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Melting curve equations at high pressure

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A number of equations for the melting temperature dependence on pressure, $T_m(P)$, based on the two- and one-phase approaches to melting have been obtained. All melting curves have the form $T_m = F(P)D(P)$, where $F(P)$ is the Simon (rising) melting equation and $D(P)$ is the damping function, which asymptotically slopes down under pressure. This form predicts that each solid phase has a maximum melting temperature at positive or negative pressure. The simplest equation of this form is $T_m = T_0(1+\Delta P/a)^b \exp(-c\Delta P)$, where $\Delta P = P - P_0$, P_0 is some reference pressure, and *a, b*, and *c* are parameter which are identified in terms of thermodynamic values. All melting curve data obey this equation. This implies that there exist no anomalous melting curves. All melting curves, rising, falling, and flattening, as well as curves with a maximum, are normal insofar as all of them can be described by the unified equation.

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There exist two basically different approaches used to solve the melting problem.

(i) Melting is considered as an ordinary first-order phase transition (the two-phase approach to melting). In accordance with the thermodynamic theory, the first-order transition occurs when the Gibbs free energies of two phases are equal at a given temperature and pressure. The theory leads to the Clausius-Clapeyron equation, the fundamental equation governing the equilibrium of two phases, in particular, the liquid and solid phases:

$$\frac{d\ln T_m}{dP} = \frac{\Delta V}{\Delta H}, \tag{1}$$

where T_m and P are the melting temperature and pressure, ΔV is the volume change, $\Delta H = T_m \Delta S$ is the enthalpy, and ΔS is the entropy change during melting, respectively. At the melting $\Delta H > 0$ $(\Delta S > 0)$, whereas ΔV can change the sign. At $\Delta V > 0$ the melting temperature grows under pressure, at $\Delta V < 0$ it decreases, and at $\Delta V = 0$ the melting curve has its maximum.[1]

This approach is used in Monte Carlo[2–4] and molecular dynamic simulations of melting[5–9] with different pair and many-body, analytical, and *ab initio* potentials. This approach is also used in thermodynamic calculations using different approximations of the equation of state for the solid and liquid phases.[10–14]

(ii) Melting is based on the lattice instability (the one-phase approach to melting). One-phase models suggest that melting can be predicted from the behavior of one phase alone, without regard to the other. It should be emphasized that the existence of one-phase approaches to melting is the result of the basic differentiates melting from any other first-order transition. Various instability-based theories of melting have been developed. Melting has been discussed in terms of the generation of vacancies,[15–17] interstitials,[18] vanishing of the static shear modulus,[19–21] thermodynamic,[22] and thermoelastic instabilities,[23] entropy criterion,[24] and spontaneous generation of dislocations.[25–29]

One of the oldest (1910) and most widespread theories for the melting instability is the Lindemann criterion of melting.[30] It states that the ratio of the mean-square amplitude of lattice vibration to the interatomic spacing is constant along the melting curve. At high temperature $T_m > \Theta_m$, where Θ_m is the characteristic temperature of solid at melting, the criterion leads to the well-known Lindemann melting-curve equation $\Theta_m^2 V_m^{2/3}/T_m = \mathrm{const}$, where V_m is the volume of solid at the melting (the same equation also follows from the entropy criterion of melting[24]). In the differential form, the Lindemann equation law of melting can be written as

$$\frac{d\ln T_m}{dP} = \frac{\Gamma_m}{B_m}. \tag{2}$$

Here $\Gamma_m = -(d\ln T/d\ln V)_m = 2(\gamma_m - 1/3)$, $\gamma_m = -(d\ln\Theta/d\ln V)_m$ is the Grüneisen melting parameter, B_m is the bulk modulus of solid along the melting curve; $B_m = -(dP/d\ln V)_m = B_T[1+2(\gamma_m - 1/3)\alpha T_m]$, where $\alpha = (d\ln V/dT)_P$ is the volume coefficient of thermal expansion and $B_T = (dP/d\ln V)_T$ is the isothermal bulk modulus, at $T = T_m$. For the rising melting curve $B_m > B_T$, for the falling melting curve $B_m > B_T$, and at the melting curve maximum $B_m = B_T$.

