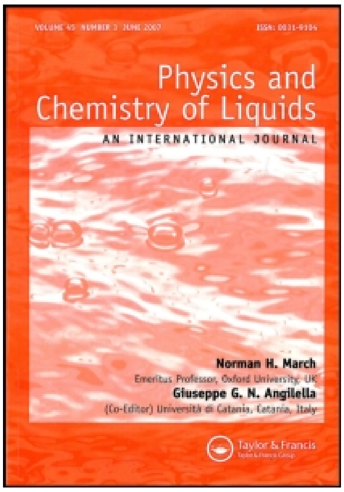

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Letter

Melting transitions in metallic elements correlated with shear modulus and atomic volume

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We show that two quite recent treatments of dislocation-mediated melting transitions result in the thermal energy associated with the melting temperature, T_m, being expressed as a product of a volume factor and a combination of elastic constants times a lattice structure-dependent factor. We further show that the result for the latent heat of fusion L_m obtained in one of these studies leads to the ratio $L_m/G\Omega$, where G is the shear modulus at melting and Ω the atomic volume, being a constant. Since the ratio of the vacancy formation energy to $G\Omega$ is also found to be roughly constant, we suggest that the factor $G\Omega$ at melting is crucial in determining the melting temperature, the latent heat of fusion and the vacancy formation energy and we comment on the reasons why this should be so.

Keywords: Melting transition; Dislocation model

1. Introduction

Following the pioneering work by [1], there now exists a quantitative statistical mechanical theory of freezing [2–5]. However, in spite of this, there has been a recent resurgence of interest in models, and also criteria, which aim to throw light on the regularities exhibited by the empirical melting temperatures; especially, to date, of the metallic crystals. The most recent contributions of this kind have been those of Kleinert and Jiang (KJ) [6], Lawson [7] and Burakovsky and co-workers [8,9]. KJ [6] constructed simple harmonic lattice models to describe the elastic fluctuations in body-centred cubic (bcc) and face-centred cubic (fcc) lattices and for the excitation of dislocations and disclinations. The resulting lowest order approximation for the melting temperatures of some bcc and fcc metallic crystals have been found to be

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more precise than that obtained by the use of Lindemann's rule. This is indeed in agreement with Lawson's analysis of the law; namely that the errors of between 20 and 30% are characteristic of its use in predicting T_m.

In the approach taken by Burakovsky *et al.* [8] (BPS), although elasticity considerations are paramount, they differ fundamentally from KJ in that the disinclinations are neglected. This is serious, since, as stressed by Kleinert [10], the melting transition, if dislocation-mediated, is only correctly first-order after incorporating disclinations. However, the simplicity of the approach of BPS allowed them to give a prediction for the latent heat of fusion, L_m, in relation to T_m and a structure-dependent factor, $\ln(z-1)$. Here, z is the local coordination number while the logarithmic term is a characteristic of line-like defects.

The outline of the article is as follows. In the next section, we compare and contrast existing formulae for T_m, and compare the predictions for T_m and L_m, with currently available experimental data. Following this, we focus on the empirical regularities between mono vacancy formation energies $E^{\mathrm{f}}_{1\mathrm{v}}$ and the thermal energy, $k_B T_m$, associated with melting for some close-packed crystals. Finally, we give a possible explanation for the observed macroscopic regularities.

2. Predictions arising from dislocation-mediated theories of melting

Starting with the recent proposal of KJ, we note that their equation (15) for the melting temperature can be rearranged to take the form

$$\frac{k_B T_m}{a^3 \mu \xi} = \frac{8^{4/3}}{2\pi n_u (2\xi - 1)} \left(1 + \frac{3\lambda}{2\xi\mu}\right)^{1/3} \exp(-l/3) \tag{1}$$

where n_u denotes the number of atoms per unit cell, while a is the near-neighbour distance. The elastic constants, μ, λ and ξ are defined in the usual way by the continuum elastic energy

$$E_{ce} = \mu \int d\mathbf{r} \left[\sum_{i \neq j} u_{ij}^2 + \xi \sum_i u_{ii}^2 + \frac{\lambda}{2\mu} \left(\sum_i u_{ii} \right)^2 \right] \tag{2}$$

While KJ tabulate the elastic constants μ, λ and ξ for the 18 metal crystals (including fcc) considered in their study, they do not give values for the least accessible quantity, l, even though it enters the previous equation through an exponential dependence. The dimensionless parameter, l, depends on the lattice structure and on the elastic constants.

