Thermodynamic model of melting

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Unlike previously used approximations, the model proposed in this paper takes into account the difference between the elastic components of the free energies for the solid and liquid phases around the melting point, as well as the so-called configurational energy of liquid, which is a measure of its disorder. Oscillations of atoms around their equilibrium positions in both solid and liquid phases are described in the Debye approximation. The general conditions of phase equilibrium are simplified using the smallness of the relative volume change and parameters of the triple point on the material phase diagram. If the solid phase volume is smaller than that of the liquid phase over the entire melting curve (normal melting), the Lindeman criterion derived by equating the derivatives of pressure with respect to volume at the the point where free energy isotherms intersect is valid. Probable causes of anomalous melting are discussed. Calculations are compared to experimental data on melting of sodium, cesium, and solidified noble gases. © *1996 American Institute of Physics.* [S1063-7761(96)02308-6]

1. INTRODUCTION

It is well known that there is no detailed theory of melting which is self-consistent and, moreover, there is no generally accepted model adequately describing physical processes in melting even qualitatively.[1] In practice, independently derived empirical relations, such as Simon's relation for the melting curve and that derived from Lindeman's hypothesis, are widely used.[1,2]

For example, thermodynamic functions describing the melting process were derived from semiempirical expressions for the free energy containing thermal and elastic (''cold'') components.[3–5] One way or another, this approach assumes that the free energies of solid and liquid phases have equal elastic components and very different thermal parts. This is the condition for the first-order phase transition between the solid and liquid state of materials, i.e., melting. In both solid and liquid states, the thermal component is largely due to oscillations of atoms around their equilibrium positions. Many years ago, however, Frenkel[6] noted that it would be incorrect to ascribe the entire change in the free energy in a crystal resulting from loss of long-range order and the transition to the liquid state only to changes in frequencies of atomic oscillations around equilibrium positions. Some of the difference between the free energies of the phases is due to the so-called configurational component of the free energy, and another part is controlled by the differences between the elastic parameters of solids and liquids. The equation of state for the liquid phase taking into account these effects was proposed in a previous publication.[7] There the elastic oscillations of the atoms about their equilibrium positions in both solid and liquid phases were described in terms of the Debye approximation modified so as to obtain the ideal-gas equation of state in the limit of high temperature and low density.[8] In contrast to the previously used approach,[3–5] the elastic component of the liquid free energy is not equal to that of the solid phase because the density and evaporation energy of the liquid phase extrapolated to zero temperature are slightly lower than those of the solid phase. In addition, the configurational entropy, which is a measure of its disorder, is introduced for the liquid phase. In this approach, the main contribution to the difference between the free energies of the solid and liquid phases around the melting point is due to the elastic components and configurational entropy.

In this paper the model of solid and liquid states proposed in previous publications[7,8] is used to describe melting. As in most other work concerning this topic, the smallness of the relative volume change is exploited to simplify the general conditions of phase equilibrium. Formally, this allows us to expand the thermodynamic functions of volume in the solid and liquid phases around the point at which the free energy isotherms cross. As is well known, in the case of normal melting, the solid phase volume is always smaller than that of the liquid phase, and this difference is nonzero even at very high temperatures.[1] This is possible if the nature of the free energy isotherms around the crossing point is the same along the entire melting curve. This paper demonstrates that this condition leads to conservation of a specific parameter, namely the ratio of pressure derivatives at the crossing point, in the case of normal melting. Typically this ratio is slightly larger than unity. In anomalous melting, it is first larger than unity, then it may become smaller than unity. In the latter case the solid volume is larger than the liquid volume. This allows us to specify for normal melting that the ratio of pressure derivatives at the isotherm crossing point be constant. This condition is equivalent to the Lindeman criterion, which naturally derives from the proposed model.

Since the crossing point lies in the ''nonphysical'' region, and the isotherms separating equilibrium volumes are purely interpolation lines, we have employed experimental parameters of the triple point. This has allowed us to eliminate the elastic components of the pressure, which are not easy to calculate, from the equations in both phases and to derive a relatively simple equation system for calculating pressure, temperature, and volume in both phases. It is remarkable that the pressure as a function of temperature is controlled by the factor $T(T/T_t-1)$, where T and T_t are the temperatures at the calculated and triple points, respectively. Given this function, one can understand the success of Simon's empirical formula, in which the pressure is proportional to T^c, where $c=0.4$–0.6.

