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Homogeneous Nucleation and the Temperature Dependence of the Crystal-Melt Interfacial Tension

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I. Introduction

When David Turnbull started his work on the undercooling of metallic melts in the late 1940s, one of his most distinguished colleagues at the General Electric Research Laboratory in Schenectady, New York, was greatly skeptical about the likelihood of success—and not without reason. The density and bonding of crystal and melt were known to be quite similar, and many regarded the melt as a highly defective crystal or a dynamic assembly of crystallites. The crystal-melt interface, unlike the crystal-vapor or liquid-vapor interfaces, therefore did not appear to be

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the major discontinuity required for an effective barrier against crystal nucleation. In fact, Turnbull's colleague was so persuaded by these factors that he promised to eat his hat if the melt of a simple metal such as copper could be undercooled more than a few degrees. David Turnbull took this as a challenge, and in a few weeks demonstrated major undercooling of a large number of such melts. At the next group meeting his colleague walked in with a headpiece made of cheese.

These experiments, which culminated in the classic demonstration of homogeneous crystal nucleation in mercury and a set of measurements of its isothermal kinetics,[1] were the basis of two fundamental insights into the structure of liquids: (1) it is fundamentally different from that of simple crystals and (2) it orders substantially near a crystal surface, with the resulting entropy decrease being the main contribution to the crystal-melt interfacial tension (or excess interfacial free energy[2]).

An important suggestion on the first point, directly inspired by Turnbull's results, was made by Frank,[3] who pointed out that the *short-range* energy minimization in a monatomic system favors icosahedral coordination shells. The fivefold symmetry and the predominance of fairly perfect tetrahedral configurations of the arrangement are incompatible with the simple close-packed lattices (face-centered cubic, hexagonal close-packed) that minimize the *overall* volume and energy.

The essential polytetrahedral nature of simple liquids and the ubiquity of fivefold symmetrical local order were confirmed in the analysis of physical models, such as the dense random packing of hard spheres[4] or computer-generated ones,[5] and formed the basis of a formal description of the liquid state in which a four-dimensional perfect polytetrahedral polytope is mapped onto three-dimensional Euclidean space by the introduction of disclination lines.[6]

The study of the structure and properties of the crystal-melt interface

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[1] D. Turnbull, *J. Chem. Phys.* **20**, 411 (1952).

[2] The identification of interfacial tension, which is defined mechanically, with the excess interfacial free energy is strictly only valid for fluid-fluid interfaces. For the crystal-melt interface, where one of the phases is solid and can sustain an elastic strain, the mechanical definition leads to the introduction of an interface *stress* [see Ref. 35 and J. W. Cahn, *Acta Metall.* **28**, 1333 (1980)]. In this paper the two phases will be assumed incompressible, so that the interface stress need not be considered.

[3] F. C. Frank, *Proc. Roy. Soc. London* **A215**, 43 (1952).

[4] J. D. Bernal, *Proc. Roy. Soc. London* **A280**, 299 (1964).

[5] For a review, see F. Yonezawa in *Solid State Physics* (H. Ehrenreich and D. Turnbull, eds.), Vol. 45, p. 179, Academic Press, New York (1991).

[6] For a review, see D. R. Nelson and F. Spaepen, in *Solid State Physics* (H. Ehrenreich and D. Turnbull, eds.), Vol. 42, p. 1, Academic Press, New York (1989).

is difficult for a number of reasons.[7] First, direct structural probes, which have been extremely successful in the study of crystal-vapor and, to a lesser degree, liquid-vapor interfaces, are as yet not available. Second, the development of structural models has long suffered from the incomplete understanding of the liquid structure.

In early models, therefore, the specifics of the liquid structure were mostly ignored. Some of those models were similar to those for intercrystalline boundaries (grain boundaries) in that their interfacial tension originates from the excess energy associated with a substantial density deficit or, equivalently, bond breaking.[8] Other authors made the analogy with the crystal-vapor interfaces[9] and used Ising models to predict interface roughening.[10]

The crystal-melt interface, however, is intrinsically different from an intercrystalline boundary. In the latter, all atomic positions are strongly correlated by one or the other of the two adjacent crystals. High-resolution microscopy shows that the two crystals extend right up to a clear dividing surface, and that all atoms can unambiguously be assigned to one or the other crystal (with an occasional shared one). This causes a substantial density deficit.[11] The positional correlations in the liquid phase, however, are not as strong as in a crystal. As a result, the atoms in the crystal-melt interface can adjust their position to the strong correlations imposed by the crystal on one side to minimize the density deficit. This leads to increased ordering of the liquid as the crystal is approached.

David Turnbull[12] first pointed out that the entropy loss associated with this ordering is the origin of the large crystal-melt interfacial tension (or excess interfacial free energy), which creates the barrier to crystal nucleation and allows sizable undercooling. As discussed in detail later (see Fig. 4), he noted that the entropy must rise more slowly than the enthalpy with distance away from the crystal surface.

Since then structural models that take proper account of the nature of the liquid state, such as static physical models,[13–17] in which the transition

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[7] A review of the early experimental work, modeling, and applications is given by D. P. Woodruff, *The Solid-Liquid Interface*, Cambridge University Press, Cambridge, UK (1973).

[8] A. D. Skapski, *Acta Metall.* **4**, 576 (1956).

[9] W. K. Burton, N. Cabrera, and F. C. Frank, *Phil. Trans. Roy. Soc.* **A243**, 299 (1951).

[10] K. A. Jackson, in *Growth and Perfection of Crystals* (R. H. Doremus, B. W. Roberts, and D. Turnbull, eds.), p. 319, Wiley, New York (1958).

[11] H. J. Frost, M. F. Ashby, and F. Spaepen, *Scripta Metall.* **14**, 1051 (1980).

[12] D. Turnbull, in *Physics of Non-Crystalline Solids* (J. A. Prins, ed.), p. 41, North-Holland, Amsterdam (1964).

[13] F. Spaepen, *Acta Metall.* **23**, 729 (1975).

[14] F. Spaepen and R. B. Meyer, *Scripta Metall.* **10**, 257 (1976).

from crystal to melt is accomplished by enforcing a polytetrahedral structure, analytic models,[18–26] and molecular dynamics simulations,[26–31] have confirmed Turnbull's view of the interface.

The neg-entropic nature of the crystal-melt interface must be reflected in the temperature dependence of the interfacial tension, and hence also in that of the frequency of homogeneous nucleation. Turnbull's original paper[1] already points out that the interfacial tension must increase with temperature if the atomic jump frequency is to have a physically reasonable value. Although the temperature coefficient indeed has a sign that appears to agree qualitatively with the entropy loss, it has thus far not been linked quantitatively to the structural models.

Part of the difficulty is that most of the models provide thermodynamic information on the equilibrium state (i.e., for flat interfaces), whereas the interfacial tension derived from homogeneous nucleation experiments is obtained under strongly nonequilibrium conditions (i.e., for curved interfaces). In this chapter, the temperature dependence of the interfacial tension under both conditions is reviewed. Considerable literature is available on flat and curved interfaces, going all the way back to Gibbs.[32,33] A simple model for the curved interface,[34] based on Turnbull's

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[15] D. R. Nelson and F. Spaepen, in *Solid State Physics* (H. Ehrenreich and D. Turnbull, eds.), Vol. 42, p. 190, Academic Press, New York (1989).

[16] A. Bonnissent, J. L. Finney, and B. Mutaftschiev, *Phil. Mag.* **B42**, 233 (1980).

[17] C. V. Thompson, Ph.D. Thesis, Harvard University (1981).

[18] W. A. Curtin, *Phys. Rev. Lett.* **59**, 1228 (1978).

[19] W. E. McMullen and D. W. Oxtoby, *J. Chem. Phys.* **88**, 1967 (1988).

[20] D. W. Oxtoby, in "Fundamentals of Inhomogeneous Fluids" (D. Henderson, ed.), p. 407, Marcel Dekker, New York (1992).

[21] A. D. J. Haymet and D. W. Oxtoby, *J. Chem. Phys.* **74**, 2559 (1981).

[22] D. W. Oxtoby and A. D. J. Haymet, *J. Chem. Phys.* **76**, 6262 (1982).

[23] B. B. Laird and A. D. J. Haymet, *J. Chem. Phys.* **91**, 3638 (1989).

[24] S. M. Moore and H. J. Raveche, *J. Chem. Phys.* **85**, 6039 (1986).

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[26] J. H. Sikkenk, J. O. Indekeu, J. M. J. van Leeuwen, and E. O. Vossnack, *Phys. Rev. Lett.* **59**, 98 (1987).

[27] J. Q. Broughton and F. F. Abraham, *J. Chem. Phys. Lett.* **71**, 456 (1980).

[28] J. Q. Broughton, A. Bonnissent, and F. F. Abraham, *J. Chem. Phys.* **74**, 4029 (1981).

[29] J. Q. Broughton and G. H. Gilmer, *J. Chem. Phys.* **84**, 5741; 5749; 5759 (1986).

[30] E. Burke, J. Q. Broughton, and G. H. Gilmer, *J. Chem. Phys.* **89**, 1030 (1988).

[31] W.-J. Ma, J. R. Banavar, and J. Koplik, *J. Chem. Phys.* **97**, 485 (1992).

[32] J. W. Gibbs, *The Scientific Papers of J. Willard Gibbs*, Dover, New York (1961).

[33] An excellent review of the thermodynamics of flat and curved surfaces can be found in J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity*, Oxford Clarendon Press, New York (1982).

[34] F. Spaepen, in *Proc. Int. Workshop on Containerless Processing of Metals—Undercooling and Solidification* (I. Egry and J. Laakmann, eds.), p. 22, DLR-Mitteilung 89-15, Deutsche Forschungsanstalt für Luft- und Raumfahrt, Köln, Germany (1989).

