Thermodynamic theory of size dependence of melting temperature in metals

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The way that small particles melt is a crucial element in the construction of a thermodynamic treatment of the relation between particle size and melting temperature. There are indications that melting is initiated at the surface and that the solid–liquid interface sweeps rapidly through the solid at the melting temperature. The formal and physical elements of the indicated nucleation and growth criterion for melting are discussed and the existence of upper and lower limits on the melting temperature is outlined. Theoretical predictions show satisfactory agreement with experimental observations.

THE effect of particle size on melting temperature has promoted explicit theoretical discussions since the early 1900s and extensive experimental investigations have been reported. The qualitative experimental features are fairly simple —a monotonic decrease in melting temperature with decreasing particle size[2][16], this variation seems to be more substantial in the lower end of the size spectrum than in the 'large' size regime[5-13,15,16].

Previous theories have considered the solid–liquid–vapour mutual equilibrium[17] (actually a size-dependent triple point[18-20]) as the chemical equilibrium condition for a solid sphere embedded in bulk liquid[18] (this, however, is related to the classical supercooling problem rather than to the melting of small particles), chemical equilibrium between solid and liquid spheres of identical radius[19]. In a later theory the 'thermodynamic melting temperature' was defined as that of Pawlow[17] (although this is not necessarily the actual transformation temperature)[21]. Several of these and other works[4][10][19] have considered solid–liquid contact to be a central point: the favoured liquid skin theory considers chemical equilibrium between a finite liquid layer and the surrounded solid at the melting temperature[4,5,7,9]. Unfortunately, no physical criterion has emerged by which to determine the liquid thickness; this quantity (assumed constant) and the solid–liquid interfacial tension are determined by fitting the theoretical expression to experimental results.

In view of these problems associated with previous treatments of the size-dependence of melting temperature we have reconsidered the problem, and we present a thermodynamic theory of the relation between particle size and melting temperature.

Size dependence of melting temperature

Unlike in bulk systems, in small particles the mode of melting is a crucial element for the construction of a thermodynamic theory of melting. The size-dependence of intensive parameters in these systems requires that the geometry and extent of both phases be determined at the melting temperature. Consequently, it is imperative to consider the question of the mechanism of melting in general, and of small particles in particular.

First, note the essential asymmetry between melting and freezing— substantial liquid supercoolings are normal, whereas there is no significant superheating in solids. There is evidence that this lack of superheating is a surface-related effect[22-24]; additional support for the important role of the surface in initiating melting is provided by kinetic studies of superheating[25,26], low-energy

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electron diffraction (LEED) studies of surface melting and freezing of (Pb, Bi and Sn) single crystal surfaces[27] and neutron scattering experiments indicating the absence of any bulk phenomena associated with melting in Al to within 10^{-1}K of the melting temperature[28]. Moreover, molecular dynamics simulations of melting in small clusters of (rare gas) atoms indicate quite unambiguously that the transition is initiated at the surface[29-31]. Finally, the fact that liquid metals wet the parent solid, energetically favours the initiation of melting at the surface[23].

Evidently, at the melting temperature a liquid layer is formed on the surface and moves at a substantial rate into the solid. It is these nucleation and growth characteristics of the melting phenomenon that may be used to construct a thermodynamic theory of the size-dependence of melting temperature.

The (closed, constant total volume) system considered is an isolated one-component collection of non-contiguous metal spheres at a uniform temperature and individually in mechanical equilibrium, resting on a non-interacting substrate. There are no dissociated species, no evaporation occurs during melting and gravitational effects are assumed negligible. Additionally, the difference between surface stress and surface free energy per unit area[32] is neglected.

It is useful to recognise that a size-dependent absolute lower limit on the melting temperature exists. Neglecting the small vapour free-energy change this temperature, T_{lb}, is defined by the condition that the Helmholtz free energy difference between the final, entirely liquid, and initial, entirely solid, particles vanishes. The Helmholtz potential is appropriate as there is a pressure discontinuity associated with the melting of small particles. In equation (1) the subscripts s and l refer to solid and liquid; σ, areal surface work, r, particle radius; v, atomic volume; T_0, bulk melting temperature; and l_0 latent heat, whence neglecting all but first order terms

$$T_{lb} = T_0\left\{1 - \frac{3}{l_0}\left[\frac{v_s\sigma_s}{r_s} - \frac{v_l\sigma_l}{r_l}\right]\right\}$$ (1)

Although T_{lb} has been discussed as the two-state melting temperature[7,9,34] it cannot be the actual melting temperature unless the mechanism by which the final state is attained is irrelevant (that is, in the limit of vanishing particle size).