The paper reports on calculations for materials with normal melting curves, such as solidified noble gases and sodium, and compares them to experimental data. The agreement for pressure versus temperature is fairly good, but poorer for the phase volumes. Melting curves for cesium, which are anomalous,[1] are also discussed. The related problems are considered.

2. EQUATIONS OF STATE FOR SOLID AND LIQUID PHASES

We express the free energy of the unit mass in the crystalline state in the Debye approximation:[2]

$$F_1=\frac{RT}{\mu}\left[3\ln(1-e^{-\Theta/T})-D\left(\frac{\Theta}{T}\right)\right]+U_1(v), \tag{1}$$

where $D(\Theta/T)$ is the Debye function, R is the universal gas constant, μ is the molecular mass of the material, v is the specific volume, and Θ is the Debye temperature, which is described by the following function:

$$\Theta(v)=\Theta_0\exp\left(-\int_{v_0}^{v}\Gamma d\ln v\right), \tag{2}$$

where v_0 and Θ_0 are the specific volume and Debye temperature at $T=0$, and $\Gamma(v)$ is the Grüneisen parameter. For most materials Γ is practically constant on the melting curve, so Eq. (2) can be simplified:

$$\Theta(v)=\Theta_0(v_0/v)^{\Gamma}. \tag{3}$$

Here $U_1(v)$ is the elastic component of the free energy satisfying the condition

$$U_1(v_0)=-q_0, \tag{4}$$

where q_0 is the sublimation energy at $T=0$.

The expressions for entropy and pressure derived from Eq. (1) have the forms

$$S_1=\frac{R}{\mu}[4D-3\ln(1-e^{-\Theta/T})], \tag{5}$$

$$p_1=3\Gamma D\left(\frac{\Theta}{T}\right)\frac{RT}{\mu v}+\Pi_1(v), \tag{6}$$

where $\Pi_1(v)=-dU_1/dv$ is the elastic component of pressure. Irrespective of its specific form, this should satisfy two general conditions. The first of these is

$$\Pi_1(v_0)=0. \tag{7}$$

The second is the normalization condition in the form

$$\int_{v_0}^{\infty}\Pi_1 dv=q_0. \tag{8}$$

If v is close to v_0, the derivative of the elastic pressure is related to the Debye temperature by the equation[2,9]

$$\Pi_1'(v)=-\frac{1}{v^2}\left(\frac{k\Theta}{\hbar}\right)^2\left(\frac{mv}{6\pi^2}\right)^{2/3}. \tag{9}$$

After differentiating Eq. (9) with respect to v and taking into account Eq. (3), we obtain

$$\Pi''v=-2(\Gamma+2/3)\Pi'. \tag{10}$$

On the other hand, the Grüneisen parameter is related to the parameters of the elastic component by the equation[2]

$$\Gamma=\frac{m-2}{3}-\frac{v}{2}\frac{(\Pi v^{2m/3})''}{(\Pi v^{2m/3})'}. \tag{11}$$

The value $m=0$ corresponds to the Landau–Slater–Stanyukovich approximation,[10,11] in which the Poisson coefficient is assumed to be constant. The Dugdale–MacDonald model ($m=1$) is obtained assuming that logarithmic derivatives of all force constants are equal,[12] and $m=2$ corresponds to the free-volume theory of Vashchenko and Zubarev,[13] which suggests that atoms oscillate in a spherically symmetrical field generated by their neighbors. Given Eq. (11), for v close to v_0 we can transform Eq. (10) to

$$\Pi''v=-2(\Gamma+2/3-2m)\Pi'. \tag{12}$$

For $m=0$ Eqs. (10) and (12) are identical, which justifies the Landau theory.[11]

In order to derive the equation of state for the liquid phase, we use the thermodynamic model of liquids developed previously.[7,8] According to this model, oscillations of atoms about their equilibrium positions are also described using the Debye approximation. The elastic components of the free energy and pressure for liquids are different from those for solids. In particular, the parameters v_0 and q_0 in Eqs. (7) and (8) characterizing solids should be replaced with v_0' and q_0' typical of liquids. The latter parameters are slightly smaller than the former. They can be estimated, given the average number of atoms per vacancy in the solid (r) and liquid (r') states:

$$q_0'\simeq q_0\frac{r'}{r},\quad v_0'\simeq v_0\frac{r}{r'}. \tag{13}$$

For noble gases, these parameters are[14] $r=6$ and $r'=5.6$. Furthermore, the liquid free energy contains the configurational component, which is a characteristic of disorder and results in a nonzero entropy at zero temperature. As a result, the liquid free energy can be expressed as[12]