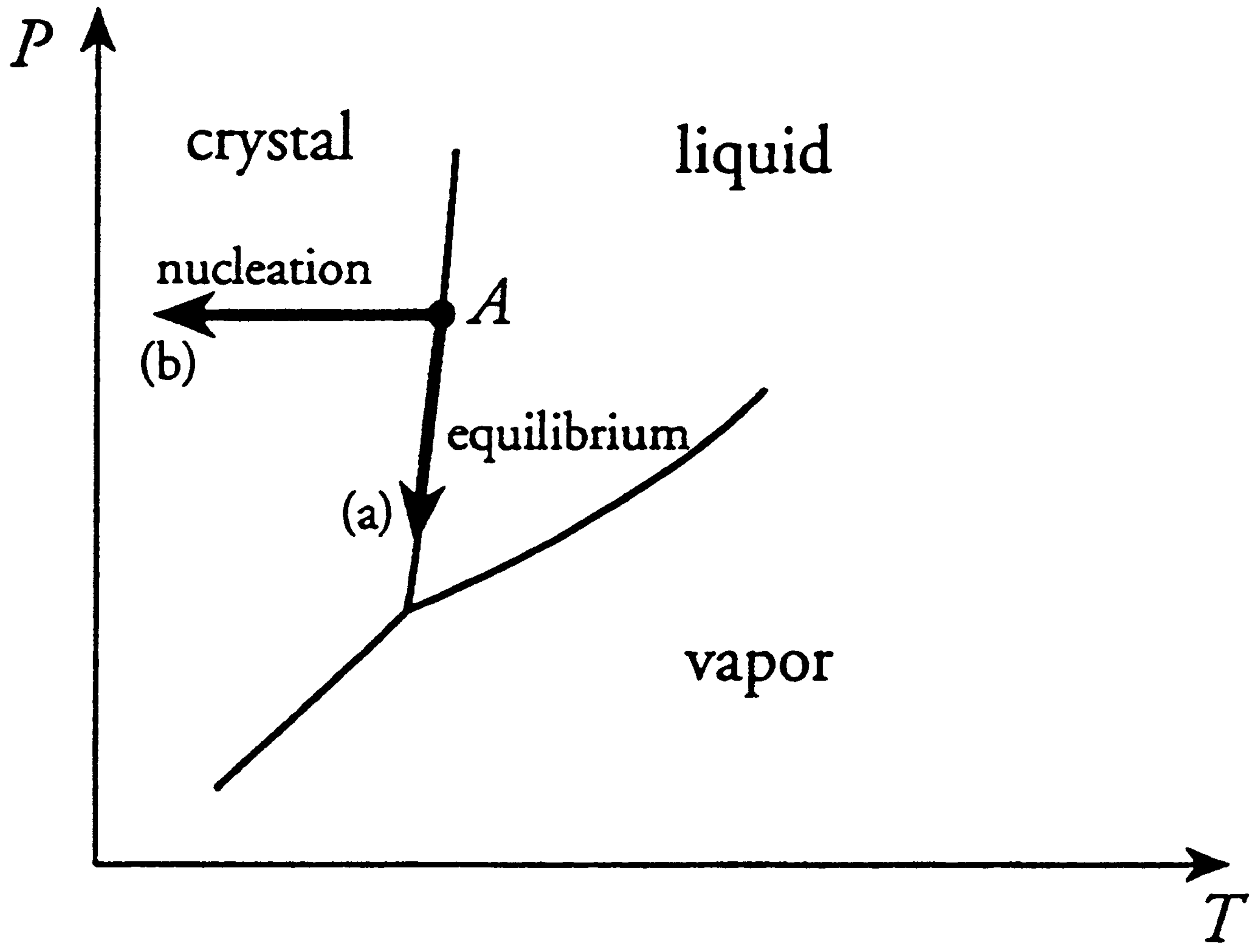

FIG. 1. Schematic phase diagram of a single component system. The change of the interfacial tension with temperature can be considered in equilibrium [path (a)] or in an undercooled melt, as in nucleation experiments [path (b)].

original proposal for the interfacial structure, is introduced, and its thermodynamic properties are related to the nucleation data.

II. The Equilibrium Interface

1. TEMPERATURE DEPENDENCE OF THE INTERFACIAL TENSION: EXCESS INTERFACIAL ENTROPY

The thermodynamic properties of an interface between two phases in equilibrium (e.g., point A on Fig. 1, the phase diagram for a single component system) have been described definitively by Gibbs.[32] The following discussion is based on Cahn's particularly clear exposition of Gibbs's approach.[35] For simplicity, only the single component system is considered.

Consider a system consisting of N moles distributed between two phases, α and β, in equilibrium, separated by an interface with area A. Equilibrium dictates that the interface be flat. The Gibbs free energy of the total system (including the interface) is:

$$G = U - TS + pV, \tag{1.1}$$

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[35] J. W. Cahn, in *Interfacial Segregation* (W. C. Johnson and J. M. Blakeley, eds.), pp. 3-23, ASM, Metals Park, OH (1979).

where U, S, and V are, respectively, the total energy, entropy, and volume of the system. The Gibbs free energy of the two phases without the interface is:

$$G_b = \mu N, \tag{1.2}$$

where μ is the chemical potential (the same in both phases in equilibrium). The interfacial tension[2] σ can then be defined as the excess free energy, per unit area, in the system due to the presence of the interface, or:

$$\sigma A = U - TS + pV - \mu N. \tag{1.3}$$

Differentiating gives:

$$\sigma dA + A d\sigma = dU - TdS - SdT + pdV + Vdp - \mu dN - Nd\mu. \tag{1.4}$$

Since σdA is the force–times–distance work done by the interfacial tension when the area is increased by dA, the combination of the first and second laws of thermodynamics gives:

$$dU = TdS - pdV + \mu dN + \sigma dA. \tag{1.5}$$

Combination of Eqs. (1.4) and (1.5) gives:

$$A d\sigma = -SdT + Vdp - Nd\mu. \tag{1.6}$$

For each of the two bulk phases a similar relation, the Gibbs-Duhem equation, holds:

$$0 = -S^{\alpha} dT + V^{\alpha} dp - N^{\alpha} d\mu, \tag{1.7}$$

$$0 = -S^{\beta} dT + V^{\beta} dp - N^{\beta} d\mu. \tag{1.8}$$

The assignment of the atoms to the two phases requires the placement of a dividing surface, which at this point is arbitrary. The only condition that must hold is, obviously:

$$N^{\alpha} + N^{\beta} = N. \tag{1.9}$$

The temperature dependence of the interfacial tension is found by solving the system of three equations [Eqs. (1.6), (1.7), and (1.8)] and three unknowns (dT, dp, and $d\mu$). Following Cahn, this is most conveniently done with Cramer's rule from linear algebra:

$$A d\sigma = -\frac{\begin{vmatrix} S & V & N \\ S^\alpha & V^\alpha & N^\alpha \\ S^\beta & V^\beta & N^\beta \end{vmatrix}}{\begin{vmatrix} V^\alpha & N^\alpha \\ V^\beta & N^\beta \end{vmatrix}} dT. \tag{1.10}$$

At this point, it is convenient to choose the position of the dividing surface such that the excess volume associated with the interface is zero (Fig. 2), or:

$$N^\alpha v^\alpha + N^\beta v^\beta = V^\alpha + V^\beta = V, \tag{1.11}$$

where v^α and v^β are the molar volumes of the two bulk phases. Subtraction of the lower two rows from the top one in the determinant in the numerator of Eq. (1.10) then makes two of the elements equal to zero [see Eq. (1.9) and (1.11)] and leads directly to the solution:

$$\frac{d\sigma}{dT} = -S_{ex}, \tag{1.12}$$

where

$$S_{ex} = \frac{1}{A}(S - S^\alpha - S^\beta) \tag{1.13}$$

is the excess entropy, per unit area, associated with the interface (Fig. 2).

It is important to keep in mind that Eq. (1.12) only holds in *equilibrium,* where the variation dT must be accompanied by *a variation in pressure, dp, along the coexistence line* [path (a) in Fig. 1]. It *cannot,* therefore, be applied, as many authors have done[14,36,37] to undercooling experiments, where the external pressure is kept constant [path (b) in Fig. 1]. In that case, only unstable equilibrium at a curved surface can be established, and a different analysis must be made.

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[36] Y. Miyazawa and G. M. Pound, *J. Cryst. Growth* **23,** 45 (1974).

[37] G. R. Wood and A. G. Walton, *J. Appl. Phys.* **41,** 3027 (1970).

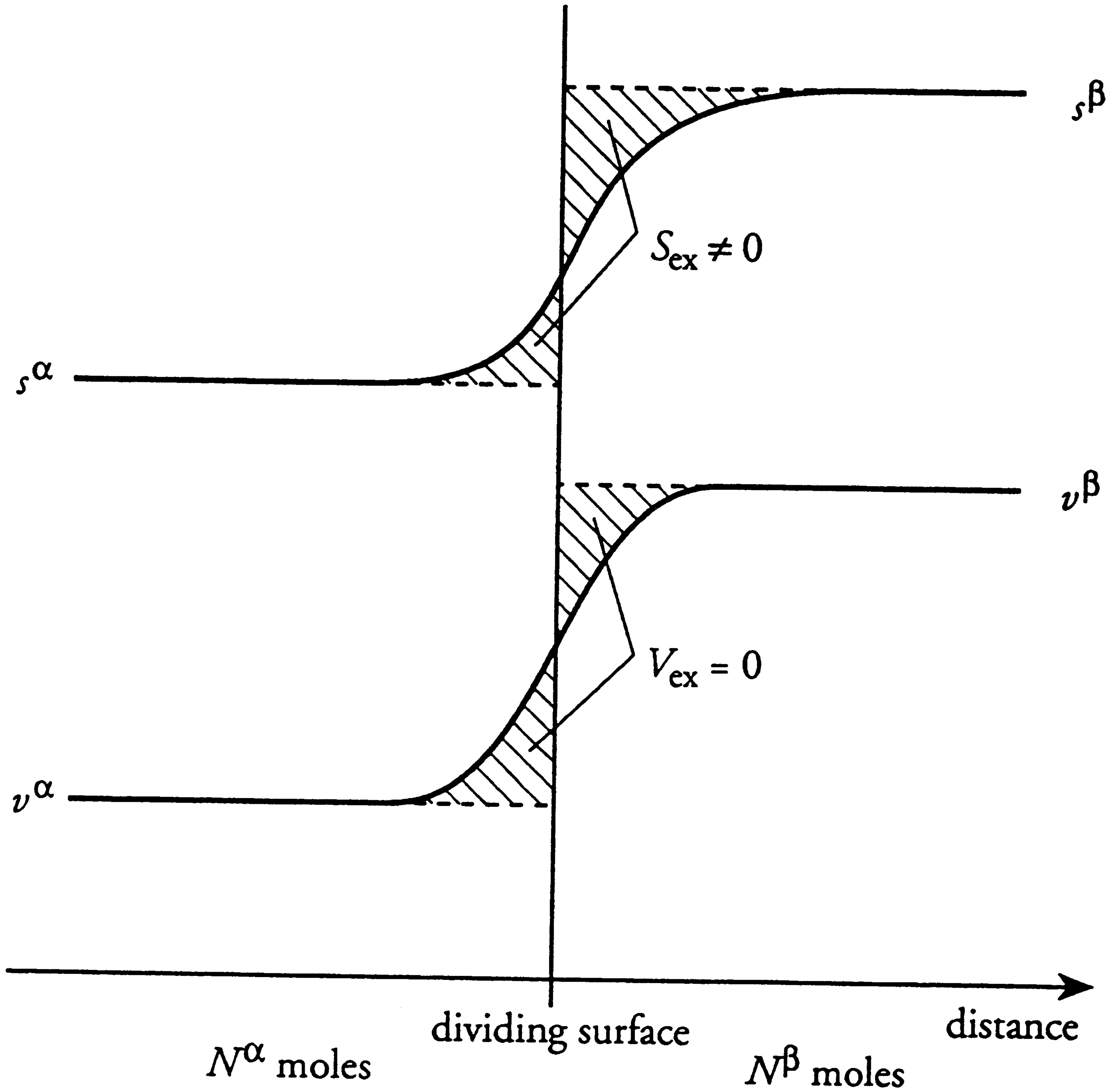

FIG. 2. Schematic diagram of the variation of the molar volume v and the molar entropy s across an interface in equilibrium. The superscripts refer to the values in the bulk phases. If the (negative) excess interfacial entropy, $-S_{ex}$, is to be equal to the temperature coefficient of the interfacial tension, the dividing surface must be chosen to give zero excess volume.