The melting mode, and consequently the actual melting temperature, involves the formation of a liquid layer and a criterion to determine its spontaneous growth to consume the solid. The derivation and formal analysis of the Helmholtz free energy difference ΔF_i between a core of solid surrounded by a concentric liquid layer and an entirely solid particle is thus complemented by the development of a melting criterion; their combined use leads directly to a quantitative estimate of the relation between particle size and melting temperature and, finally, to a comparison with experimental results. For brevity and simplicity we reproduce the principal features of the results of this energetic analysis by considering (where appropriate) only first-order terms. The superscript prime denotes quantities of the combined (solid–liquid) system. Those of the entirely solid system have no superscript. Pressure, temperature, chemical potential, number of atoms, volume and area are respectively, P, T, μ, N, V, A. The double subscript sl denotes quantities of the solid–liquid interface. Matter conservation is assumed between the solid and liquid states. Formally, ΔF_1 is given by

$$\Delta F_i = -P_s' V_s' + P_s V_s - P_l' V_l + (\mu_s' - \mu_s)N_s' +$$
$$+ (\mu_s' - \mu_s)N_l' + \sigma_{sl}A_{sl} + \sigma_l A_l - \sigma_s A_s \qquad (2)$$

Explicit integration of the relevant Gibbs–Duhem relations provides a lengthy and analytically intractable expression for ΔF_i (ref. 1). Fortunately there are two simplifying approximations which retain all essential physical insight of the problem and provide an expression amenable to formal qualitative investigation: the liquid and solid atomic volumes are taken to be identical ($v_s = v_l \equiv v$) and both of these phases are assumed incompressible. These approximations yield the following expression

$$\Delta F_i = \frac{l_o(T_0 - T)}{T_0} \times \frac{4}{3}\frac{\pi}{v}[r^3 - (r-t)^3] +$$
$$+ \sigma_{sl}4\pi(r-t)^2 + (\sigma_l - \sigma_s)4\pi r^2 \qquad (3)$$

where r denotes the initial solid (and here, final liquid) radius and t the liquid thickness. This function may be shown to have a stationary value (σ_{sl}, σ_l and σ_s are here approximated as size-independent) with respect to t (or, here, N_l) at constant temperature, when

$$\frac{l_0}{T_0}(T_0 - T) = \frac{2\sigma_{sl}v}{(r-t)} \qquad (4)$$

This is simply the condition that the solid core has the same chemical potential as the surrounding liquid layer. For $\sigma_{sl} < 0$, physical solutions of this relation demand that $t > r$ and $T > T_0$. The extremum of equation (4) is then a maximum

$$\frac{1}{8\pi}\left(\frac{\delta^2 \Delta F_i}{\delta t^2}\right)_r = -\sigma_{sl} \qquad (5)$$

and thus, equation (4) defines an unstable chemical equilibrium. An approximate upper limit, T_{ub}, on the melting temperature may be inferred from the condition $\delta\Delta F_i/\delta N_l)_T > 0$ for vanishing t

$$T_{ub} = T_0\left(1 = \frac{2\sigma_{sl}v}{l_0 r}\right). \qquad (6)$$

Below T_0 the transformation of solid to liquid is favoured by the surface term (due to the wetting condition) and retarded due to the volume (latent heat) term. This is the converse of the classical nucleation problem and is consistent with the surface-induced nature of melting[35].

If the non-wetting condition $\sigma_s > \sigma_l + \sigma_s$ is obeyed, the possibility of superheating exists; the condition $T < T_0$ restores the latent heat as the driving force for melting. It seems that a theory of the size-dependence of solid superheating analogous to the melting theory is possible. This explanation and such a theory relate to Peppiatt's experiments[22].