$$F_2=\frac{RT}{\mu}\left[3\ln(1-e^{-\Theta/T})-D\left(\frac{\Theta}{T}\right)-\frac{sv_0'}{v}\right]+U_2(v), \tag{14}$$

where s is the zero-temperature entropy of the liquid. The entropy and pressure are given by the equations

$$S_2=S_1+\frac{R}{\mu}\frac{sv_0'}{v}, \tag{15}$$

where S_1 is the Debye component of the entropy determined by Eq. (5), and

$$p_2=\frac{RT}{\mu v}\left[3\Gamma D\left(\frac{\Theta}{T}\right)-\frac{sv_0'}{v}\right]+\Pi_2(v). \tag{16}$$

3. CROSSING OF ISOTHERMAL CURVES. LINDEMAN'S MELTING CRITERION

It is noteworthy that the isothermal curves of free energy versus specific volume for the solid and liquid phases described by Eqs. (1) and (14) in the melting region curve downward curvature and cross at some point. The position of the crossing point can be easily determined in terms of temperature as a function of specific volume by equating the solid and liquid free energies given by Eqs. (1) and (14):

$$T=\frac{\mu v_0(U_1-U_2)}{Rsv_0'}. \qquad (17)$$

If two downward curving curves have a crossing point, they also have a common tangent with a negative slope passing through the points at v_1 and v_2. These points are described by the condition of phase equilibrium,

$$F_1-F_2+p(v_1-v_2)=0, \qquad (18)$$

where F_1 and F_2 are the free energies of the phases, v_1 and v_2 are their specific volumes, and p is the pressure at the phase-transition point. The pressures at the points v_1 and v_2 satisfy

$$p=p(v_1)=p(v_2). \qquad (19)$$

The qualitative behavior of the isothermal curves is shown in Fig. 1. Note that the point v is always between the points v_1 and v_2. In the melting region, the isothermal curves 1 and 2 always curve downward, so

$$p_1'(v)<0, \quad p_2'(v)<0. \qquad (20)$$

Moreover, at the crossing point in Fig. 1a the following inequalities hold:

$$p_2(v)>p_1(v), \quad p_2'(v)>p_1'(v). \qquad (21)$$

For some parameters of the elastic components in Eqs. (1) and (14), two crossing patterns different from that in Fig. 1a are possible (Fig. 1b,c). The pattern of Fig. 1b corresponds to the tangency of the isothermal curves, when the phase transition is degenerate. In this case $p=p_1(v)=p_2(v)$, and the specific volumes in both phases at the transition point are equal, $v_1=v_2=v$. But unlike the critical point, the derivatives p' and p'' are nonzero in this case. Figure 1c shows behavior opposite to that in Fig. 1a. In this case $p_2(v)<p_1(v)$ and the volume v_2 is smaller than v_1. In this model, the melting mode is considered "normal"[1] if the pattern of isothermal curves at the crossing point corresponds to Fig. 1a on the entire melting curve. The case when the crossing pattern changes from that of Fig. 1a through Fig. 1b to Fig. 1c is defined as "anomalous" melting,[1] i.e., the solid-phase volume is smaller than that of the liquid phase in some region of thermodynamic parameters, but larger in another region. Note that the crossing point corresponds to a thermodynamically nonequilibrium state and belongs to the "nonphysical" region. Here the isothermal curves described by Eqs. (1) and (14) are mere interpolations of physical curves. Mathematically, however, they are smooth without any singularities.