Taking the elastic constants and T_m given in KJ together with equation (1), we find that, although l itself does not vary a great deal, lying between 12 and 17, such a variation is of course significant when appearing in an exponential factor. It is of greater significance, however, to note the presence of the a^3 term in equation (1) which allows the *shape* of the KJ formula for T_m to be expressed in terms of the atomic volume Ω as

$$k_B T_m = \Omega C_e(\mu, \xi, \lambda) \times S_{KJ} \tag{3}$$

Here, S_{KJ} is a purely structure-dependent factor including, not only the term $\exp(-l/3)$, but also the residual dependence on structure in going from a^3 to the volume Ω. The factor C_{e} is simply a combination of the elastic constants.

Turning now to the predictions of BPS, we note that the melting temperature can also be expressed in the form

$$k_{\mathrm{B}}T_{\mathrm{m}} = \Omega G \times S_{\mathrm{B}} \tag{4}$$

where, now, G is the shear modulus and S_{B} is once again, a structure-dependent factor. Thus, both treatments allow us to write the melting temperature as a product of a volume factor and a combination of elastic constants times a lattice structure-dependent factor. The result expressed in equation (4) is in a way not very surprising, as a reduction in the shear modulus is intimately connected with a reduction in the melting temperature.

In their theory of melting as a dislocation-mediated phase transition, BPS also relate the latent heat of fusion to the melting temperature. Combining this relationship together with equation (4) yields the result

$$\frac{L_{\mathrm{m}}}{G\Omega} = \text{constant} \tag{5}$$

Unlike the relations for the melting temperature, there is now no structure-dependent quantity in this equation. Thus, equations (4) and (5) may be taken as predictions arising from dislocation-mediated theories of melting. We now confront these model predictions with the available experimental data.

The values of T_{m}, L_{m}, the atomic volume Ω and the shear modulus values at both the melting temperature (G_{m}) and at room temperature (G_{r}) are given in table 1. Also tabulated are the ratios $k_{\mathrm{B}}T_{\mathrm{m}}/G\Omega$ for both sets of G values. Taking the shear modulus values at melting, this ratio is seen to be approximately constant for the different structures; with a value of about 5 ± 0.4 for most of the fcc elements and $\sim 7 \pm 1$ for the bcc structures. Thus, it would appear that a central result coming

Table 1. Shear modulus, atomic volume and heats of formation, melting temperatures and vacancy formation energies for 13 elements [14–17].

Element	G_{r} (GPa)	G_{m} (GPa)	Ω (A^3)	L_{m} (eV/atom)	T_{m} (K)	$k_{\mathrm{B}}T_{\mathrm{m}}/G_{\mathrm{m}}\Omega$ ($\times 10^{-5}$)	$k_{\mathrm{B}}T_{\mathrm{m}}/G_{\mathrm{r}}\Omega$ ($\times 10^{-5}$)	$E^{\mathrm{f}}_{1\mathrm{v}}$ (eV)	$E^{\mathrm{f}}_{1\mathrm{v}}/G_{\mathrm{m}}\Omega$ ($\times 10^{-4}$)
Al	26.1	14.31	16.61	0.112	934	5.4	3.0	0.67	4.5
Cu	47.7	29.00	11.78	0.136	1357	5.5	3.3	1.28	6.0
Ag	29.8	18.33	17.07	0.118	1235	5.4	3.4	1.11	5.7
Au	28.0	16.05	16.93	0.131	1338	6.8	3.9	0.89	5.2
Ni	85.8	41.77	10.95	0.183	1726	5.2	2.5	1.40	4.9
Pb	8.6	5.75	30.32	0.053	601	4.8	3.2	0.53	4.9
Pd	48.0	37.24	14.71	0.179	1825	4.6	3.6	1.85	5.4
Li	3.85	3.69	21.59	0.048	454	7.9	7.5	0.34	6.8
Na	1.98	1.97	39.33	0.027	371	6.6	6.6		
K	0.9	0.81	75.33	0.025	336	7.6	6.8		
Rb	0.63	0.60	92.66	0.023	312	7.7	7.4		
Cs	0.65	0.39	118.06	0.021	302	9.1	5.4		
Nb	37.6	35.00	18.01	0.279	2741	6.0	5.6	2.48	6.3