It is evident that the dependence of the right-hand-side parts of Eqs. (1) and (2) on pressure are identical. We suggest that this dependence can be written as a fractional-form function. (The fractional-form function approximates a very wide classes of functions.) Hence we suggest that Eqs. (1) and (2) can be written—and this is a main point of the article—in a unified form as

$$\frac{d\ln T_m}{dP} = \frac{c_0 + c_1\Delta P + \cdots + c_L(\Delta P)^L}{b_0 + b_1\Delta P + \cdots + b_M(\Delta P)^M}, \tag{3}$$

where $\Delta P = P - P_0$, P_0 is some reference (for example, the triple point) pressure, and $c_0, c_1, \ldots, c_L$ and $b_0, b_1, \ldots, b_M$ are constants. Equation (3) combines both one- and two-phase approaches to melting. The integration of Eq. (3) with respect to pressure leads to the melting-curve equations $T_m = F_{[L/M]}(x)$:

For $M=1$

$$T_m=F_{[0/1]}(x)=T_0(1+x)^{a_2}, \tag{4}$$

$$T_m=F_{[1/1]}(x)=F_{[0/1]}(x)\exp(-a_3x), \tag{5}$$

$$T_m=F_{[L/1]}(x)=F_{[0/1]}(x)\exp\left(-\sum_{k=1}^{L} a_{k+2}x^k\right). \tag{6}$$

For $M=2$,

$$T_m=F_{[0/2]}(x)=F_{[0/1]}(x)(1+a_3x)^{-a_2}, \tag{7}$$

$$T_m=F_{[1/2]}(x)=F_{[0/1]}(x)(1+a_3x)^{-a_4}, \tag{8}$$

$$T_m=F_{[2/2]}(x)=F_{[1/2]}(x)\exp(-a_5x), \tag{9}$$

$$T_m=F_{[L/2]}(x)=F_{[1/2]}(x)\exp\left(-\sum_{k=2}^{L} a_{k+3}x^{k-1}\right). \tag{10}$$

Here $x=\Delta P/a_1$ is the reduced pressure, a_1 has the dimensionality of pressure, and the other parameters are dimensionless. The parameters a_k in Eqs. (4)–(11) can be expressed in terms of c_k and b_k and vice versa.

Melting curves have universal features irrespective of whether they rise or fall, are smooth (do not oscillate), and are concave towards pressure. It follows from these conditions that the parameters a_k in Eqs. (4)–(10) are positive.

It was *suggested* above that Eqs. (1) and (2) can be written in the form (3). However, the form (3) can be also *obtained* from Eqs. (1) and (2) by different methods:

(A) Expanding $y=\Delta V/\Delta H$ (or Γ_m/B_m) in the right-hand-side part of Eq. (1) [or Eq. (2)] at the point $P=P_0$ up to the order $L+M$, and performing the Padé $[L/M]$ approximation we obtain Eq. (3), where the values of $c_0,c_1,\ldots,c_L$ and $b_0,b_1,\ldots,b_M$ are determined by y_0 and its derivatives. In this case, the parameters a_k in Eqs. (4)–(10) can be identified now in terms of the ratios $\Delta V/\Delta H$ (or Γ_m/B_m) and their derivatives. This method was used in Ref. 1.

(B) Expanding the values in the numerator up to the order L and the denominator up to the order M in the right-hand-side part of Eq. (1) [or Eq. (2)] at the point $P=P_0$, we again obtain Eq. (3). In this case the parameters a_k in Eqs. (4)–(10) can be identified in terms of the two-phase approach to melting, ΔV and ΔH, or in terms of the one-phase approach to melting, Γ_m and B_m, and their derivatives.