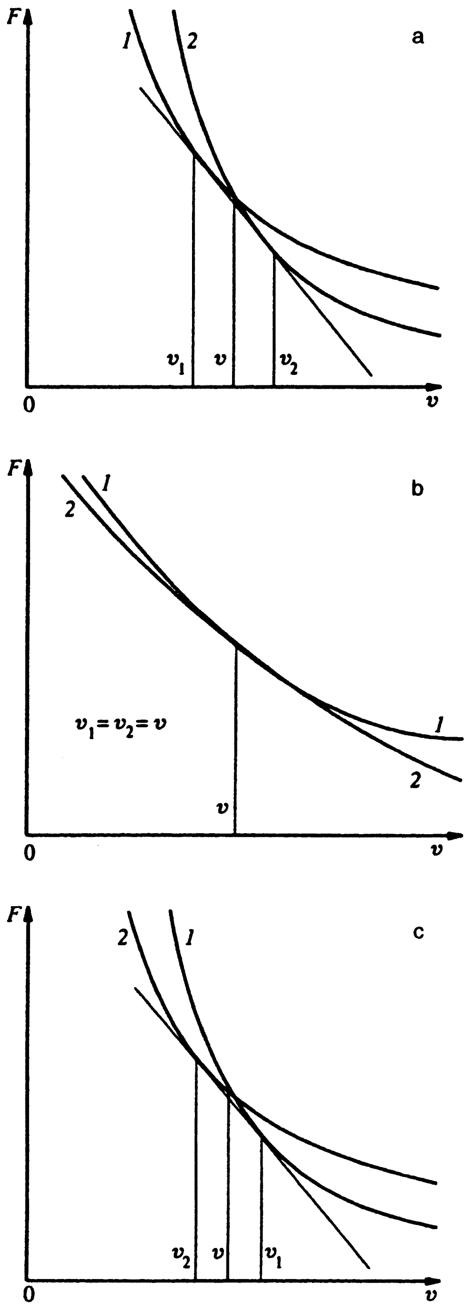

FIG. 1. Behavior of the free-energy isothermal curves for (*1*) solid and (*2*) liquid phases around the melting point versus volume there. v denotes the crossing point. The tangent determine the equilibrium pressure and phase volumes v_1 and v_2.

It is known from experimental data that the relative volume change due to melting is small but nonzero even at very high temperatures.[1] Thus the following conditions are satisfied:

$$\frac{v-v_1}{v}\ll 1, \quad \frac{v_2-v}{v}\ll 1. \qquad (22)$$

Therefore the functions $F_1(v_1)$, $F_2(v_2)$, $p_1(v_1)$, and $p_2(v_2)$ can be represented as power series around the point

v. By retaining only derivatives of pressure through first order and substituting the resulting expressions into Eqs. (18) and (19), we obtain

$$p_1'(v)(v-v_1)^2=p_2'(v)(v_2-v)^2, \tag{23}$$

$$p=p_1(v)-p_1'(v)(v-v_1)=p_2(v)+p_2'(v)(v_2-v). \tag{24}$$

After some transformations, we derive the following formulas for the pressure and the volumes of the phases from Eqs. (23) and (24):

$$p=\frac{\xi p_2+p_1}{\xi+1}, \tag{25}$$

$$v_1=v-\frac{p_1-p_2}{p_1'(\xi+1)}, \tag{26}$$

$$v_2=v+\frac{p_1-p_2}{p_1'(\xi+1)\xi}, \tag{27}$$

where

$$\xi=p_2'/p_1'. \tag{28}$$

From Eqs. (26) and (27) we derive

$$\frac{v_2-v_1}{v}=\frac{p_1-p_2}{vp_1'\xi}, \tag{29}$$

which should tend to a constant as $T\to\infty$. The pressures of the phases, p_1 and p_2, and the derivative p_1' increase with the temperature. Assuming $p_1\neq p_2$ and eliminating the indeterminacy on the right-hand side of Eq. (29), we obtain in the limit of high temperature

$$\frac{v_2-v_1}{v}=\frac{\xi-1}{\xi(1+vp_1''/p_1')}. \tag{30}$$

Note that the dominant contributions to the first and higher-order derivatives of pressure are due to the elastic component of the free energy determined by the repulsion branch of the potential curve. If it is described by a power function, the parameter vp_1''/p_1' is constant. Then the function in Eq. (30) tends to a constant if

$$\xi\to\text{const}, \tag{31}$$

where ξ is, according to Eq. (28), the ratio of the derivatives of phase pressures. Note that the condition for $(v_2-v_1)/v$ to be small is that ξ should be close to unity. Hence the parameter ξ may be slightly larger than unity on the initial part of the melting curve in the case of "normal" melting, and then it should drop and tend to a constant, but remain larger than unity. This means that the parameter ξ should vary little on the melting curve.

The anomalous melting is quite a different case. Initially, the factor ξ should be higher than unity, then it should drop and tend to a constant smaller than unity. Concurrently the pattern of isothermal curves around the crossing point should sequentially change from that of Fig. 1a to Fig. 1c.