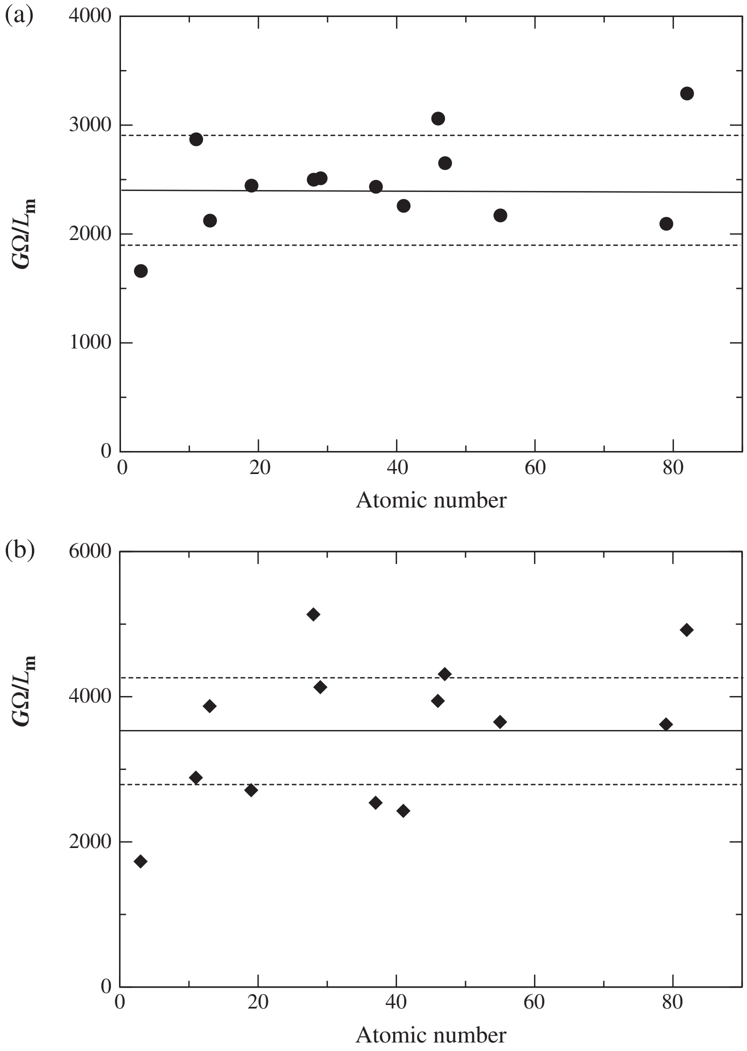

Figure 1. Plot of the ratio $G\Omega/L_{\mathrm{m}}$ *vs*. the atomic number for the 13 elements in table 1 with G at its (a) melting temperature and (b) the room temperature values. The full curve denotes the average value and the dashed lines represent the values to within 20% on either side of the average.

from these theories of melting is in general agreement with the experimental observations within the same degree of accuracy, or better, as the Lindemann rule. To examine the validity of the second prediction, the variation of the ratio $G\Omega/L_{\mathrm{m}}$ with atomic number is displayed in figure 1. With the shear modulus values taken at the melting temperature, this ratio has a range of values which lie in a narrow band, within about 20% of the mean. It may be noted that when the room temperature shear modulus values are used, the variation is much more scattered. Thus, it may be concluded that the prediction that $L_{\mathrm{m}}/G\Omega$ is a constant is correct within the same degree of accuracy as the melting temperature prediction, providing the values of G at melting are used.

