to melting to be known. Comparing the calculated results with available experimental data, we can conclude that the calculation accuracy is fairly high and the phase equilibrium condition can be used for calculating the melting curves for the metals considered.

Acknowledgment

The study was conducted within the framework of the basic part of state task of the Khristianovich Institute of Theoretical and Applied Mechanics SB RAS (GR No. AAAA-A17-117030610136-3).
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