Let us differentiate Eqs. (6) and (16) with respect to v and substitute into Eq. (28), neglecting the zero-temperature entropy and the weak dependence of Γ and D on v. Then the parameter ξ is determined by the equation

$$\xi=\sqrt{\left(1+\frac{\Pi_2'mv^2}{3\Gamma DkT}\right)\Big/\left(1+\frac{\Pi_1'mv^2}{3\Gamma DkT}\right)}. \tag{32}$$

It follows from Eq. (32) that ξ is constant if the parameters

$$\frac{\Pi_2'mv^2}{3\Gamma DkT}\quad\text{and}\quad\frac{\Pi_1'mv^2}{3\Gamma DkT} \tag{33}$$

are constant. After substituting Π_1' from Eq. (9) and the similar expression for Π_2' into Eq. (33), we obtain

$$\frac{m(mv)^{2/3}\Theta^2}{3\Gamma DkT}=\text{const.} \tag{34}$$

On the melting curve the product ΓD depends weakly on v since the Grüneisen parameter is constant and the function D is close to saturation. In this case Eq. (34) is fully identical to the Lindeman criterion.

Note that since the elastic component of the pressure is a steep function of the volume, the parameters in Eq. (33) are much larger than unity, which implies a simple formula for ξ:

$$\xi\simeq\sqrt{\frac{\Pi_2'}{\Pi_1'}}\simeq\left(\frac{v_0'}{v_0}\right)^{\Gamma-1/3}=\left(\frac{r}{r'}\right)^{\Gamma-1/3}. \tag{35}$$

For noble gases the average values are $\Gamma\simeq2.7$ and $\xi\simeq1.18$. We see that if the volumes or the numbers of vacancies per atom in the solid and liquid phases are equal, the parameter ξ is constant on the melting curve, which corresponds to the case of normal melting. In contrast, if r' or r changes on the melting curve, the pattern of isothermal curves around the crossing point also changes, and the melting is anomalous. The parameter r may change in the solid or liquid phase as a result of a phase transition without a change in the material structure. In cesium, for example, a gradual phase transition is assumed to take place in the liquid state at a pressure of about 10^4 atm.[1] It is ascribed to a transition of the valence electron from the s- to d-shell.

Stishov[1] proved that, in systems whose potential energy is a homogeneous function of coordinates, the Lindeman relation is a direct consequence of the self-similar nature of the nonideal part of the partition function. In this case, it is equivalent to the condition that the ratio of potential to thermal energy on the melting curve should be constant. This assertion is also valid for the ratio of the derivatives of these energies. In our discussion, we have not exploited the assumption that the potential is described by a homogeneous function. One can see that Eq. (32) contains the ratio of the derivatives of potential and thermal components in pressure. On the melting curve, the derivative of the potential pressure component is largely determined by the repulsive branch of the potential (which cannot be said about the potential component proper that is determined by an accurate balance between attractive and repulsive forces). In this context, the potential may be considered as a quasi-homogeneous function, as concerns the derivatives of the potential pressure component. Hence the ratio of the potential to thermal pressure component is not constant on the melting curve. The attractive forces, however, are less significant for the derivatives of the pressure components, and the results obtained for systems with a uniform potential can be applied to approximately describe our system. In this sense, our results are consistent with the conclusions reached by Stishov.[1]

4. THERMODYNAMIC FUNCTIONS ON THE MELTING CURVE

The approximate system of equations (17), (25)–(27) describes the parameters T, p, v_1, and v_2 on the melting curve as functions of the parameter v, which is defined as the position where the isothermal curves intersect and, generally speaking, belongs to the "nonphysical" region of parameters. Besides, a calculation using these equations demands information about the elastic components of the energy and pressure in the liquid and solid phases, and the parameters v_0' and q_0' of the liquid phase, which cannot be easily calculated. All these difficulties, as well as doubts about whether the thermodynamic functions can be expanded in powers around the point v, can be largely eliminated if one exploits experimental data on the thermodynamic functions at the triple point. For most materials, the pressure p_t, temperature T_t, specific volumes of the phases v_{1t} and v_{2t}, and the entropy jump ΔS_t at the triple point are available. Let us take advantage of the fact that the volumes v_1 and v_2 on the melting curve are quite close to v_{1t} and v_{2t}. Assuming $\xi=\text{const}$, we expand the elastic components of energy and pressure around the point $v=v_t$, where we have $p=p_t$ and $T=T_t$, in powers of small parameters v_1-v_{1t} and v_2-v_{2t} and retain the terms with derivatives of pressure up to the first order. After this procedure and simple algebra, we obtain the following equations valid in the case of normal melting:

$$T=T_t\left[1+L_t(v_t-v)(v_{2t}-v_{1t})\frac{(1+\xi)\zeta}{v_0' s v_t}\right], \tag{36}$$