3. Other predictions for the melting temperature

Books on materials science have, over decades, recorded beyond reasonable doubt an empirical correlation between the thermal energy at melting, $k_B T_m$, and the monovacancy formation energy, E^f_{1v}. Roughly, the *rule of thumb* used in such discussions is that $E^f_{1v}/k_B T_m \sim 10$. In contrast to the dislocation-mediated phase transition at the heart of the present discussion, with clear implications for the mechanism of melting, point defect correlations have no such underlying mechanism, as there is no experimental evidence for any major build-up of the (small) concentration of monovacancies as the melting temperature T_m is approached. Therefore, first principle discussions of such a correlation between E^f_{1v} and $k_B T_m$ have had recourse to a (assumed) force field. As a specific example, Bhatia and March ([11] (BM) have utilised, for close-packed solids, a pair potential formulation by Minchin *et al.* [12] for E^f_{1v}. Although, the BM discussion is most appropriate for solid Ar and Kr, it does lead to a quite clear cut prediction for the ratio $E^f_{1v}/k_B T_m$. This ratio, they observed, is the sum of two parts, with the first involving the ratio $B\Omega/k_B T_m$ where B is the bulk modulus. A refinement of the aforesaid pair potential treatment by invoking an embedded atom potential led Johnson [13] to predict that for the close-packed metals, E^f_{1v} correlates better with $G\Omega$ than with $B\Omega$. The correlation, resulting from dislocation-mediated theories of melting between $k_B T_m$ and $G\Omega$, through a structure-dependent factor, when combined with Johnson's work on a Cu-like *model metal* yields, for a given structure such as fcc, the relationship $E^f_{1v}/k_B T_m = \text{constant}$; which is found to be in fair accord with the experimental data.

A presumably more refined form for this same ratio, but now in terms of other thermodynamic quantities, and in particular the ratio of the specific heats γ of the liquid near freezing is discussed in the appendix. This results in an equation relating E^f_{1v} to the factor $G\Omega$. In particular, it may be expected that $E^f_{1v}/G\Omega$ is nearly constant. In table 1, we have tabulated this ratio for some of the elements for which the vacancy formation energy data is readily available. The relative constancy of this ratio suggests that the vacancy formation energy is also determined by the factor $G\Omega$.

4. Discussion

The dislocation-mediated melting transition, as advocated in recent studies, leads to the thermal energy $k_B T_m$ being written as a product of atomic volume and a combination of elastic constants, times a factor depending on the lattice structure. This multiplicative factor appears to be 5×10^{-5} for the fcc crystal structures and 7.5×10^{-5} for the bcc structures. In addition, it has been shown that one of the consequences of such theories, namely, the result that the ratio $L_m/G\Omega$ is roughly a constant, is also approximately borne out by the experimental evidence. The empirical relationship between the vacancy formation energy and the melting temperature is manifest in the connection between E^f_{1v} and the factor $G\Omega$; the ratio of which is also found to be roughly a constant. This suggests that the factor $G\Omega$ plays the crucial role in determining not only the melting properties but also the defect formation energies in elemental crystals. All the anisotropy of the crystal is manifest in the value of the quantity, $G\Omega$.

One can understand this by noting that $G\Omega$ is a measure of the energy required to distort the crystal. We therefore put forward the suggestion that it is this distortion that results in the formation of both line defects, such as dislocations (which in turn lead to melting) *and* of point defects. The relationship between $L_{\rm m}$ and $G\Omega$ reinforces this idea as $L_{\rm m}$ is a measure of the energy absorbed by the crystal before the shear modulus drops. Thus, it is reasonable to expect that all three quantities are determined by the ability of the crystal to withstand a shear force. This, in turn, depends on the electron–phonon interactions in a crystal.

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Appendix

Relationship between $E^{\rm f}_{\rm 1v}$ and the thermal energy, $k_{\rm B}T_{\rm m}$, at melting.

One of the authors [18] had earlier related the monovacancy formation energy, $E^{\rm f}_{\rm 1v}$, to departures from Joule's Law. In this appendix, we show how the ratio $E^{\rm f}_{\rm 1v}/k_{\rm B}T_{\rm m}$ can be related to the atomic volume, Ω times an elastic constant.

