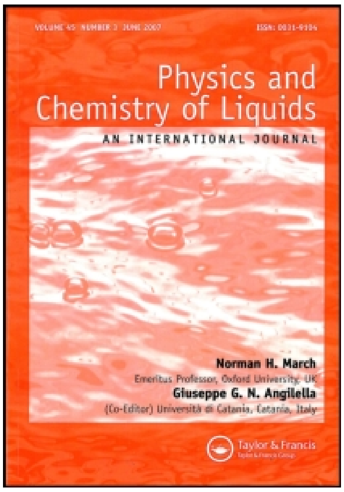

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Review Article

Vacancy Formation Energy, Liquid Structure and Criteria for Liquid–Solid Phase Transitions

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Theoretical models are discussed for close-packed materials which relate vacancy formation energy, Debye temperature and melting temperature. Available theory linking vacancy energy to melting temperature intimately involves the liquid structure at melting. This leads to discussion of three criteria for the solid-liquid phase transition, with particular reference to condensed rare gases. Some directions for further investigation are proposed.

Key words: Vacancy formation energy, Debye temperature, melting temperature, rare gases.

1 INTRODUCTION

Empirical relations between vacancy formation energy E_v, melting temperature T_m, and Debye temperature θ have been known for a long time. Although a fully satisfactory theory of these intimate connections has yet to be supplied, recent progress has proved possible by direct appeal to liquid state properties at the melting point and the aim of this brief article is to review this work.

The outline of the article is as follows. In Section 2 an admittedly oversimplified model, based on electron theory, is used to provide insight into the way the vacancy formation energy E_v may be related to the Debye temperature in close-packed metals. Attention is then focussed in Section 3 on condensed rare gases, both thermodynamics and then liquid state theory being employed to relate E_v approximately to the thermal energy $k_B T_m$ at melting. This leads naturally in Section 4 to the discussion of criteria for solid–liquid phase transitions, with reference specifically to condensed rare gases. A summary is provided in Section 5, where some directions for further investigation are proposed.

2 ELECTRON THEORY MODEL RELATING E_v AND θ FOR CLOSE-PACKED SIMPLE METALS

To motivate the theory outlined below, Table 1 records the way in which E_v for a variety of close-packed metals correlates with the Debye temperature θ, following Mukherjee,[1] Ω being the atomic volume and M the ionic mass.

To gain insight into the origin of this relation, consider an elementary free-electron model of a metal of valence Z. Remove an ion at the origin by the device of placing there a point charge $-Ze$. Electrons will be repelled from this defect and one will consequently find a screened potential energy $V(r)$ describing the vacancy:

$$V(r) = \frac{Ze^2}{r}\exp(-qr), \tag{2.1}$$

where q^{-1} is the Thomas–Fermi screening radius given by $(2\pi/\omega_p)v_f$ with v_f the Fermi velocity and ω_p the electronic plasma frequency $(4\pi\rho_0 e^2/m)^{1/2}$, ρ_0 being the conduction electron density. First-order perturbation theory using plane waves enables one to calculate the change in the sum of the one-electron energies as $\Omega^{-1}\int V(r)\,d\mathbf{r} = (\frac{2}{3})ZE_f$ with E_f the Fermi energy.[2] Plainly, this result, being perturbative, is strictly valid only for low valency Z. One must next account for the fact that in creating a vacancy by removing an atom from the bulk and placing it on the surface, one increases the volume occupied by the

Table 1 Empirical relation between vacancy formation energy E_v and Debye temperature θ (after Mukherjee[1])

Metal	θ(K)	E_v(eV)	$\theta/(E_v/M\Omega^{2/3})^{1/2}$
Cu	245	1.17	32
Ag	225	1.09	32
Au	165	0.94	34
Mg	406	0.89	34
Al	428	0.75	33
Pb	94.5	0.5	33
Pt	229	1.4	37
Ni	441	1.5	33

conduction electrons by the atomic volume Ω, if we neglect atomic relaxation round the vacancy; a useful approximation only in close-packed metals. This reduces the kinetic energy of the conduction electron gas, and one finds, following Fumi,[3] a decrease of $(\frac{2}{5})ZE_f$. Thus, one may write as a first approximation to the vacancy formation energy E_v:

$$E_v = (\tfrac{2}{3} - \tfrac{2}{5})ZE_f = \alpha ZE_f \tag{2.2}$$

where in this model α is simply $(\frac{4}{15})$.