The Helmholtz free energy difference, ΔF_i, required to form a liquid layer on and from the completely solid particle is a maximum at the critical liquid thickness, t_c, defined by equation (4). In nucleation theory the probability of attaining this critical fluctuation will determine the speed of movement of the solid–liquid interface into the solid. A formal relation between temperature, the critical Helmholtz energy fluctuation ΔF_c and a measure, J, of this rate of movement is given by

$$J = C\exp[-\Delta F/kT] \qquad (7)$$

where the pre-exponential factor C is only mildly temperature dependent and is taken as constant[35] and equal to that calculated by Stowell[36]. The critical melting fluctuation ΔF_c, is formally given here by equation (3) evaluated at the chemical potential equality condition of equation (4). The various dependences (calculated, estimated or measured) of quantities needed to determine correction terms to the first-order expression quoted here are discussed in detail elsewhere[1].

Comparison of theory with experiment

A comparison of the predictions of this theory with experimental results is given in Figs 1–3. Sn, In and Au were chosen because these
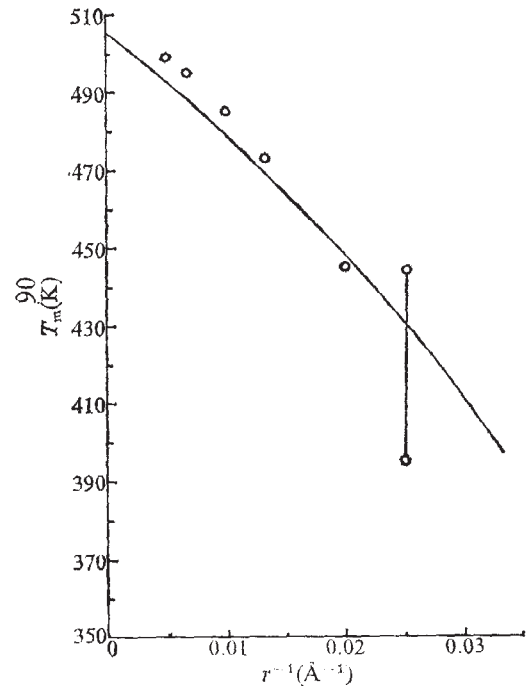

Fig. 1 Relation between melting temperature (T_m) and reciprocal particle radius (r^{-1}) for tin. $-$, Calculated; $\bigcirc$, experimental. The latter were obtained directly or by interpolation from Wronski[5] and are (except at $r^{-1} = 0.025\,\text{Å}^{-1}$) midway between the experimental scatter. The scatter increases as particle size decreases and consequently is largest (and mostly unavoidable) at smallest r. At $r^{-1} = 0.025\,\text{Å}^{-1}$ the apparent upper and lower values of T_m are illustrated. The solid curve represents the results of the calculation using equations (3, 4 and 7).
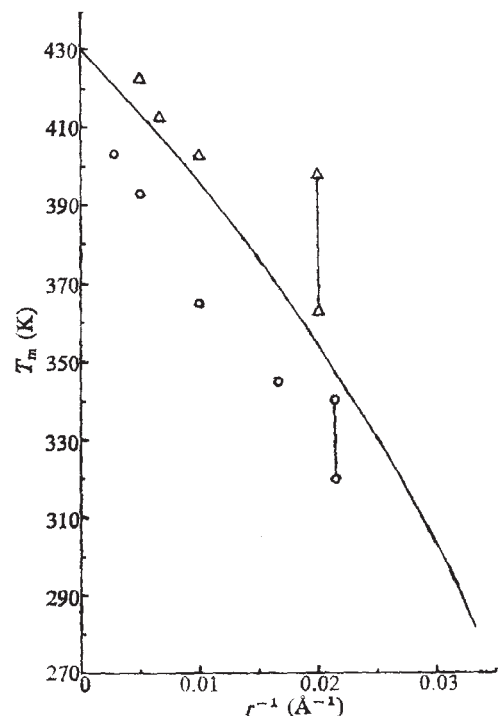