Both of methods (A) and (B) can be also combined by performing the Padé approximation separately to the series of numerator and denominator.

Thus, we have shown that Eq. (3) [and hence the melting curves Eqs. (4)–(10)] is quite general.

It follows from Eqs. (5)–(10) that melting curves have the same structure:

$$T_m=F_{[0/1]}(x)D_m(x), \tag{11}$$

where $F_{[0/1]}(x)$ is the rising and $D_m(x)$ is the damping function that asymptotically slopes down under pressure.

The function $F_{[0/1]}(x)$ is the well-known Simon-Glatzel empirical equation for melting Eq. (4), which we write as

$$T_m=T_0(1+\Delta P/a)^b. \tag{12}$$

This two-parameter equation[31] was proposed by Simon and Glatzel in 1929, when they studied the melting of solid gases under pressure.[32,33] The Simon-Glatzel equation gives a form of the melting curve which rises indefinitely with increasing pressure. It is widely used for the analytical representation of experimental data for the ‘‘normal’’ melting curves.[34]

Equation (5) represents the simplest form of Eq. (11). It may be rewritten as

$$T_m=T_0(1+\Delta P/a)^b\exp(-c\Delta P). \tag{13}$$

With methods (A) and (B), one can identify the parameters *a*, *b*, and *c* appearing in Eq. (13) in terms of the thermodynamic values for the one- or two-phase approach of melting.

In case (A),

$$a=-2y_0'/y_0'', \tag{14}$$

$$b=-a^2y_0', \tag{15}$$

$$c=-ay_0+b, \tag{16}$$

where $y_0=(\Delta V/\Delta H)_0$ [or $(\Gamma_m/B_m)_0$]. It was shown in Ref. 1 that the relationships on the right-hand side of Eqs. (14)–(16) are indeed constants.

In case (B),

$$a=(\Delta H)_0/(\Delta H)_0'=B_{m0}/B_{m0}', \tag{17}$$

$$b=(\Delta V)_0/(\Delta H)_0'-ac=\Gamma_{m0}/B_{m0}'-ac, \tag{18}$$

$$c=-(\Delta V)_0'/(\Delta H)_0'=-\Gamma_{m0}'/B_{m0}'. \tag{19}$$

Case (B) implies that ΔV and ΔH, and Γ_m and B_m, are the linear functions of pressure. However, analysis of experimental data[35–37] shows that the dependence ΔV and Γ_m on pressure is more complicated.

Note that the melting curve can be predicted if the thermodynamic values at the reference pressure are known.[38].

On surveying the literature available (more than 100 substances were examined) it is shown that Eq. (13) accurately approximates, as good as experimental data, the rising, falling, and flattening curves, as well as the curves with a maximum for different classes of substances: solid gases, metals, nonmetals, and compounds.[1] As an example, Fig. 1 illustrates Eq. (13) for Te (Ref. 39), Cs-I Cs-II (Refs. 41–43), and the peculiar melting curve of Ca(OH)$_2$ (Ref. 40) (see also Figs. 1 and 2 in Ref. 1).

Figure 2 demonstrates the extrapolation of Eq. (13) for rubidium. The parameters of Eq. (13) were computed by a least-squares fit of the high-precision data of Nikolaenko *et al.* up to 1.3 GPa.[37] It is seen that the extrapolation of Eq. (13) from 1.3 to 10 GPa predicts the melting curve in very good agreement with available high-pressure experimental data.[44–46]

Very recently, Datchi, Loubeyre, and LeToullec have measured the melting curve of solid gases and water at high pressure with a diamond anvil cell.[47] Their unique high-precision experiments show that Eq. (13) fits very well ex-