III. The Interface in an Undercooled Melt

2. THE INFINITELY THIN INTERFACE

If, in the Gibbsian sense, abstraction is made of the interfacial structure and the interface is reduced to a mathematically two-dimensional surface with interfacial tension σ separating a crystal and melt with bulk properties, the (unstable) equilibrium condition at a curved surface is established as follows.

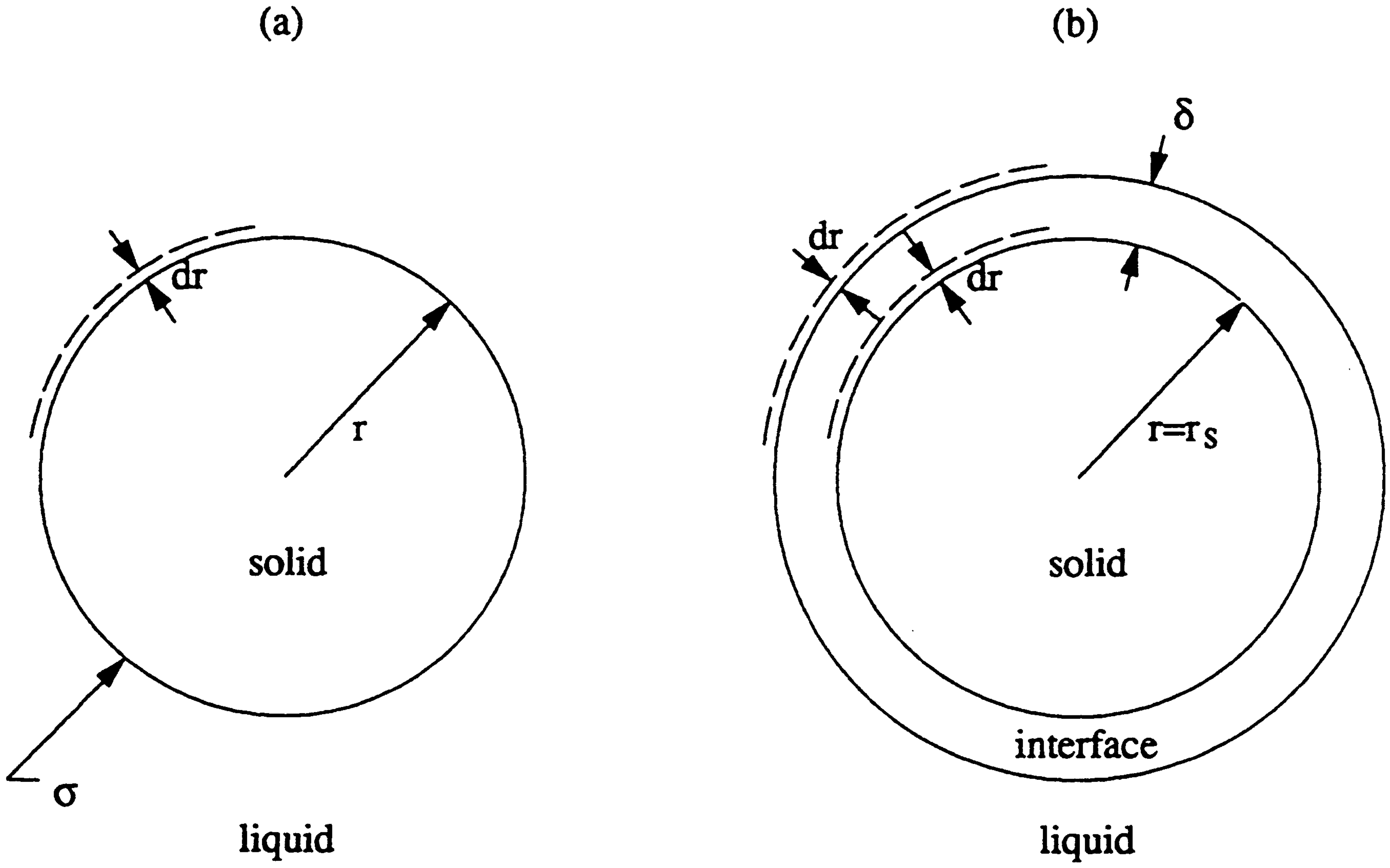

FIG. 3. Schematic diagram illustrating unstable equilibrium of a spherical crystal (solid) in an undercooled melt (liquid) with (a) an infinitely thin interface and (b) a physical interface of width δ.

Consider the case of a single-component, incompressible, spherical, and isotropic crystal of radius r, surrounded by its melt [Fig. 3(a)]. The work required to form this crystal from the melt is[32,38]:

$$W_G = \frac{4\pi r^3}{3}\Delta G_{sl} + 4\pi r^2 \sigma, \tag{2.1}$$

where ΔG_{sl} is the difference in Gibbs free energy, per unit volume of the crystal, between the bulk crystal (solid) and its undercooled melt (liquid).

The condition for equilibrium is that W_G be at an extremum for a variation dr of the radius:

$$\frac{dW_G}{dr} = 4\pi r^2 \Delta G_{sl} + 8\pi r \sigma = 0. \tag{2.2}$$

This gives the condition for the radius of curvature:

$$r_G^* = -\frac{2\sigma}{\Delta G_{sl}}. \tag{2.3}$$

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[38] D. Turnbull, in *Solid State Physics* (F. Seitz and D. Turnbull, eds.), Vol. 3, p. 225, Academic Press, New York (1956).

The work to form the crystal in (unstable) equilibrium is then

$$W_G^* = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G_{sl}^2}. \tag{2.4}$$

We will return to the question of the location of the interface after the discussion of the physical interface of finite width. This requires first a brief review of its structure.

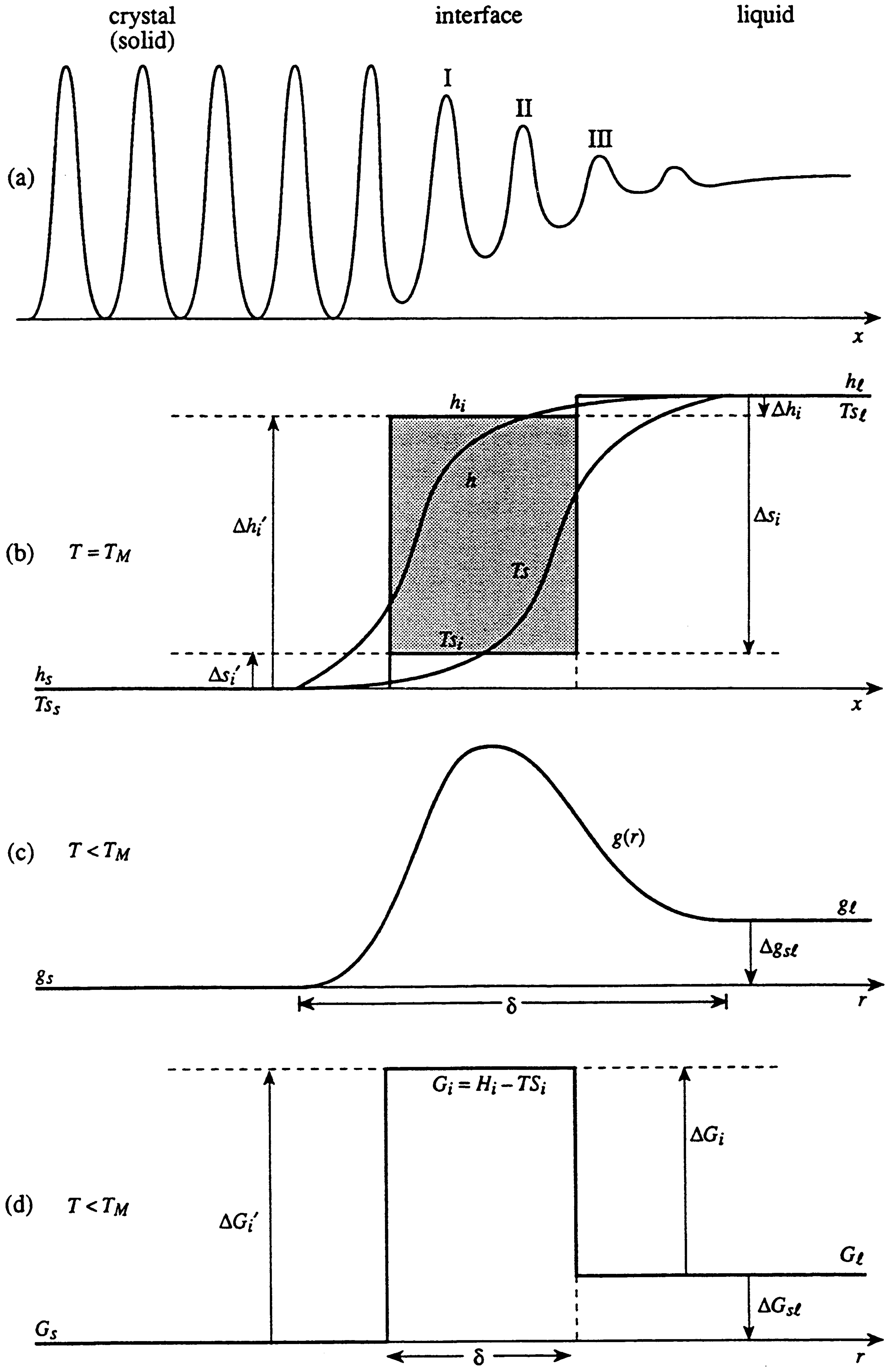
3. STRUCTURE AND PROPERTIES OF THE PHYSICAL INTERFACE

Physical modeling,[13–17] analytic studies,[18–25] and computer simulation[26–31] of the crystal-melt interface in simple systems (hard sphere, Lennard-Jones, or metallic) produce atomic density profiles that are all qualitatively similar to the one sketched in Fig. 4(a). The interface has a thickness on the order of a few interatomic distances and consists of atoms that are localized, to a degree that depends on the distance from the crystal, in layers parallel to the interface.

Note that the apparent width of the interface in simulations of the interface is an upper limit of the intrinsic transition width of interest here. This is due to the formation of crystal terraces, which have only a slight effect on the thermodynamics of the interface. The intrinsic width is more clearly identifiable in static physical modeling, where the planarity of the crystal can be enforced.

Since the structure of the interfacial layers is different from that of the two bulk phases, the enthalpy and entropy in the interface are different from their bulk values in the two phases as well. For example, the localization makes the entropy lower than in the bulk liquid. If the interface had a substantial density deficit, as in a grain boundary, its enthalpy could be higher than that of both bulk phases. If, as is found in most structural models, the density deficit is small, the interfacial enthalpy is expected to be intermediate between the two bulk values.