$$p=p_t+\frac{3\Gamma DRT}{\mu v_t(1+\xi)}\left(\frac{T}{T_t}-1\right)\left[1+\frac{v_0' s}{3\Gamma D(v_t-v_{1t})\zeta}\right], \tag{37}$$

$$v_1=v-(v_t-v_{1t})+(\xi-1)(v_t-v), \tag{38}$$

$$v_2=v+(v_{2t}-v_t)-\frac{\xi-1}{\xi}(v_t-v), \tag{39}$$

$$v_t=\frac{v_{1t}+v_{2t}\xi}{1+\xi}, \tag{40}$$

$$\zeta=1+\frac{(\xi-1)(v_t-v)}{2(v_t-v_{1t})}. \tag{41}$$

The factor L_t in Eq. (36) is, in fact, the Lindeman parameter derived from the Debye temperature and volume at the triple point. It is defined as

$$L_t=\left(\frac{k\Theta_0}{\hbar}\right)^2\left(\frac{mv_0}{2}\right)^{2/3}\left(\frac{v_0}{v}\right)^{2\Gamma-2/3}\frac{m}{kT}. \tag{42}$$

All the thermodynamic functions in Eqs. (36)–(41) are functions of v. At $v=v_t$ they equal their values at the triple point. The pressure varies slowly with v (via the factor ζ), and its dependence on the temperature is determined by the product $T(T/T_t-1)$, so for $T\geqslant T_t$ it satisfies $p\propto T$. In the high-temperature limit we have $p\propto T^2$. At intermediate temperatures it behaves as $p\propto T^c$, where $1<c<2$. The latter condition is consistent with Simon's empirical law, according to which the parameter c of some materials ranges between 0.4 and 0.6.[4,5]

One can see that Eqs. (38) and (39) for the volumes of phases contain only terms linear in the volume deviation $v-v_t$ with the proportionality factor $\xi-1$. From Eqs. (38) and (39), we derive

$$v_2-v_1=v_{2t}-v_{1t}-\frac{\xi^2-1}{\xi}(v_t-v). \tag{43}$$

Formally, the difference v_2-v_1 may drop to zero as v decreases, which would contradict the initial assumption.

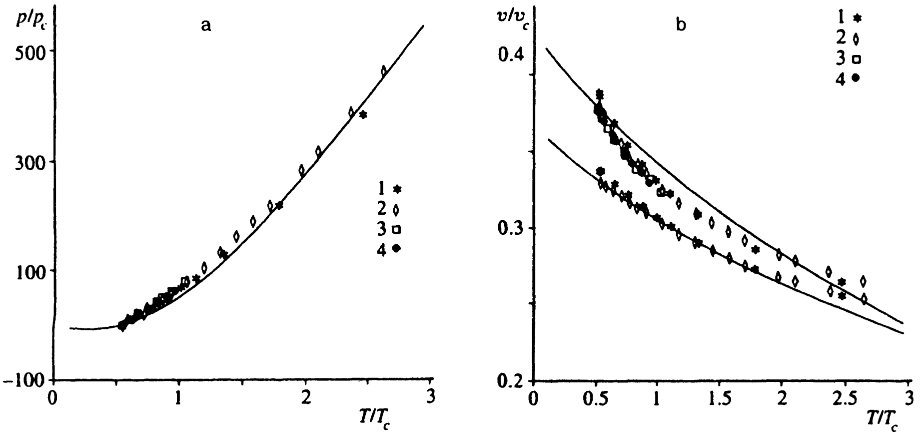

FIG. 2. Reduced (a) pressure and (b) volumes of solid (v_1/v_c, upper curve) and liquid (v_2/v_c, lower curves) phases versus reduced temperature T/T_c for noble gases on the melting curve. The symbols correspond to the following materials: 1) Ne; 2) Ar; 3) Kr; 4) Xe. Solid curves show calculations of this work.

TABLE I.

	p_t, atm	T_t, K	v_{1t}, cm^3/g	v_{2t}, cm^3/g	v_0 cm^3/g	v'_0, cm^3/g	s	Θ_0, K	Γ	ξ	L_t	ξ'	L'_t
Ar	0.69	83.8	0.63	0.71	0.57	0.61	0.7	92	2.73	1.18	27.5	1.18	19
Na	35	371	1.05	1.08	1.02	1.09	0.87	158	1	1.05	23	1.05	21
Cs	1	301	0.53	0.54	0.45	0.5	0.87	38	1	1.05	15	1.05	16

This determines the application domain of the expansions in Eqs. (39) and (40). These equations are valid until the following condition is satisfied:

$$v>v_t-\frac{(v_{2t}-v_{1t})\xi}{\xi^2-1}. \qquad (44)$$

For argon at $\xi=1.18$, the right-hand side of Eq. (44) equals 0.43 cm^3/g.