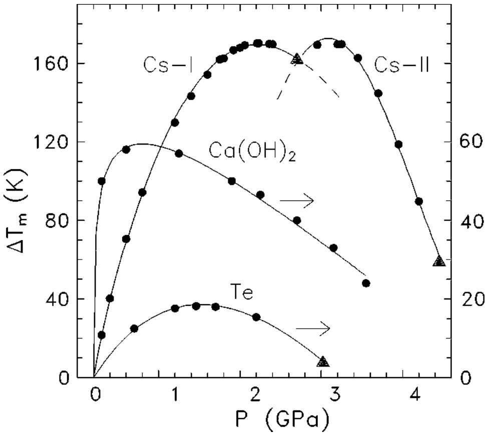

FIG. 1. Melting temperature difference $\Delta T_m = T_m - T_0$ for Cs-I, Cs-II, Ca(OH)$_2$, and Te. Lines are the fitting of Eq. (13). For Cs-I, $T_m = 302(1+P/1.4041)^{1.3497}\exp(-0.3788P)$; for Cs-II, $T_m = 464(1+\Delta P/6.1270)^{11.7612}\exp(-1.8370\Delta P)$, $\Delta P = P - 2.54$ GPa; for Ca(OH)$_2$, $T_m = 1023(1+P/0.0008)^{0.0136}\exp(-0.0236P)$; for Te, $T_m = 723(1+P/1.421)^{0.1535}\exp(-0.0573P)$. Triangles are the triple points.

perimental data up to 41.2 GPa for He and up to 15.2 GPa for H_2. They also have demonstrated that the 20-fold extrapolation of Eq. (13) for hydrogen from 15.2 to 300 GPa is in excellent agreement with *ab initio* molecular dynamic calculations.[48–50]

Equations (6)–(10), in comparison with Eq. (13), describe more accurately the falling branch of the melting curves. However, the available data precision is not sufficient for a detailed analysis of this equations.

The results obtained in this work can be summarized as follows.

A number of melting-curve equations based on the two- and one-phase approaches to melting have been obtained. The parameters appearing in the equations are identified in terms of thermodynamic values.

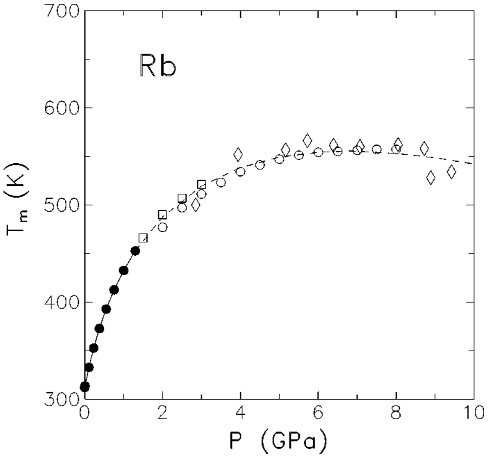

FIG. 2. Melting curve of Rb. The dashed line is extrapolation of Eq. (13) based on the data up to 1.3 GPa, solid circles (Ref. 37): $T_m = 312.12(1+P/0.4287)^{0.3064}\exp(-0.04258P)$; open circles (Ref. 44), open squares (Ref. 45), and open diamonds (Ref. 46).

The melting curves have the form $T_m = F(P)D(P)$, where $F(P)$ is the rising (Simon-Glateel) melting function and $D(P)$ is the damping function, which asymptotically slopes down under pressure. Therefore, every solid phase has a maximum (but no minimum[51,52]) melting temperature at positive or negative pressure.[53,54] The melting curves have the inflection point at $P = P_{\text{infl}}$, where $d^2T_m/dP^2 = 0$, so that at $P > P_{\text{infl}}$ the melting curves are upward from pressure. (Note that in the neighborhood of the inflection point, the melting curve can be approximated by a falling linear function of pressure.)

Among all the melting curves, the simplest three-parameter equation (13) can be well used for the analytical representation and extrapolation of the melting data.

We can conclude that there exist no anomalous melting curves. All melting curves, rising, falling, and flattening, as well as curves with a maximum, are normal insofar as they can be described by the unified equation (13).

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