FIG. 4. Schematic illustration of the variation of the structure and thermodynamic properties of the crystal-melt interface with distance across the interface: (a) average atomic density; (b) atomic enthalpy and entropy, in equilibrium at the melting temperature T_M; the horizontal lines correspond to the interfacial enthalpy h_i and entropy s_i in the approximate model of a uniform interface; (c) free energy per atom below the melting temperature (crystal in an undercooled melt); r is the distance from the center of the crystal (solid); and (d) the free energy per unit volume for the uniform interface below the melting temperature.


crystal (solid)
interface
liquid
I
II
III
(a)
x
h_ℓ
h_i
Δh_i
Ts_ℓ
$\Delta h_i'$
h
Δs_i
(b) $T = T_M$
Ts
Ts_i
h_s
$\Delta s_i'$
Ts_s
x
(c) $T < T_M$
$g(r)$
g_ℓ
$\Delta g_{s\ell}$
g_s
δ
r
$G_i = H_i - TS_i$
ΔG_i
(d) $T < T_M$
$\Delta G_i'$
G_ℓ
$\Delta G_{s\ell}$
G_s
δ
r

We should emphasize from the outset that the description of the interface as a region with its own thermodynamic parameters does *not* imply that it is being treated as a separate phase.[39] It can only exist between the two bulk phases, and its thermodynamic parameters only have meaning as transition parameters between the bulk values. The approach developed next has, in fact, the same basis as that of the so-called "quasi-" or "local" thermodynamic methods used for the study of interfaces.[33]

Figure 4(b) shows a plausible variation of the entropy and enthalpy, per atom, as a function of position through the interface between the two phases in equilibrium (the bulk free energies, $g_s = h_s - T_M s_s$ and $g_l = h_l - T_M s_l$, are equal and have been made equal to zero). The interfacial tension is proportional to the area between the two curves (normalized by the atomic volume). As Turnbull first pointed out,[12] for the interfacial tension to be positive, and hence for the undercooling of liquids to be possible, the entropy in the interface must rise more slowly with distance from the crystal than the enthalpy.

4. INTERFACIAL TENSION OF THE PHYSICAL INTERFACE

The arguments of Section 2 can be repeated for a spherical crystal with a full interface of thickness δ [see Fig. 3(b)], if the variation of the free energy, per atom, in the radial direction, $g(r)$, is known, as sketched in Fig. 4(c). The approach is similar to that of Cahn and Hilliard for the formation of nuclei with a diffuse interface[40] and has been outlined in an earlier publication.[34] Again, it is assumed that the system has one component, and that the crystal and interface are isotropic and incompressible.

The work W required to create a crystal of radius r_s in the liquid is then the sum of the work to form concentric spherical shells of the crystal and the interface:

$$W(r_s) = \int_0^\infty [g(r) - g_l] \frac{4\pi r^2}{\Omega(r)} dr, \tag{4.1}$$

where $\Omega(r)$ is the local atomic volume and

$$\begin{aligned} g(r) &= g_s && \text{for } r \leq r_s, \\ g(r) & && \text{for } r_s \leq r \leq r_s + \delta, \\ g(r) &= g_l && \text{for } r_s + \delta \leq r, \end{aligned} \tag{4.2}$$

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[39] E. A. Guggenheim, *Thermodynamics*, North-Holland, Amsterdam (1967).

[40] J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **31**, 688 (1959).

where g_s and g_l are the free energies, per atom, of the crystal and the liquid, respectively.

The radius of the crystal in (unstable) equilibrium with the melt, r_s^*, is again obtained by requiring that W be an extremum for a variation of r_s [see Fig. 3(b)]:

$$\left.\frac{dW}{dr_s}\right|_{r_s^*} = 0. \tag{4.3}$$

Inserting r_s^* into Eq. (4.1) gives the work needed to create the crystal in equilibrium with the melt:

$$W^* = W(r_s^*). \tag{4.4}$$

This work is now equated to W_G^* of Eq. (2.1), the work required to form a crystal in equilibrium with its melt through a Gibbsian dividing surface, for the same difference in free energy between the bulk phases, ΔG_{sl}:

$$W^* = \frac{16\pi}{3}\frac{\sigma^3}{\Delta G_{sl}^2}. \tag{4.5}$$

Since W^* has been calculated from the properties of the interface, and ΔG_{sl} is known from the bulk thermodynamics of the two phases, Eq. (4.5) is in fact a *definition* of the interfacial tension, or:

$$\sigma = \left(\frac{3}{16\pi}\Delta G_{sl}^2 W^*\right)^{1/3}. \tag{4.6}$$

The interfacial tension defined this way is also the one obtained from homogeneous nnucleation, since the critical work measured in those experiments is precisely that of Eq. (4.5).

Finally, the position of the Gibbsian dividing surface, r_G^*, for the particular interface model used in the calculations is found by substituting the known value of σ [Eq. (4.6)] and of ΔG_{sl} into Eq. (2.3). As shown in Appendix A, the position of r_G^* is such that the excess free energy, computed spherically, with respect to that dividing surface equals σA_G^*, where A_G^* is the area of the dividing surface and σ is given by Eq. (4.6).

In Appendix B explicit formulas are given for σ and r_G^* in terms of the moments of the free energy $g(r)$. The method is actually most clearly illustrated by working out a simple example, as shown in the next section.

5. A SIMPLE MODEL: THE UNIFORM INTERFACE

a. *Calculation of the Interfacial Tension at Constant Temperature*

The interface model under consideration in this section has the following properties [see Figs. 4(b) and 4(d)]: (1) The interface has a thickness δ; (2) the entropy and enthalpy, and hence the free energy are uniform throughout the interface; (3) the entire system—crystal, liquid, and interface—is incompressible; and (4) all atoms in the system have the same atomic volume.

Properties (1) and (2) are the essential features of the model. Assumption (3) is a common, and quite accurate one for condensed phases; it is essential for the formulation of the work according to Eqs. (2.1) and (4.1); it also obviates the need to consider the interface stress[2] and effects of pressure. Assumption (4) is made for computational convenience; it, too, applies fairly accurately to the bulk crystal and liquid phases, as well as to the interface, which has a low density deficit.

The quantities used for the computation of the interfacial tension are indicated on Fig. 4(d). The G_s and G_l represent, respectively, the free energies per unit volume of the crystal and the liquid. Their difference, $\Delta G_{sl} = G_s - G_l$, is negative below the melting temperature. The H_i, S_i, and $G_i = H_i - TS_i$ represent, respectively, the enthalpy, entropy, and free energy per unit volume in the interface. Two additional free energy differences can be defined. On the liquid side, $\Delta G_i = G_i - G_l$; and on the solid side, $\Delta G_i' = G_i - G_s$. For the interface to be stable, both of these quantities must be positive. It is useful to remember that $\Delta G_i' = \Delta G_i - \Delta G_{sl}$.

In equilibrium, $T = T_M$ and $\Delta G_{sl} = 0$, so that $\Delta G_i = \Delta G_i'$. The interfacial tension is then simply

$$\sigma = \delta \Delta G_i. \tag{5.1}$$

In the following, T_M, ΔG_i, and $\Delta G_i'$ are different, and σ must be a symmetrical function of both of them. The method outlined in the previous section is now used to determine that function.

The work required to create the crystal and the interface in the undercooled liquid is, from Eq. (4.1) or by inspection,

$$W = \frac{4\pi r_s^3}{3}\Delta G_{sl} + \frac{4\pi}{3}[(r_s + \delta)^3 - r_s^3]\Delta G_i. \tag{5.2}$$

This can be simplified by introducing a dimensionless measure for the driving free energy:

$$a = \frac{\Delta G_{sl}}{\Delta G_i}, \tag{5.3}$$

which is a negative quantity. Equation (5.2) then becomes:

$$W = \frac{4\pi}{3} \Delta G_i (a r_s^3 + 3 r_s^2 \delta + 3 r_s \delta^2 + \delta^3). \tag{5.4}$$

The condition that establishes the equilibrium radius, $dW/dr_s = 0$ [Eq. (4.3)], becomes:

$$a r_s^2 + 2 r_s \delta + \delta^2 = 0. \tag{5.5}$$

The equilibrium radius is then:

$$r_s^* = -\frac{\delta}{a}(1 + \sqrt{1 - a}), \tag{5.6}$$

which by introduction of

$$b^2 = 1 - a, \tag{5.7}$$

simplifies to

$$r_s^* = -\frac{\delta}{1 - b}, \tag{5.8}$$

Note that the length scale of the problem is set by the thickness of the interface δ—the only length introduced into the model.

The work required to form the equilibrium crystal and its interface is now obtained from Eq. (4.4), i.e., by substitution of Eq. (5.8) into (5.4):

$$W^* = \frac{4\pi}{3} \Delta G_i \delta^3 \frac{b^2}{(1 - b)^2}. \tag{5.9}$$

The interfacial tension is then obtained from Eq. (4.6):

$$\sigma^3 = \frac{1}{4} \delta^3 \Delta G_i^3 \left(\frac{ab}{1 - b} \right)^2. \tag{5.10}$$

This can be put in a more transparent form by eliminating a and b using their definitions of Eqs. (5.3) and (5.7):

$$\sigma = \delta(\Delta G_i \cdot \Delta G_i' \cdot \Delta G_{i,\mathrm{ave}})^{1/3}, \tag{5.11}$$

where

$$\begin{aligned} \Delta G_{i,\mathrm{ave}} &= \frac{1}{4}[(\Delta G_i)^{1/2} + (\Delta G_i')^{1/2}]^2 \\ &= \frac{1}{2}\left[\frac{1}{2}(\Delta G_i + \Delta G_i') + (\Delta G_i \cdot \Delta G_i')^{1/2}\right]. \end{aligned} \tag{5.12}$$

Note that the last form of this expression states that $\Delta G_{i,\mathrm{ave}}$ is the arithmetic average of the arithmetic and geometric averages of ΔG_i and $\Delta G_i'$. Equations (5.11) and (5.12) also have the desired symmetry between the solid and liquid side.

b. *Temperature Dependence of the Interfacial Tension*

To apply Eq. (5.11) at different temperatures, the model must be specified further. For example, the following, quite plausible additional assumptions suffice: (1) The interface thickness δ is independent of temperature; (2) the difference between the enthalpy or entropy of the interface (both per unit volume) and its respective value in the bulk *liquid,* $\Delta H_i = H_i - S_l$ or $\Delta S_i = S_i - S_l$, is independent of temperature; and (3) the difference in specific heat between the liquid and crystal is zero; as a result, the enthalpy of fusion, $\Delta H_f = H_l - H_s$ (positive) and entropy of fusion $\Delta S_f = S_l - S_s$ (positive) are independent of temperature, and $\Delta G_{sl} = \Delta S_f(T - T_M)$.