In addition to the thermodynamic functions at the triple point, the calculation according to Eqs. (36)–(39) requires the parameters Θ_0, v_0, and Γ of the solid phase at zero temperature (these data are available for most materials), and the parameters v'_0 and s of the liquid phase. By equating the difference between the entropies in the liquid [Eq. (15)] and solid [Eq. (5)] phases at the triple point to the entropy jump ΔS_t, we obtain

$$sv'_0=\frac{\mu}{R}[\Delta S_t-S_1(v_{2t})+S_1(v_{1t})]. \qquad (45)$$

The parameter s follows from this equation.

The parameters ξ and L_t can be calculated using Eqs. (35) and (42). These equations, however, have been derived with some assumptions and simplifications. Given sufficient experimental data, one can select the parameters ξ' and L' to obtain the best fit of the calculations using Eqs. (36)–(39) to measurements. In the next section both these methods will be used to determine ξ and L_t.

5. COMPARISON TO EXPERIMENTAL DATA

We take solidified noble gases, whose melting mode is normal and measurements of melting parameters are abundant, as the first object for verifying our model. In addition, the law of corresponding states is valid in these materials. All the thermodynamic functions can be expressed in terms of three parameters,[15] namely, the potential well depth D_e, the equilibrium separation R_e between nuclei, and the atomic mass m. In particular,[16] the Debye frequency is

$$\omega_D=\frac{k\Theta_0}{\hbar}=\frac{C}{R_e}\sqrt{\frac{D_e}{m}}, \qquad (46)$$

where C is a constant. It is calculated in Ref. 16. The average value for noble gases is $C\simeq 25.7$. The triple-point temperature is $T_t=0.58D_e$, the specific volume is $v_0=R_e^3/\sqrt{2}m$. For noble gases we have $v_0/v_t\simeq 0.85, \Gamma\simeq 2.73$, and $s=0.7$. Substituting these values into Eq. (42) we calculate $L_t\simeq 27.3$. Table 1 lists triple-point parameters for argon, sodium, and cesium.

Note that for noble gases the Debye function at the triple point is considerably smaller than unity. For neon we have $T_t=24.55$ K and $\Theta_0=0.75$ K, so $D(\Theta_0/T_t)\simeq 0.42$.

Figure 2 shows measurements[15] of the reduced pressure p/p_c and reduced phase volumes v_1/v_c and v_2/v_c as functions of the reduced temperature T/T_c, where the index c denotes the critical point. In these variables, the points corresponding to different elements fall on the same curves. The best fit to experimental data is achieved at $\xi'=1.18$, which conforms to the calculations, whereas the parameter $L'_t=19$

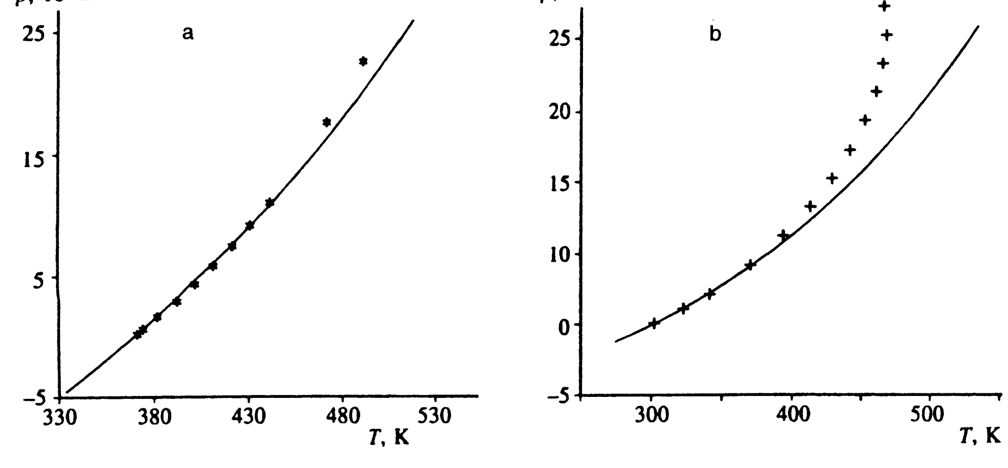

FIG. 3. Melting curves of (a) sodium and (b) cesium. Experimental data are taken from Ref. 1, solid lines are calculations of this work.