Next one employs a closely related argument to calculate the Debye temperature θ, which for an isotropic solid is related to the velocity of sound v_s by[4]

$$\theta = \frac{v_s}{\Omega^{1/3}}\left(\frac{3}{4\pi}\right)^{1/3}\frac{h}{k_B}. \tag{2.3}$$

One then follows Bohm and Staver[5,6] in deriving v_s by starting from the ionic plasma frequency $(4\pi\rho_i(Ze)^2/M)^{1/2}$, replacing ρ_i by (ρ_0/Z) and, in the resulting expression, screening Z by Fourier transforming Eq. (2.1) to get

$$\frac{4\pi Ze^2}{k^2} \to \frac{4\pi Ze^2}{k^2 + q^2}, \tag{2.4}$$

the electrons this time piling up round the ion of charge Ze to rapidly screen out its Coulomb field. In the long wavelength limit $k \to 0$, Eq. (2.4) means that Z is to be replaced in the ionic plasma frequency, after substituting $\rho_i = (\rho_0/Z)$, by Zk^2/q^2, which converts an ‘optic’ mode into the acoustic mode

$$\omega = v_s k, \tag{2.5}$$

the above argument leading to the result

$$v_s = \left(\frac{Zm}{3M}\right)^{1/2} v_f \tag{2.6}$$

showing that in a metal the velocity of sound is related to the Fermi velocity v_f times a factor of order $(m/M)^{1/2}$.

The final step in relating E_v and θ is to use Eqs (2.2) and (2.6) to eliminate ZE_f, to find

$$\alpha^{-1}E_v = \tfrac{3}{2}Mv_s^2, \tag{2.7}$$

which shows that E_v is basically related to a 'phonon energy' Mv_s^2. Combining Eqs (2.3) and (2.7) leads immediately to the relation exhibited in Table 1:

$$\theta = \frac{\text{constant}}{\Omega^{1/3}} \left(\frac{E_v}{M}\right)^{1/2}. \tag{2.8}$$

To recover the constant correctly in Table I, one could choose α, say, in Eq (2.2) to be $\frac{1}{6}$, rather than $\frac{4}{15}$ given by the above model.

We reiterate that the above argument has related θ and E_v by studying the response of the free electron gas to (i) the repulsive potential (2.1) created by a vacancy and (ii) the attractive potential of a (vibrating) ion. Eliminating the response function between θ and E_v, and thereby some of the free-electron nature of the model, demonstrates the deeper connection of E_v with a phonon energy in Eqs (2.7) and (2.8). To press this latter point, Table 2 records results from non-linear electron theory, for essentially the same model as above, due to Stott *et al.*[7] for valencies from 1 to 5. The main point to be emphasized here is that the first row of this Table shows the non-linear analogue of Eq. (2.2). However, Stott *et al.* correct these results for the self-energy of the charge displaced round the vacancy and for exchange (they find correlation to be minor in this application), these contributions being seen from Table 2 to be large and opposite in sign. Huge cancellation is then seen to occur for polyvalent metals, so that the linear model result E_v/ZE_f = constant is replaced by the non-linear finding that E_v/ZE_f decreases strongly with increasing valency Z, as is quite clear from the final row of Table 2.