With these assumptions, numerical computation of $\sigma(T)$ from Eqs. (5.11) and (5.12) is straightforward. For application and generalization, it is useful to have an expression in dimensionless form. The obvious dimensionless variables are:

$$\begin{aligned} \tilde{\sigma} &= \sigma/(\lambda T_M \Delta S_f), \\ \tilde{h} &= \Delta H_i/\Delta H_f, \\ \tilde{s} &= \Delta S_{i/\Delta} S_f, \\ \tilde{T} &= T/T_M, \\ \tilde{\delta} &= \delta/\lambda, \end{aligned} \tag{5.13}$$

where λ is an atomic dimension, for example, $(V/N)^{1/3}$ (where V = molar volume and N = Avogadro's number). Keeping in mind that $T_M \Delta S_f = \Delta H_f$, and $\Delta G_i' = \Delta G_i - \Delta G_{sl}$ [see Fig. 4(d)], Eqs. (5.11) and (5.12) yield:

$$\tilde{\sigma} = \tilde{\delta} \left\{ (\tilde{h} - \tilde{T}\tilde{s}) \cdot (\tilde{h} - \tilde{T}\tilde{s} - \tilde{T} + 1) \cdot \frac{1}{4} [(\tilde{h} - \tilde{T}\tilde{s})^{1/2} + (\tilde{h} - \tilde{T}\tilde{s} - \tilde{T} + 1)^{1/2}]^2 \right\}^{1/3} . \tag{5.14}$$

Of the assumptions made here, (2) is the essential one: It reflects the idea that the interfacial tension originates from the accommodation of the liquid structure to the structural constraint posed by the crystal plane. An alternative assumption, of constant differences in enthalpy and entropy between the interface and the *crystal*, $\Delta H_i'$ and $\Delta S_i'$, would be based on considering the interface as a disordered crystal. Assumption (3) can easily be modified if specific heat data are available, and (2) could then be adjusted so that ΔS_i would be, for example, a constant fraction of ΔS_f. Keep in mind that the changes in ΔH_i and ΔS_i with temperature are linked through the interface specific heat, and therefore cannot be varied independently. Assumption (2) used here, for example, is consistent with the interface specific heat being zero.

A similar model has recently been proposed by Gránásy.[41] It is essentially a special case of the one discussed earlier, in that the interfacial entropy and enthalpy are kept at, respectively, the bulk liquid and crystalline values. The interfacial width δ then needs to be adjustable and can no longer simply be related to structural models of the interface as is done below.

6. The Simple Model at Low Undercooling

The quickest insight into the problem is found by introducing the further simplification of low undercooling. A treatment of the entire problem under these conditions is very brief, and has been published elsewhere.[42] The simplification of the preceding results proceeds as follows.

At low undercooling, i.e., for $T \lesssim T_M$, $|\Delta G_{sl}| \ll G_i$ and $\Delta G_i' \cong \Delta G_i$. Since the geometric and arithmetic averages in Eqs. (5.11) and (5.12) are

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[41] L. Gránásy, *J. Non-Crystalline Solids,* **162,** 301 (1993).

[42] F. Spaepen, *Mat. Sci. Eng. A,* **178,** 15 (1994).

the same to first order in their difference, ΔG_{sl}, Eq. (5.11) depends simply on the arithmetic average:

$$\sigma = \delta \frac{1}{2}(\Delta G_i + \Delta G_i'), \tag{6.1}$$

or

$$\sigma = \delta\left(\Delta G_i - \frac{1}{2}\Delta G_{sl}\right), \tag{6.2}$$

or, in dimensionless form,

$$\tilde{\sigma} = \tilde{\delta}\left(\tilde{h} - \tilde{T}\tilde{s} - \frac{\tilde{T}}{2} + \frac{1}{2}\right). \tag{6.3}$$

This is illustrated in the lower part of Fig. 5. Keeping in mind that

$$\frac{\partial \Delta G_i}{\partial T} = -\Delta S_i \quad \text{and} \quad \frac{\partial \Delta G_{sl}}{\partial T} = -\Delta S_f, \tag{6.4}$$

the temperature coefficient at low undercooling is easily found:

$$\frac{d\sigma}{dT} = -\delta(\Delta S_i + \frac{1}{2}\Delta S_f), \tag{6.5}$$

or, in dimensionless form, directly from Eq. (6.3):

$$\frac{d\tilde{\sigma}}{d\tilde{T}} = -\tilde{\delta}\left(\tilde{s} + \frac{1}{2}\right). \tag{6.6}$$

The location of the Gibbsian dividing surface, defined by Eq. (2.3), can also be easily found under these conditions. Keeping in mind the definition of the dimensionless driving force a [Eq. (5.3)], Eq. (6.2) gives:

$$r_G^* \equiv -\frac{2\sigma}{\Delta G_{sl}} = -2\delta\left(\frac{\Delta G_i}{\Delta G_{sl}} + 1\right) = \delta\left(-\frac{2}{a} + 1\right). \tag{6.7}$$

Expansion of the expression for the radius of the solid [Eq. (5.6)] to first order in a gives:

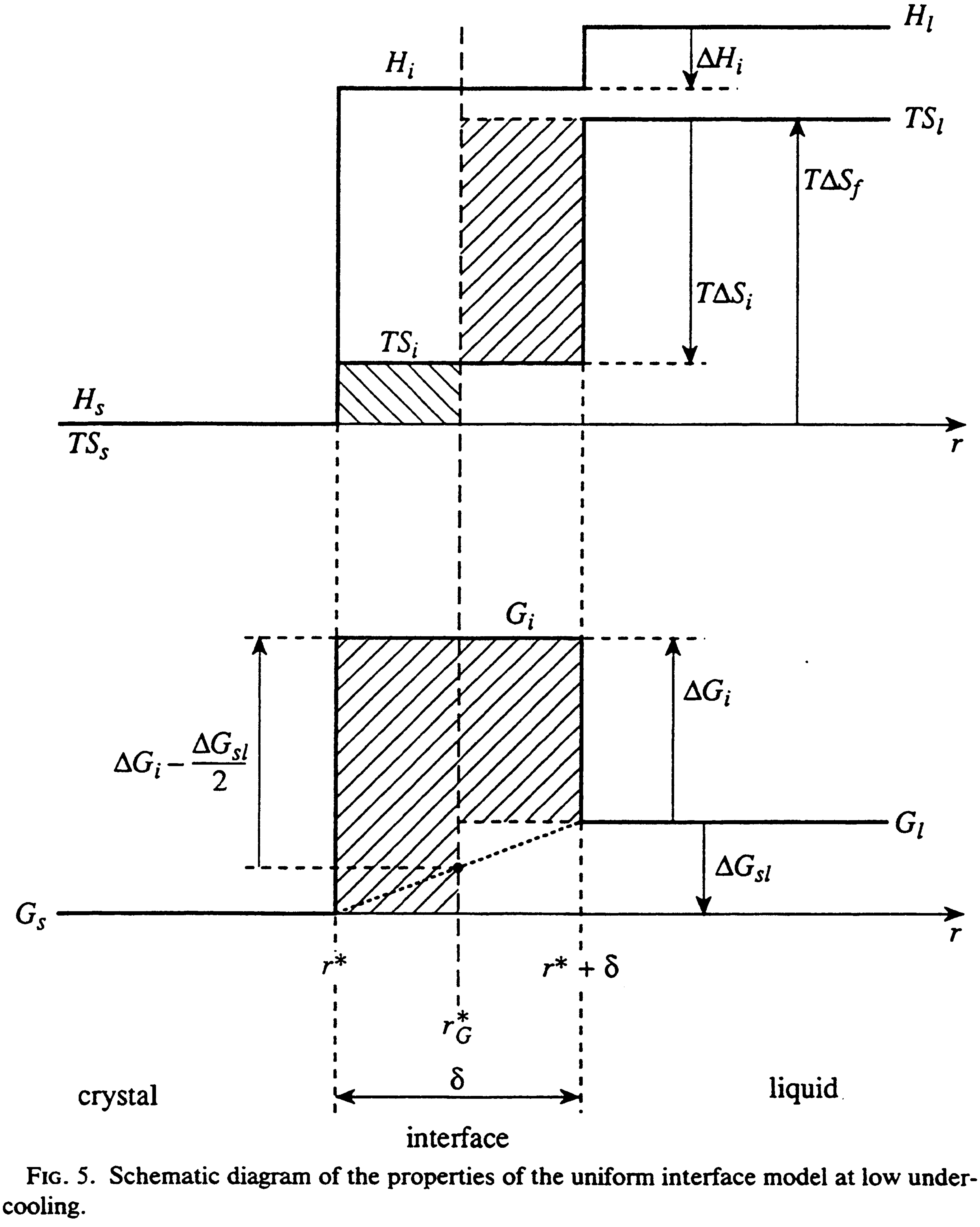

FIG. 5. Schematic diagram of the properties of the uniform interface model at low undercooling.

$$r_s^* = \delta\left(-\frac{2}{a} + \frac{1}{2}\right). \tag{6.8}$$

To lowest order, the two radii are the same and are equal to the classical radius of Eq. (2.3), since to that order $\sigma = \delta\Delta G_i$. The difference between them in the next order shows that the Gibbsian dividing surface in this model, at low undercooling, lies right at the middle of the interfacial layer:

$$r_G^* - r_s^* = \frac{\delta}{2}. \tag{6.9}$$

Figure 5 shows the location of the surface. Note that the interfacial tension is indeed the excess free energy computed with respect to this interface (cross-hatched area in the lower part of the figure), as discussed at the end of Section 4 and in Appendix B.

Figure 5 and Eq. (6.5) also show that the temperature coefficient of the interfacial tension is the (negative) entropy excess computed with respect to this same surface.

IV. Application to the Analysis of Homogeneous Nucleation Experiments

7. REANALYSIS OF THE DATA FOR MERCURY

As pointed out in Kelton's recent review in this series,[43] there are only two sets of quantitative data on the kinetics of homogeneous crystal nucleation from the melt in metals: those of Turnbull[1] on mercury and those of Miyazawa and Pound[36] on gallium. Both make use of the emulsion technique to isolate the heterogeneous nucleants.

To establish that homogeneous nucleation has been measured, two conditions must be met[44]: (1) The maximum undercooling should be independent of the nature of the surface of the droplets and (2) the steady state nucleation rate I should be stochastic in volume and time. The latter can be established in two ways: (a) by a detailed analysis of the kinetics on the size distribution of each dispersion or, more convincingly, (b) by showing that for dispersions with *different average size d*, the nucleation probability of a droplet scaled with d^{-3}.

In Turnbull's experiments on mercury all of these conditions were met. In those on gallium, however, condition 2b was not met: For reasons that are not understood, I scaled with d^{-1}. Nevertheless, similar conclusions on the temperature dependence of the interfacial tension emerged from the two sets of experiments.

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[43] K. F. Kelton, in *Solid State Physics* (H. Ehrenreich and D. Turnbull, eds.), Vol. 45, p. 75, Academic Press, New York (1991).

[44] D. Turnbull, in *Undercooled Alloy Phases* (E. W. Collings and C. C. Koch, eds.), p. 3, The Metallurgical Society of AIME, Warrendale, PA (1986).

TABLE I. DATA (FROM REF. 1) AND ANALYSIS OF THE KINETICS OF HOMOGENEOUS CRYSTAL NUCLEATION FROM THE MELT IN MERCURY

T (K)	$\log I$ ($\mathrm{cm}^{-3}\mathrm{s}^{-1}$)	Δg_{sl} (J/mole)	σ ($\mathrm{erg/cm^2}$)	$f(T)$ ($\times 10^3$)
Dispersion 1				
153.62	7.105	814.50	30.270	1.0058
153.89	6.970	812.10	30.277	1.0099
154.34	6.686	808.08	30.308	1.0170
Dispersion 2				
154.15	6.948	809.78	30.244	1.0140
154.36	6.790	807.91	30.268	1.0173
154.64	6.592	805.41	30.294	1.0218
154.91	6.444	803.00	30.303	1.0262
155.12	6.244	801.12	30.340	1.0296
155.40	6.077	798.62	30.354	1.0342

In the mercury experiments, the steady state isothermal nucleation rate was measured at several temperatures in the range of 153.62 to 155.40 K, and the results are listed in Table I.