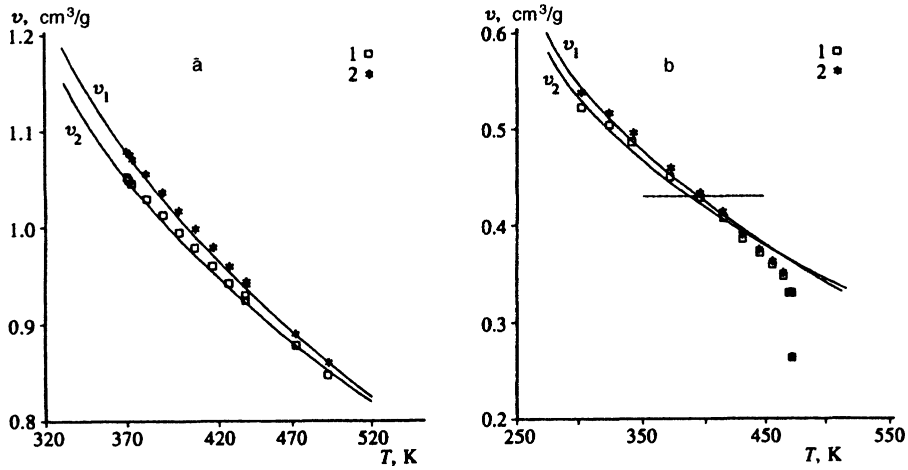

FIG. 4. Volumes of solid (v_1) and liquid (v_2) phases versus temperature for (a) sodium and (b) cesium. Experimental data are taken from Ref. 1; *1*) solid phase; *2*) liquid phase. Solid lines show calculations of this work. The dashed line defines the application domain of the model.

is considerably smaller than the calculated value of 27.3. The calculations these parameters are shown by solid curves. The parameters of noble gases at the triple point were also taken from Ref. 15. One can see that the calculated pressure coincides with experimental data. The calculated phase volumes differ from measurements much more, especially at high temperatures. This may be caused by the insufficient accuracy of power expansions used in calculations of these parameters. It seems, in particular, that the calculation of v_1 and v_2 [Eqs. (38) and (39)] taking into account only the terms linear in $v-v_t$ is inaccurate. The deviation of the calculations from the measurements may also be ascribed to the approximate nature of the theory.

The theory was also tested on the alkali metals Na and Cs. Kozhevnikov *et al.*[17] determined the specific volume of the cesium liquid phase by formally extrapolating it to zero temperature. Their result was $v_0'=0.5$ cm^3/g. The specific volume of solid Cs at $T=0$ was $v_0=0.451$ cm^3/g. The Grüneisen parameter for alkali metals is $\Gamma\simeq 1$.[18] Given these data, Eq. (36) yields $\xi\simeq 1.05$. Other parameters of Na and Cs used in the calculation are given in Table I.

Figures 3 and 4 show the pressure and specific volumes of the phases for Na and Cs. Experimental measurements were taken from Ref. 1. One can see that the agreement between measurements and calculations of pressure and volume for sodium is quite satisfactory.

As is well known, cesium is classified as a material with an anomalous melting mode.[1] The experimental data shown in Fig. 3b indicate that at lower pressures the melting temperature of cesium increases with the pressure, achieves a maximum, and then drops. At temperatures higher than 470 K the phase volumes drop abruptly, and the liquid-phase volume becomes smaller than that of the solid phase (Fig. 4b). Stishov[1] suggested that such a behavior may be due to a restructuring of the liquid phase, which is a gradual process taking place under a pressure of about 10^4 atm. Consistently with the concept underlying the present work, the factor ξ in this case should be smaller then unity, whereas on the low-pressure section of the melting curve the melting proceeds in the normal mode, so this section of the experimental curve can be compared with the calculation based on the proposed model. For Cs the limiting value of v calculated by Eq. (45), which determines the applicability of Eqs. (39) and (40), is 0.43 cm^3/g. The calculations are shown in Figs. 3b and 4b by solid lines. As expected, the low-pressure section of the melting curve is in good agreement with the experimental data, and at higher pressures the calculations deviate from the measurements. The low-pressure sections of the phase volume curves are also in satisfactory agreement with experimental data.

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