To lead into the following section, if we use measured melting temperatures to form $k_B T_m/ZE_f$, this is found to parallel closely, as a function of Z, the variation of E_v/ZE_f in Table 2. Another way of

Table 2 Non-linear electron theory results for vacancy formation energy E_v in units of ZE_f (after Stott *et al.*[7])

	Cu	Mg	Al	Pb	Sb
Change in eigenvalue sum plus kinetic energy change	0.194	0.166	0.156	0.138	0.134
Exchange energy correction	0.153	0.130	0.098	0.096	0.087
Self-energy correction	−0.24	−0.21	−0.22	−0.19	−0.19
E_v/ZE_F	0.11	0.09	0.03	0.04	0.03

N.B. Stott *et al.*[7] estimate errors in last row to range from ±0.04 for Cu to about 0.02 for Sb.

expressing this is to note that Lindemann's law of melting is precisely of the same form, when E_v in Eq. (2.8) is replaced by $k_B T_m$. Therefore, in Section 3 a quite different approach will be introduced, designed to expose such a relation between E_v and T_m in simpler systems than the close-packed metals, namely the condensed rare gases.

3 VACANCY FORMATION ENERGY E_v RELATED TO $k_B T_m$ IN CONDENSED RARE GASES

The writer[8] has recently studied the relation between the vacancy formation energy E_v in crystalline forms of the condensed rare gases and departures from Joule's law in the liquid phase at T_m. This work was, at least in part, motivated by the fact that a hard sphere system, which satisfies Joule's law since $(\partial U/\partial V)_T = 0$, U being the internal energy, is totally inadequate for studying E_v in the hot crystal.

Starting from the well known thermodynamic formula for the difference $c_p - c_v$ of the specific heats:

$$c_p - c_v = -\frac{T}{\rho V}\left(\frac{\partial p}{\partial T}\right)_V^2\left(\frac{\partial V}{\partial p}\right)_T \tag{3.1}$$

it is a straight forward matter to express this in terms of pressure p and $(\partial U/\partial V)_T$ since

$$p = -\left[\frac{\partial}{\partial V}(U - TS)\right]_T = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial p}{\partial T}\right)_V, \tag{3.2}$$

the second step in Eq. (3.2) following from one of Maxwell's thermodynamic relations. Hence Eq. (3.1) becomes

$$\frac{c_p - c_v}{S(0)} = \left\{\frac{p}{\rho k_B T} + \frac{1}{\rho k_B T}\left(\frac{\partial U}{\partial V}\right)_T\right\}^2 k_B \tag{3.3}$$

In order to relate hot solid and liquid properties, which is the basic aim below, it is natural to put $T = T_m$ and noting that $p/\rho k_B T_m \ll 1$ one finds

$$\frac{1}{\rho k_B T_m}\left(\frac{\partial U}{\partial V}\right)_{T_m} = \left[\left\{\frac{c_v(\gamma - 1)}{k_B S(0)}\right\}_{T_m}\right]^{1/2} \tag{3.4}$$

where $\gamma = c_p/c_v$ while $S(0)$ is the long wavelength limit of the liquid structure factor $S(k)$, related via fluctuation theory to the isothermal compressibility $K_T = -1/V(\partial V/\partial p)_T$ appearing in Eq. (3.1) by

$$S(0) = \rho k_B T K_T \tag{3.5}$$

where ρ is the atomic number density in the liquid.

It is striking that the values of the departure from Joule's law represented by Eq. (3.4), namely 9.0, 7.1 and 7.2 using empirical data for Ne, Ar and Kr[9] agree very closely with the experimentally determined ratios $E_v/k_B T_m$ which are respectively 9.3, 7.2 and 7.3. We shall return to this point in Section 4, but let us next link the above thermodynamic treatment with the theory of Bhatia and March,[10] which relates the same ratio $E_v/k_B T_m$ for the condensed rare gases with the Ornstein-Zermike direct correlation function $c(r)$ of the liquid, together with its Fourier transform $\tilde{c}(k)$, at the melting temperature. Their result,[10] based on pair potential theory with neglect of relaxation round the vacancy, takes the form

$$\frac{E_v}{k_B T_m} = \tfrac{1}{2}[\tilde{c}(k=0) - c(r=0) - 3]_{T_m}. \tag{3.6}$$