In classical nucleation theory, the nucleation rate is determined by the work to form the critical nucleus [Eq. (2.4)] according to the expression:

$$I = I_o \exp\left(-\frac{16\pi\sigma^3}{3kT\Delta G_{sl}^2}\right), \tag{7.1}$$

where k is Boltzmann's constant and I_o is a prefactor that takes into account the jump frequency across the interface of the critical nucleus.

In the original analysis, a value for σ was extracted from the $I(T)$ data, under the assumption that it was independent of temperature and that the difference in specific heat between crystal and liquid was zero. This gave $\sigma = 31.2\ \mathrm{erg/cm^2}$ and $I_o = 10^{42}\ \mathrm{cm^{-3}\ s^{-1}}$. A theoretical estimate[1] of the prefactor, based on absolute rate theory and viscosity data for Hg, is $I_o \doteq 10^{35}\ \mathrm{cm^{-3}\ s^{-1}}$. Turnbull pointed out in his original paper that this discrepancy must be explained by the temperature dependence of σ and ΔG_{sl}.

We will therefore reexamine the analysis of these nucleation data by taking into account the experimentally measured difference[45–47] in specific

[45] R. H. Busey and W. F. Giauque, *J. Phys. Chem.* **75**, 806 (1953).

[46] J. H. Perpezko and D. H. Rasmussen, *Met. Trans.* **A9**, 1490 (1978).

[47] C. V. Thompson and F. Spaepen, *Acta Metall.* **27**, 1855 (1979).

heat between crystal and liquid, ΔC_p, in the computation of $\Delta G_{sl}(T)$. The undercooled temperature range was divided into three regions; in each ΔC_p (in J/mole K) was approximated by a linear relation:

$$\begin{array}{llll} 234.28\,\text{K} & -\ 195\,\text{K} & \Delta C_p = 10.274 - 0.0473T, & \\ 175\,\text{K} & -\ 195\,\text{K} & \Delta C_p = 13.506 - 0.0604T, & (7.2) \\ 150\,\text{K} & -\ 175\,\text{K} & \Delta C_p = 13.679 - 0.0614T. & \end{array}$$

Integration gives the difference in the bulk free energies, Δg_{sl}, at the undercooled temperature. The molar volume of the crystal at 154 K was computed from crystallographic data[48] (14.086 cm^3/mole at 227 K) and the thermal expansion[49] (average value over the relevant range: $14 \times 10^{-5}\ \text{K}^{-1}$) to be 13.945 cm^3/mole.

First, we reconsider the case of a constant interfacial tension. Equation (7.1) can be rewritten as:

$$\log I = \log I_o - \sigma^3 f(T), \tag{7.3}$$

where all the temperature-dependent factors are collected in a function:

$$f(T) = \frac{16\pi}{3}\frac{\log e}{\Delta G_{sl}^2 kT}, \tag{7.4}$$

which is listed in the last column of Table I. A linear fit of log I versus $f(T)$ for all of the data of Table I gives $\sigma = 33.26$ erg/cm^2 and $I_o = 10^{44}\ \text{cm}^{-3}\ \text{s}^{-1}$. The even larger discrepancy with the theoretical prefactor must be attributed to the only remaining temperature dependence, that of σ.

To find the temperature dependence of the interfacial tension, the pre-exponential factor in Eq. (7.1) is set equal to the theoretical value, $I_o = 10^{35}\ \text{cm}^{-3}\ \text{s}^{-1}$, and $\sigma(T)$ is computed for each temperature. The results are listed in Table I and plotted in Fig. 6. A linear fit to all the data gives:

$$\sigma = 22.46 + 0.0507T, \tag{7.5}$$

where σ is in erg/cm^2 and T is in K. A fit to the just data from dispersion 2, for which most data were taken, gives, in the same units:

$$\sigma = 16.74 + 0.0876T. \tag{7.6}$$

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[48] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 1, p. 683, Pergamon Press, New York (1958).

[49] G. Borelius, in *Solid State Physics* (F. Seitz and D. Turnbull, eds.), Vol. 15, p. 13, Academic Press, New York (1963).

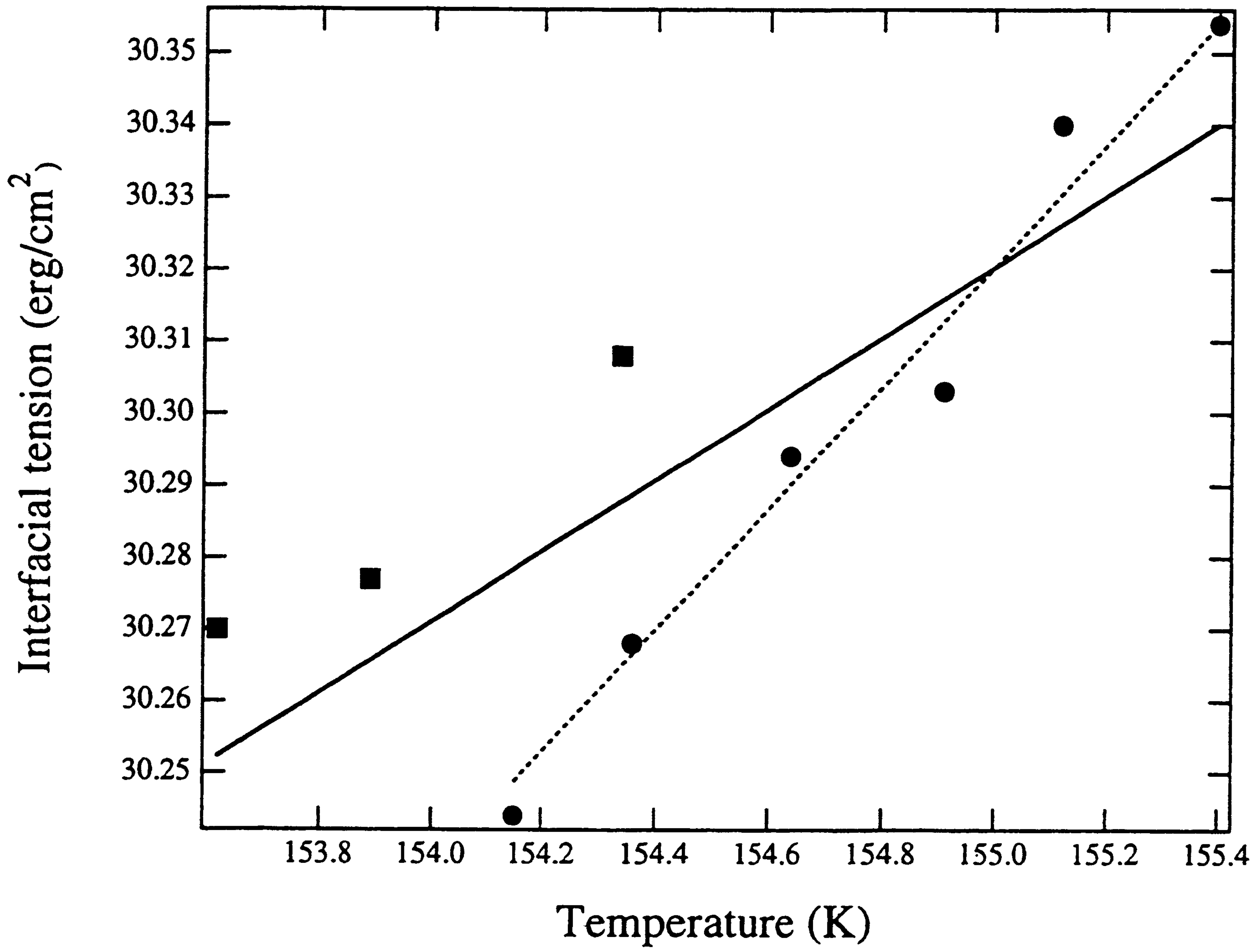

FIG. 6. Experimental temperature dependence of the crystal-melt interfacial tension for mercury, derived from Turnbull's homogeneous nucleation data (Ref. 1). The squares and circles correspond, respectively, to dispersions 1 and 2 of Table I. The solid line is a linear fit to all the data; the dashed line is a linear fit to the data for dispersion 2.

Although the data for gallium[36] do not as unambiguously correspond to homogeneous nucleation, it is still interesting to note that an analysis similar to the preceding one above also gives a positive temperature coefficient (same units):

$$\sigma = 53.8 + 0.055T. \tag{7.7}$$

A positive temperature coefficient of a crystal-melt interfacial tension obtained from homogeneous nucleation data was also found for water[37] (same units):

$$\sigma = -25.67 + 0.211T. \tag{7.8}$$

This case is of interest because the value of the interfacial tension at the melting temperature is known[50]: $\sigma(T_M) = 33 \pm 3$ erg/cm^2, in agree-

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[50] P. V. Hobbs and W. M. Ketcham, in *Physics of Ice* (N. Riehl et al., eds.), p. 95, Plenum Press, New York (1969).

ment with the linear extrapolation of Eq. (7.8) at $T_M = 273$ K: $\sigma(T_M) = 31.9$ erg/cm^2. No such comparison can as yet be made for the metals. The linear extrapolation needs to be reconsidered as well.

8. Interpretation of the Temperature Dependence of the Interfacial Tension

The uniform interface model of Sections 5 and 6 has three unknowns: δ, ΔS_i, and ΔH_i; Turnbull's data provides two values to fit (both in the narrow undercooled temperature range): σ and $d\sigma/dT$ in Eq. (7.5) or (7.6). One of the model parameters must therefore be estimated first. For example, the width of the interface, *assumed uniform,* in a physical hard sphere model of the interface[14,15] is 1.46 monolayers, or 3.69 Å for mercury.[51]

The results of Section 6 can be used by inspection for a first estimate of the remaining interface parameters. Equations (6.3) and (6.6) give $\tilde{s} = -0.70$ and $\tilde{h} = -0.13$ for the data of Eq. (7.5); and $\tilde{s} = -0.84$ and $\tilde{h} = -0.22$ for the data of Eq. (7.6). Note that Eq. (6.6) also implies generally that, since the interface thickness δ must obviously be positive, a positive temperature coefficient can only be obtained if $\tilde{s} < -0.5$, i.e., if there is a substantial entropy loss.