If E is the internal energy and V is the volume, the departure from Joule's Law, which states that E is independent of V in the dense liquid resulting from melting a close-packed crystal like Ar or Cu can be estimated from the pressure, p, via

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\rm T} = -\left(\frac{\partial E}{\partial V}\right)_{\rm T} + T\left(\frac{\partial S}{\partial V}\right)_{\rm T} \tag{A1}$$

in the usual thermodynamic notation. Using the Maxwell thermodynamic relation

$$\left(\frac{\partial S}{\partial V}\right)_{\mathrm{T}} = \left(\frac{\partial p}{\partial T}\right)_{\mathrm{V}} \tag{A2}$$

in equation (A1) then yields

$$T\left(\frac{\partial p}{\partial T}\right)_{\mathrm{V}} = p + \left(\frac{\partial E}{\partial V}\right)_{\mathrm{T}}. \tag{A3}$$

Employing the well-known formula for the difference of specific heats $c_{\mathrm{p}} - c_{\mathrm{V}}$ in terms of the thermal expansion and compressibility, one is led to

$$c_{\mathrm{p}} - c_{\mathrm{V}} = \rho\left[\frac{p}{\rho k_{\mathrm{B}} T} + \frac{1}{\rho k_{\mathrm{B}} T}\left(\frac{\partial E}{\partial V}\right)_{\mathrm{T}}\right]^2 k_{\mathrm{B}}^2 T K_{\mathrm{T}}. \tag{A4}$$

where ρ is the atomic number density and K_{T} the isothermal compressibility of the liquid. Recalling that for, say, liquid Ar near its triple point, $p \ll \rho k_{\mathrm{B}} T$, one is led to a quantitative expression for the departure from Joule's Law, namely,

$$\frac{1}{\rho k_{\mathrm{B}} T}\left(\frac{\partial E}{\partial V}\right)_{\mathrm{T}} \approx \left(\frac{(\gamma - 1)(c_{\mathrm{V}}/k_{\mathrm{B}})}{S(0)}\right)^{1/2}, \tag{A5}$$

where $\gamma = c_{\mathrm{p}}/c_{\mathrm{V}}$, and K_{T} has been written in terms of the long wavelength limit $S(0)$ of the liquid structure factor $S(q)$, using $S(0) = \rho k_{\mathrm{B}} T K_{\mathrm{T}}$. For liquid Ar near its triple point, $\gamma = 2.2$, $c_{\mathrm{V}}/k_{\mathrm{B}} = 2.3$, $S(0) \approx 0.06$, and the RHS of equation (A5) is ~ 7, confirming the dominance of the term denoting the departure from Joule's Law in this specific example.

We next invoke pair potential theory for the internal energy of the liquid:

$$E = \frac{3}{2} N k_{\mathrm{B}} T + \frac{N\rho}{2}\int g\phi \,\mathrm{d}r \tag{A6}$$

where $g(r)$ is essentially the Fourier transform of $S(q)$ and $\phi(r)$ the (assumed) density-independent pair potential appropriate for Ar, say. From the work of Minchin *et al.* [12], one has

$$E_{1\mathrm{v}}^{\mathrm{f}} = -\frac{\rho}{2}\int g\phi \,\mathrm{d}r - k_{\mathrm{B}} T, \tag{A7}$$

leading to the result

$$\frac{E_{1\mathrm{v}}^{\mathrm{f}}}{k_{\mathrm{B}} T_{\mathrm{m}}} \approx \left(\frac{(\gamma - 1)(c_{\mathrm{V}}/k_{\mathrm{B}})}{S(0)}\right)^{1/2}, \tag{A8}$$

where a term involving $(\partial g/\partial\rho)$ has been omitted since it contributes only a few percent to $E^{\mathrm{f}}_{1\mathrm{v}}$ for Ar and Kr. Inserting the aforesaid data for γ, etc., for Ar used earlier in this appendix, one finds that $E^{\mathrm{f}}_{1\mathrm{v}}/k_{\mathrm{B}}T_{\mathrm{m}}$, in this example, is $\sim$7 , in fair accord with experiment.

In an attempt to transcend pair potential theory, which is appropriate for Ar as discussed previously, but not for transition metals where glue models are needed, one of us [19] used Johnson's embedded atom result to obtain a weaker inequality

$$\frac{E^{\mathrm{f}}_{1\mathrm{v}}}{k_{\mathrm{B}}T_{\mathrm{m}}} \leq \frac{5}{3}\frac{c_{\mathrm{V}}}{k_{\mathrm{B}}}\frac{(\gamma-1)^{1/2}}{\gamma J}\frac{G\Omega}{k_{\mathrm{B}}T_{\mathrm{m}}}, \tag{A9}$$

where J is approximately constant.