Noting that in the Percus-Yevick solution for hard spheres

$$c_{\mathrm{PY}}^{hs}(r=0) - \tilde{c}_{\mathrm{PY}}^{hs}(k=0) = -1 \tag{3.7}$$

it is again clear that the ratio $E_v/k_B T_m$ must reflect very directly departures from Joule's law.[8,9] An alternative way of writing Eq. (3.6) is to utilize Eq. (3.5) together with the identity

$$\tilde{c}(k) = \frac{S(k) - 1}{S(k)} \tag{3.8}$$

which follows directly by Fourier transform of the Ornstein-Zernike definition of the direct correlation function $c(r)$, when Eq. (3.6) reads

$$\frac{E_v + \frac{1}{2}B\Omega}{k_B T_m} = -\tfrac{1}{2}\{c(r=0)\}_{T_m} - 1, \tag{3.9}$$

with $B = (K_T)^{-1}$ written for the bulk modulus. If one uses the Percus-Yevick hard sphere result

$$c_{\mathrm{PY}}^{hs}(r=0) = -\frac{(1+2\eta)^2}{(1-\eta)^4} \tag{3.10}$$

where η is the packing fraction $(\pi/6)\rho\sigma^3$, with σ the hard sphere diameter, together with the empirical fact that at T_m, $\eta \simeq 0.45$, then it follows that the right-hand side of Eq. (3.9) is indeed a large number ~ 20 as required by experiment. As in Mukherjee's relation (2.8), together with Eq. (2.3), for close-packed metals, E_v and $B\Omega$ are again related, but now via liquid structure and melting temperature. Bernasconi and the writer[11] have utilized experimental diffraction data on some fifteen liquids near the melting temperature T_m to confirm that $\{c(r=0)\}_{T_m}$ is usefully approximated by Eq. (3.10) with $\eta \sim 0.45$, whereas it is $\tilde{c}(k = 0)$ which is very poorly correlated with the hard sphere prediction in Eq. (3.7).

These intimate connections between E_v, $B\Omega$ and $k_B T_m$, displayed directly in this and the previous section, prompt us to conclude this review by comparing and contrasting criteria for solid–liquid phase transitions. More specifically we shall do this in the following section for the condensed rare gases while the possible relevance of these criteria for other classes of condensed matter will be briefly referred to in Section 5.

4 CRITERIA FOR SOLID–LIQUID PHASE TRANSITIONS

Of long-standing is Lindemann's criterion which states that crystals will melt when the root mean square amplitude of atomic vibration reaches a fixed fraction of the lattice spacing.

Subsequently, a criterion for freezing emerged from the work of Verlet[12] on liquids described by Lennard–Jones pair interactions. This is now often referred to as the Verlet criterion, which states that simple liquids such as Ar will freeze when the principal peak of the liquid structure factor reaches a height of about 2.8. Some first-principles justification of this is afforded by the density wave theory of freezing due to Ramakrishnan and Yussouff.[13]

These two criteria, one for melting and the other for freezing, have been shown by Bhatia and March[14] to be intimately related by the property of the pair function $g(r)$ of a dense liquid that

$$g(r = 0) = 0 \tag{4.1}$$

This relation (4.1) leads to the approximate relation[14]

$$S(q_m) = \text{constant}\,\frac{q_m}{\Delta q};\ \text{constant} \simeq \tfrac{3}{8} \tag{4.2}$$

for the principal peak height, at position q_m, of the static structure factor $S(q)$ in terms of the peak width $2\Delta q$ defined precisely as the distance between the two adjacent nodes of $S(q) - 1$ which embrace the peak position q_m.

Bhatia and March[14] estimate similarly that

$$\frac{q_m}{\Delta q} \sim \frac{r_m}{\Delta r} \tag{4.3}$$

with entirely parallel definitions of r_m and Δr from the pair function $[g(r) - 1]$. For example, for liquid Ar at 85 K the left-hand side of Eq.