A more precise determination requires the use the results of Section 5. The numerical determination was made by differentiating Eq. (5.14), which gives:

$$\frac{d\tilde{\sigma}/d\tilde{T}}{\tilde{\sigma}} = -\frac{1}{3}\left(\frac{\tilde{s}}{\tilde{g}} + \frac{\tilde{s}+1}{\tilde{g}'} + \frac{\tilde{s}}{\tilde{g} + \sqrt{\tilde{g}\tilde{g}'}} + \frac{\tilde{s}+1}{\tilde{g}' + \sqrt{\tilde{g}\tilde{g}'}}\right), \tag{8.1}$$

where

$$\tilde{g} = \tilde{h} - \tilde{T}\tilde{s} \quad \text{and} \quad \tilde{g}' = \tilde{h} - \tilde{T}\tilde{s} - \tilde{T} + 1, \tag{8.2}$$

are the values of ΔG_i and $\Delta G_i'$ normalized by the enthalpy of fusion. After choosing a value for $\tilde{s}$, Eq. (8.1) can be solved numerically for $\tilde{h}$. The interface thickness is then obtained directly from Eq. (5.14):

$$\tilde{\delta} = \tilde{\sigma}\left[\frac{4}{\tilde{g}\tilde{g}'(\sqrt{\tilde{g}} + \sqrt{\tilde{g}'})^2}\right]^{1/3}. \tag{8.3}$$

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[51] Data used for mercury calculations: CN12 radius: 3.10 Å, which gives an effective close-packed plane spacing of 2.53 Å. $\Delta S_f = 0.70919$ J/K · cm^3 at 154 K, using $V = 13.945$ cm^3/mole, discussed on p. 22; see Refs. 48 and 49.

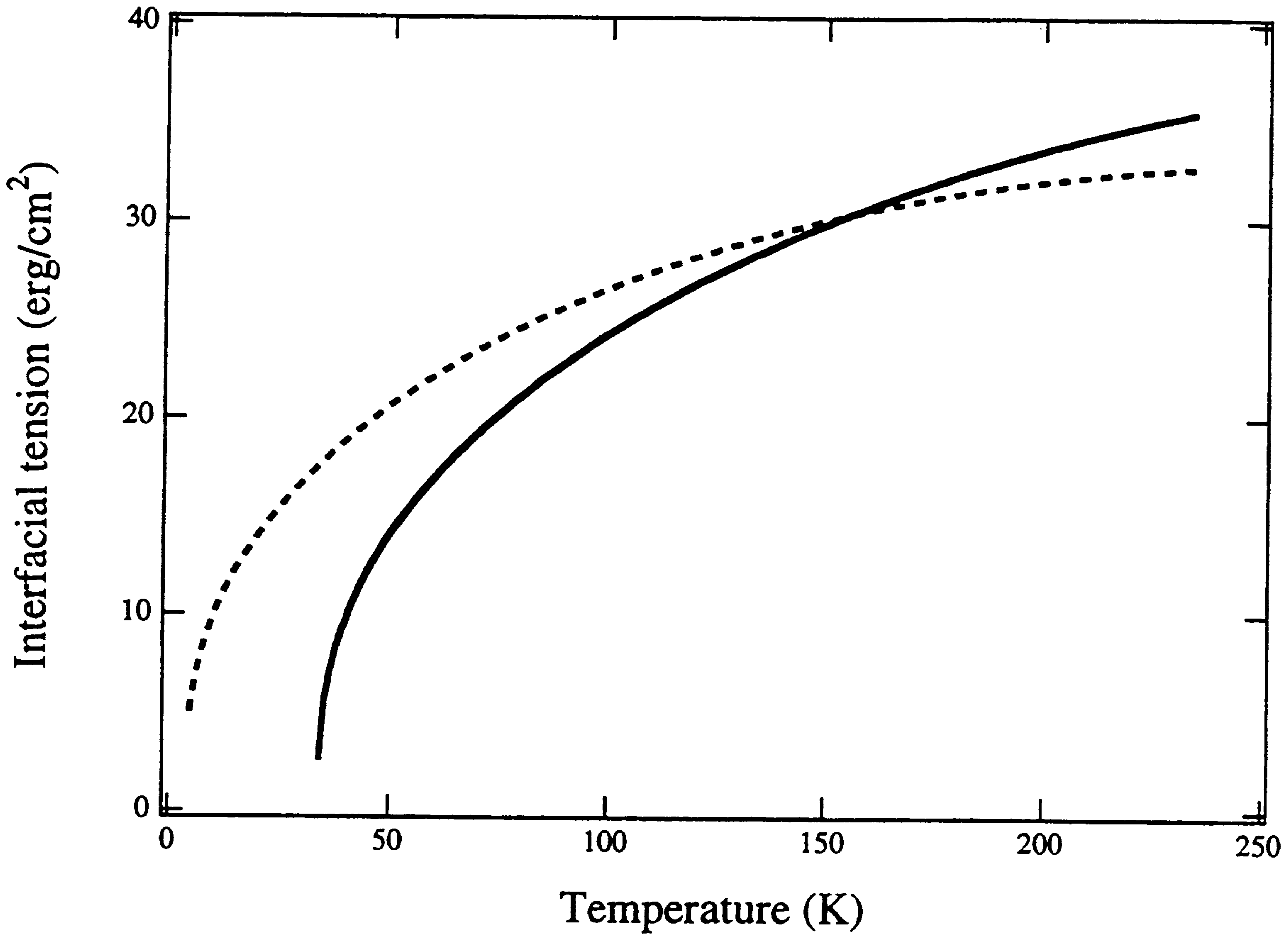

FIG. 7. Temperature dependence of the interfacial tension for mercury computed according to Eq. (5.14) for an interface thickness $\delta = 3.69$ Å. Dashed line: fit to all the data of Fig. 6, with $\bar{s} = -0.55$ and $\bar{h} = -0.01$; solid line: fit to the data of dispersion 2 in Fig. 6: $\bar{s} = -0.68$ and $\bar{h} = -0.10$.

The requirement of a positive interface thickness is satisfied as long as $\bar{g}$ and $\bar{g}'$ are both positive, which is, of course, an essential condition for the stability of the interface (see above). Furthermore, since the left-hand side of Eq. (8.1) is positive, it can only be satisfied if $\bar{s} < 0$, i.e., if there is a loss of liquid entropy in the interface.

Iterative solution of Eq. (8.1) and (8.3) with the chosen value of the interface thickness ($\delta = 3.69$ Å) gives for the two remaining parameters: $\bar{s} = -0.55$ and $\bar{h} = -0.01$ for the data of Eq. (7.5); and $\bar{s} = -0.68$ and $\bar{h} = -0.10$ for the data of Eq. (7.6). Figure 7 shows the temperature dependence of the interfacial tension computed over the entire undercooled temperature range using Eq. (5.14) and the two sets of fit parameters.

The values of the fit parameters can now be compared to those in the physical model chosen to provide the value for δ. The enthalpy in the hard sphere system is, of course, zero by definition. However, since the density of the interface is close to that of the liquid, one would expect the interfacial enthalpy in the presence of an interatomic potential to be close to the value in the liquid, or $\bar{h} \approx 0$.

The entropy of the static, hard sphere interface was first calculated approximately[14] using an assumption similar to those used by Pauling for proton disorder in ice.[52] A more accurate value was obtained later based on an exact solution for the dimer disorder on a honeycomb lattice.[15,53,54] The results can be summarized as follows.

Since the density of the interface is close to that of the liquid, its vibrational entropy is similar; the vibrational contribution to the heat of fusion in metals is estimated[13] at $\Delta s_v = 0.2$ k/atom. The configurational entropy of the atoms in the first interfacial layer, i.e., the one closest to the last crystal plane and labeled "I" in Fig. 4(a), is very small ($s_{\mathrm{I}} = 0.113$ k/atom). This is because the layer is fully localized in the direction normal to the interface and, because of its high density (close to that of the liquid), derives only little entropy from its lateral noncrystallinity. The next layer in the interface [labeled "II" in Fig. 4(a)] is less localized than the first one; analysis of the model shows that 46% of the atoms in that layer need to be localized, and hence derive their entropy from the configuration of the first layer.[13] The contributions from the next layers (III, etc.) are considered negligible. Since there are, then, 1.46 atoms in the interface per atom in the first layer, the average fractional loss of entropy per atom in the interface is

$$\bar{s} = \frac{s_{\mathrm{I}} + 1.46\,\Delta s_v}{\Delta s_f} - 1. \tag{8.4}$$

The entropy fusion per atom, Δs_f, is close to 1.2 k for metals. Using the value for Hg, $\Delta s_f = 1.17$ k/atom, gives $\bar{s} = -0.76$. This value is slightly higher than the parameters for the rigorous fit. This may reflect the approximation of a uniform interface in the model. Computation of the tension for a layered interface, which is a straightforward extension (see Appendix B), will be undertaken to test this. The interfacial entropy may also be raised slightly by the introduction of crystal terraces, which are not present in the static hard sphere model. Finally, it should be kept in mind that the fit is sensitive to the choice of the interface thickness. For example, if the interfacial entropy is kept fixed at the model value $\bar{s} = -0.76$, the interfacial thicknesses become 2.09 and 3.17 Å for the data of Eq. (7.5) and (7.6), respectively.

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[52] L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).

[53] V. Elser, *J. Phys.* **A17**, 1509 (1984).

[54] P. W. Kasteleyn, *J. Math. Phys.* **4**, 287 (1963).

V. Conclusions

A classical analysis, based on the Gibbsian description of interfaces, of the temperature dependence of the crystal-melt interfacial tension *at constant external pressure* (i.e., for a finite crystal in an undercooled melt) shows that the temperature coefficients obtained from homogeneous nucleation experiments can be accounted for, as originally proposed by Turnbull, by the entropy loss in the liquid due to ordering near the crystal surface. Analysis of the equilibrium interface[18,19] in the hard sphere system confirms that the interfacial entropy losses are sufficiently large to account entirely for the magnitude of the interfacial tension, since the enthalphic contribution in this system is by definition zero.

Equation (5.14) can be used as an improved expression for the temperature dependence of the interfacial tension in modeling of nucleation. The fit to the nucleation data for mercury suggests that $\tilde{h} = 0$, $\tilde{s} = -0.6$, and $\tilde{\delta} = 1.3$ [see Eqs. (5.13) for the definitions] are reasonable average parameters for close-packed metals.

In a nonequilibrium system, the interfacial tension is only a parameter introduced in the Gibbsian accounting for the work to form a critical nucleus [see Eq. (4.6)], and experimentally only that work can be measured. It is therefore entirely possible to analyze the nucleation data with a model of the interface without explicitly defining an interfacial tension. In equilibrium, however, the tension can be measured directly[7,55] and a determination at undercooled temperatures is then useful for comparison with the equilibrium value. The experiments on water are an example.[37,50] Note that the linear extrapolation that gave agreement between the two sets of measurements needs to be reconsidered (see Fig. 7). Measurements of the tension in equilibrium for mercury, for example, or determinations of the tension from homogeneous nucleation of succinonitrile, for example, would be most valuable to test the models further.

Finally, keep in mind that the analysis presented here has the classic limitation of the Gibbsian approach: It assumes that the bulk properties of the crystal are also valid at least at the center of very small nuclei. Obviously, at the smallest sizes, where all but a few atoms are at the surface, this assumption must break down. In Turnbull's experiments on mercury, there are almost 1000 atoms in the nucleus, so that its center is probably rather bulk-like. The Gibbsian approach is surprisingly successful in the description of the nucleation of liquids from the vapor,[38,56] indicating that the extrapolation of the thermodynamic properties can be

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[55] R. J. Schaefer, M. E. Glicksman, and J. D. Ayers, *Phil. Mag.* **32**, 725 (1975).