Fig. 2 Relation between melting temperature (T_m) and reciprocal particle radius (r^{-1}) for indium. $-$, Calculated; $\bigcirc$, experimental (Pócza, Barna and Barna[13]); $\triangle$, (Berman and Curzon[11]). The points are taken directly from Pócza *et al.* and directly or by interpolation from Berman and Curzon. The scatter in the small size regime is illustrated for Berman and Curzon's data; the error bars reported by Pócza *et al.* for small r are likewise given. The solid curve represents the results of the calculation using equations (3, 4 and 7).
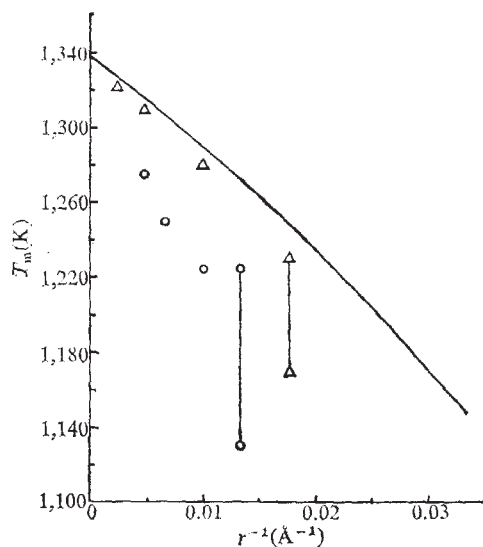
Fig. 3 Relation between melting temperature (T_m) and reciprocal particle radius (r^{-1}) for gold. −, Calculated; △, experimental (Sambles[10]); ○, (Buffat and Borel[16]). Data obtained and treated as for Fig. 1.

were the only metals with both a sufficient number of surface parameters available (latent heats and heat capacities are relatively well documented) to allow theoretical calculations and a sufficient number of experimental results to allow a significant comparison between theory and experiment. The qualitative agreement is good. Further, the quantitative agreement is satisfactory in view of the approximations involved in the theory, the known lack of precision (and accuracy) in some of the quantities and their variation and the difficulty in obtaining accurate melting temperature and size measurements over such a large range. Actually, the only surface parameter we used which had any substantial experimental disagreement is σ_{sl}. We have used values consistent with the strong evidence that its direct determination from grain boundary grooving measurements[37] yields a significantly larger value than that inferred from supercooling measurements—the latter give a lower limit to σ_{sl}.

These calculations indicate that the critical liquid thickness (t_c) is not constant for each metal[4,5,7,9] but decreases monotonically with decreasing particle size.

Conclusion

The thermodynamic theory of the size-dependence of melting temperature outlined here seems to provide a satisfactory and physically acceptable explanation of the phenomenon and is in reasonable agreement with experimental observations. Although other treatments have implied that solid-liquid interface movement is important in the transition[4-9,15,19] (Tammann[38] was the first to suggest that melting is a surface phenomenon) none has sought to explore the surface nucleation and liquid layer growth characteristics of melting in order to provide a formal treatment of the size-dependence of melting temperature.

One expected and important feature of melting in small systems that this treatment predicts is the 'smearing out' of the transition as particle size decreases. This effect stems from the basic (nucleation and growth) characteristics of the melting phenomenon although its predicted extent is minimal; and the transition is predicted as extremely sharp down to very small particle size. ($< \sim 1$ K even at the small end of the size spectrum.)

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Corrected age of the Pliocene/Pleistocene boundary

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Calcareous plankton datum-events are referred to the Pliocene/Pleistocene boundary at Le Castella, the stratotype Calabrian at Santa Maria di Catanzaro, and to deep-sea sediments in six piston cores. The boundary is correlated by multiple overlapping criteria to a level equivalent to, or slightly younger than, the top of the Olduvai Event, giving a revised estimate of about 1.6 Myr for the age of the boundary. The Pliocene/Pleistocene boundary is thus coeval with the earliest of four major climatic deteriorations in the Pleistocene, reconciling palaeoclimatic concepts with the chronostratigtaphical definition of the epoch.

ESTIMATES of the age of the Pliocene/Pleistocene boundary have varied from about 0.6 Myr[1] to >4 Myr[2,3]. The absence of reliable palaeomagnetic measurements on the stratotype of the Calabrian at Santa Maria di Catanzaro[4] and the boundary-stratotype section at Le Castella[5,6] in southern Italy has prevented direct correlation with the palaeomagnetic polarity 'scale'. Over the last decade biostratigraphical studies on the critical sections in southern Italy and also on palaeomagnetically-dated deep-sea cores have resulted in essentially two estimates for the age of the boundary: 1.6–1.8 Myr, by association with the Olduvai Event[7-11] and 2.8 Myr, by association with the Kaena Event[4,12 14]. Those who agree with the younger date have generally believed that the base of the Calabrian, as defined at Santa Maria di Catanzaro[15], was stratigraphically equivalent to the 'marker-bed' at Le Castella[16]; these workers have