(4.3) is 7.2 while the right-hand-side is 6.7. Using the Verlet criterion for freezing, namely $S(q_m) = 2.8$ at $T = T_m$ one estimates that $(\Delta r/r_m)_{T_m} \sim 0.11$. But Lindemann's law of melting, according to Faber,[15] gives $(\Delta r/R_A)_{T_m} \sim 0.2$, where R_A is the mean interatomic spacing given by $\rho = 3/(4\pi R_A^3)$ and Δr is identified with the root mean square displacement of the atoms. Since $r_m \simeq 1.8R_A$, these results are roughly consistent. There is no conflict therefore between $S(q_m)_{T_m} = 2.8$ on the one hand and Lindemann's law on the other.

We turn then to the third criterion, stemming from the success of the study reported in Section 3 of the relation between departures from Joule's law and the vacancy formation energy in the condensed rare gases. This makes it attractive to propose a further criterion for a solid–liquid phase transition in these materials. We shall formulate this as follows. When the internal energy, E_v, in the hot crystal, required to create a localized hole in the lattice with volume increase equal to one atomic volume becomes equal to the increase in internal energy needed to expand the liquid by this atomic volume, at the same temperature T_m, namely $U(N\Omega + \Omega) - U(N\Omega) = \Omega(\partial U/\partial V)_{T_m}$, then the solid–liquid phase transition will occur.

It was demonstrated in Section 3 that $E_v/(k_B T_m) = (\Omega/k_B T_m)(\partial U/\partial V)_{T_m}$, confirming the usefulness of the above criterion for the condensed rare gases.

While the criteria of Lindemann for melting, and of Verlet for freezing, appear to involve in each case knowledge of the properties of only one phase (see, however Ref. 14), the third criterion proposed above does have the merit that it directly invokes explicit properties of the two phases involved. We shall see, however, in the following section, that it must only be applied to a restricted class of materials; and, at best, only to those crystals where atomic relaxation round the vacant site can be neglected.

5 SUMMARY AND DIRECTIONS FOR FURTHER WORK

In this review, theoretical models have been employed to exhibit intimate relations between the vacancy formation energy E_v, the Debye temperature θ and the melting temperature T_m, as required by experiment. Not altogether surprisingly, liquid structure figures prominently in existing theory relating E_v to T_m, as in Eq. (3.4) where the long wavelength limit $S(0)$ appears in the formula for $(1/(\rho k_B T_m))(\partial U/\partial V)_{T_m} = E_v/(k_B T_m)$ for condensed rare gases, or in the result (3.6) of Bhatia and the writer[10] for the same systems.

That such relations must not be applied non-critically is already quite clear by work on metals. Equation (3.6), for instance, rests on the use of the mean spherical approximation of liquid state theory which, while very valuable in Ar say, is a very poor approximation in liquid metals.[15] Furthermore, the equating of Eq. (3.4) to $E_v/(k_B T_m)$ is crucially dependent on the absence of lattice relaxation round the vacancy, and is therefore quite inappropriate for the open body-centred-cubic alkali metals, where relaxation energy is a dominant term in the calculation of E_v.[16]

This prompts the question as to whether the introduction of the vacancy formation volume Ω_v into the theory will again allow E_v in the hot crystals to be linked directly with departures from Joule's law in the liquid for a much wider class of materials. This is tempting because it is known that for Schottky defects in the alkali halides, the vacancy formation volumes reflect major relaxation effects.[17–19] Yet there is still an intimate relation between the formation energy of a Schottky defect and the melting temperature in these materials; the so-called Barr–Dawson–Lidiard relation. A little further from the main theme of this article, but relevant in the sense of involving the theory of a liquid in a periodic potential, is the relation in the fluorites between the formation energy of a Frenkel defect and the superionic transition temperature.[20,21] Further studies on these Coulomb systems seem very worthwhile in the light of the progress reviewed here on monatomic metals and condensed rare gases.

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