[56] J. L. Katz, *J. Chem. Phys.* **52**, 4733 (1970).

extended to quite small nucleus sizes. This is confirmed by an analysis of the surface and bulk contributions to the energy of small clusters.[57] The recent enormous expansions in computer power will make it possible to test this on dynamic models of crystal nuclei in the melt.[58–60]

ACKNOWLEDGMENTS

It has been my privilege to be associated with David Turnbull for many years. He introduced me to the problems of the crystal-melt interface when I was still a graduate student, and I have benefited enormously from his insights on this and many other subjects. I congratulate him on his retirement as editor of the *Solid State Physics* series, knowing that his will be a hard act to follow. I also thank him, Mike Aziz, Peter Voorhees, and John Hirth for useful discussions and comments on this chapter. This work has been supported by the National Aeronautics and Space Administration under contract NAGW2838, and by the National Science Foundation through the Harvard Materials Research Laboratory under contract DMR-89-20490.

Appendix A: Calculation of the Interfacial Tension as an Excess Quantity for a Curved Interface

These are simple, definitional arguments that will be obvious to many by inspection. For ease of reading, they are spelled out. First, define some volumes associated with the various spherical surfaces in the problem (Fig. A.1): V_s^* is the volume of the sphere with radius r_s^*; V_1 is the volume between the spheres with radius r_s^* and r_G^*; V_2 is the volume between the spheres with radii r_G^* and $r_s^* + \delta$; V_G^* is the volume of the sphere with radius r_G^*. Hence,

$$\mathrm{V}_G^* = V_s^* + V_1. \tag{A.1}$$

The work to form a crystal with radius r_s^* is, according to Eqs. (4.1) and (4.2), with Ω kept constant for convenience (see also Appendix B):

$$W = G_s V_s + I_1 + I_2 - G_l(V_s + V_1 + V_2), \tag{A.2}$$

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[57] An analysis of the energy of small clusters in a Lennard-Jones potential [M. R. Hoare and P. Pal, *Adv. Phys.* **20,** 161 (1971)] shows that the surface tension starts deviating from the macroscopic prediction below about 30 atoms (F. Spaepen, unpublished results).

[58] M. J. Uttormark, S. J. Cook, M. O. Thompson, and P. Clancy, *MRS Symp. Proc.* **205,** 417 (1992).

[59] J. D. Honeycutt and H. C. Andersen, *J. Phys. Chem.* **90,** 1585 (1986).

[60] J. S. van Duijneveldt and D. Frenkel, *J. Chem. Phys.* **96,** 4655 (1992).

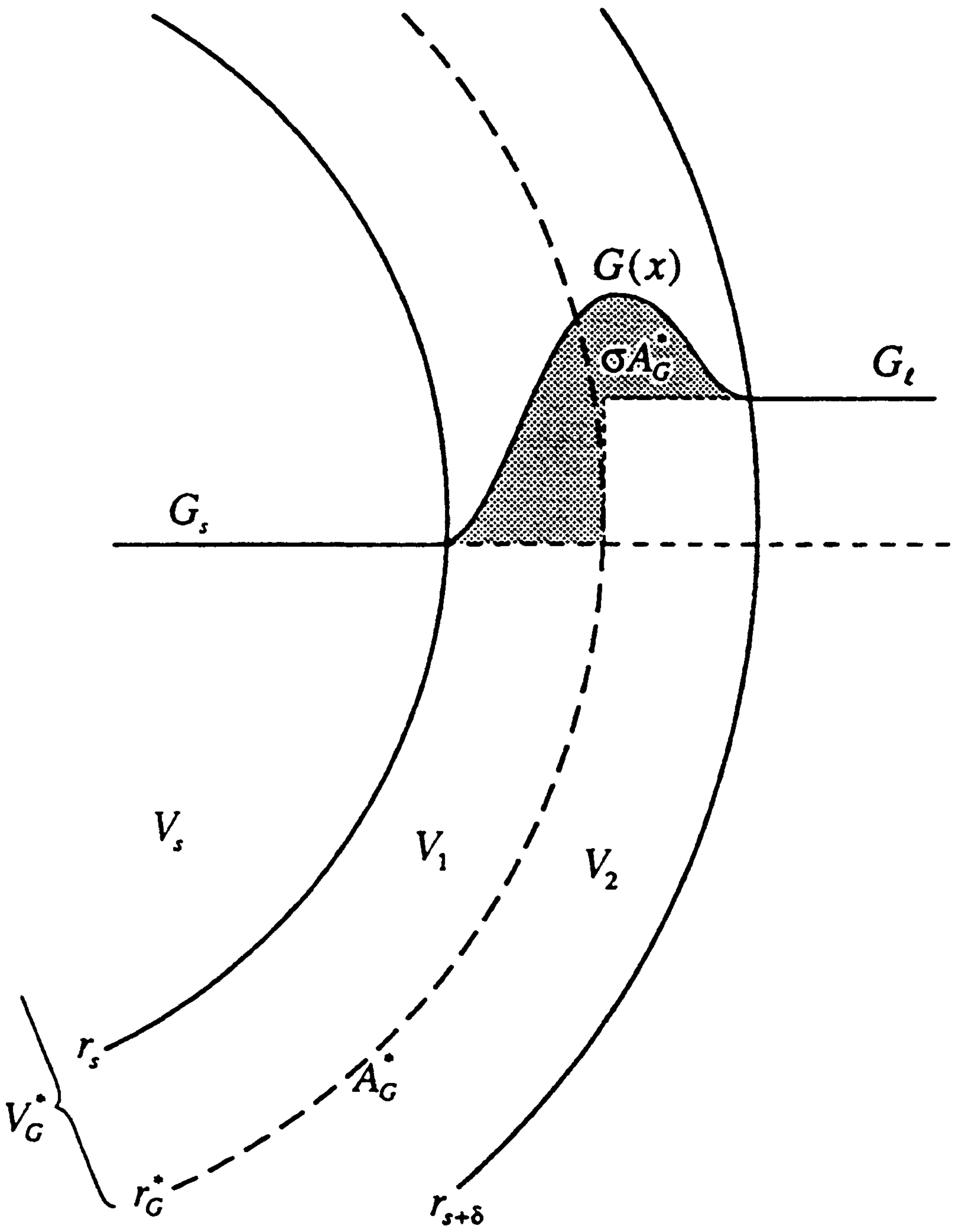

FIG. A.1. Schematic diagram of the radii, volumes, and area defined in the calculation of the interfacial tension as an excess quantity for a curved surface. The shaded area corresponds to the (spherical) excess free energy with respect to the Gibbsian dividing surface.

where

$$I_1 = \int_{r_s^*}^{r_G^*} G(r)4\pi r^2 \, dr, \tag{A.3}$$

and

$$I_2 = \int_{r_G^*}^{r_s^*+\delta} G(r)4\pi r^2 \, dr. \tag{A.4}$$

The Gibbsian definition of σ as an excess quantity is based on the same work being written as:

$$\begin{aligned} W &= (G_s - G_l)V_G^* + \sigma A_G^* \\ &= (G_s - G_l)(V_s + V_1) + \sigma A_G^*. \end{aligned} \tag{A.5}$$

Equating Eqs. (A.2) and (A.5) then gives for the interfacial term:

$$\sigma A_G^* = (I_1 - G_s V_1) + (I_2 - G_l V_2), \tag{A.6}$$

which is the excess free energy with respect to the Gibbsian dividing surface (shaded area in Fig. A.1).

The interfacial tension is defined in the text based on the work to form a critical nucleus [see Eqs. (4.5) and (4.6)]:

$$W = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G_{sl}^2}. \tag{A.7}$$

Equating this work to that defined in Eq. (A.5) and expressing A_G^* and V_G^* in terms of their radii gives an equation for r_G^*:

$$r^3 + 3pr^2 - 4p^3 = 0, \tag{A.8}$$

where

$$p = \frac{\sigma}{\Delta G_{sl}}. \tag{A.9}$$

The only positive root of Eq. (A.8) is

$$r_G^* = -2p, \tag{A.10}$$

in accord with the Gibbsian definition of Eq. (2.3).

It is interesting to note that for a *given* r_s and a choice of the location of the dividing surface, the Gibbsian radius, r_G^* of Eqs. (2.3) and (A.10) also corresponds to the *minimum* value for σ defined as an excess free energy.[33]

Appendix B: Calculation of the Interfacial Tension for a General Spatial Variation of the Free Energy

Assume that the atomic volume $\Omega(r)$ in Eq. (4.1) is the same for all atoms in the system, and that the free energy profile as a function of radius through the interface is *independent of the size of the crystal*. The variation of the free energy per unit volume given in Eq. (4.2) can then be specified as:

$$\begin{aligned} G(r) &= G_s && \text{for } r \leq r_s, \\ G(r) &= G_i(r - r_s) && \text{for } r_s \leq r \leq r_s + \delta, \\ G(r) &= G_l && \text{for } r_s + \delta \leq r. \end{aligned} \tag{B.1}$$

Using a change of variables

$$x = r - r_s, \tag{B.2}$$

the work to form a crystal of radius r_s [Eq. (4.1)] can be written as:

$$W(r_s) = \frac{4\pi r_s^3}{3}\Delta G_{sl} + \int_0^\delta (G_i(x) - G_l)4\pi(x + r_s)^2\, dx. \tag{B.3}$$

Define the n'th moment of $G_i(x)$ as:

$$I_n = \frac{n+1}{\delta^{n+1}}\int_0^\delta G(x)x^n\, dx \qquad n = 0, 1, 2, \ldots \tag{B.4}$$

Define the corresponding dimensionless coefficients:

$$a_n = \frac{I_n - G_l}{\Delta G_{sl}}. \tag{B.5}$$

Equation (B.3) then becomes:

$$W(r_s) = \frac{4\pi}{3}\Delta G_{sl}(r_s^3 + 3a_0\delta r_s^2 + 3a_1\delta^2 r_s + a_2\delta^3) = 0. \tag{B.6}$$

The equilibrium condition of Eq. (4.3) is then:

$$\left.\frac{dW}{dr_s}\right|_{r_s^*} = 4\pi\Delta G_{sl}(\mathrm{r}_s^2 + 2a_0\delta r_s + a_1\delta^2) = 0. \tag{B.7}$$

The radius of the crystal in equilibrium with an undercooled melt is the positive root of the factor in parentheses:

$$r_s^* = -\delta a_0(1 + \beta), \tag{B.8}$$

where

$$\beta^2 = 1 - \frac{a_1}{a_0^2}. \tag{B.9}$$

The work to form the crystal is found by inserting the value of r_s^* into Eq. (B.6):

$$W^* = \frac{16\pi}{3}\Delta G_{sl}\delta^3 c^3, \tag{B.10}$$

where c^3 is a dimensionless factor that depends on the shape of $G(x)$ and the undercooling:

$$c^3 = \frac{1}{4}[-a_0^3(1 + \beta)^3 + 3a_0^3(1 + \beta)^2 - 3a_0 a_1(1 + \beta) + a_2]. \tag{B.11}$$

The combination of Eqs. (B.10) and (B.13) then gives:

$$\sigma = c\delta\Delta G_{sl}. \tag{B.12}$$

The location of the Gibbsian dividing surface is found from Eq. (2.3):

$$r_G^* = -2c\delta. \tag{B.13}$$