Ginzburg-Landau theory for the solid-liquid interface of bcc elements

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We describe a simple order-parameter theory for the interfacial tension of body-centered-cubic solids. The principal order parameter is the amplitude of the density wave at the smallest nonzero reciprocal-lattice vector of the solid, but the density difference between solid and liquid is included to second order. The parameters entering the theory are fitted to the measured heat of fusion, melting temperature, and solid-liquid density difference, and to the liquid structure factor and its temperature derivative at freezing as calculated by a variational technique. Agreement with experiment is good for Na and Fe, and the calculated anisotropy of the surface tension among different crystal faces is of order 2%, in agreement with earlier calculations of Oxtoby and Haymet. With certain additional assumptions about universal behavior of bcc crystals at melting, the formalism predicts that the surface tension is proportional to the heat of fusion per surface atom, in agreement with the empirically derived relation of Turnbull [J. Appl. Phys. **24**, 1022 (1950)].

I. INTRODUCTION

The interfacial free energy τ between a solid and its coexisting liquid is a very important parameter in metallurgy.[1] For example, it plays a central role in the nucleation theory, determining the minimum size of a crystallite forming from the melt. It also enters into many models of crystal growth.[2] The dependence of τ upon crystal face—that is, its anisotropy—is of equal relevance in models of crystal growth.

Until recently, relatively few attempts had been made to calculate τ from a microscopic starting point—probably because of the obvious difference in symmetry between solid and liquid of the same element. This symmetry difference causes the solid-liquid transition to be first order. As a result, most theories of solid and liquid free energies have started from very different points of view and calculations of the melting curves have typically been carried out by comparing these differently calculated free energies curves and noting their crossing point in the pressure-temperature plane.[3]

A major advance in the theory of freezing of simple solids occurred with the work of Ramakrishnan and Youssouff (RY).[4] These authors developed a theory of freezing based on a unified treatment of both solid and liquid, the density-functional (DF) formalism.[5] According to this approach, a solid is treated as an inhomogeneous liquid with spatially varying singlet number density $n(\mathbf{x})$. The Helmholtz free energy is then a functional of $n(\mathbf{x})$. At any given pressure and temperature, the system goes into the state (solid, liquid, or vapor) which minimizes this functional. RY proposed a simple approximation for their density functional, and showed that their form does indeed give a reasonable value for the melting temperature of simple elements such as Na.

Recent workers have proposed more elaborate forms for the density functional, and have shown that the DF theory can indeed give quite reasonable predictions for the equilibrium phase diagrams, and in particular, the liquid-solid phase boundaries, several elements. Haymet and Oxtoby[6] have obtained good results with the inclusion a fairly small number of Fourier components in the density expansion. Baus and co-workers[7] have shown that excellent results can be obtained for the hard-sphere fluid, and for mixtures of hard spheres of different diameters, by using a theory in which the higher Fourier components are included by a Debye-Waller-like approximation. More recently, Curtin and Ashcroft[8] have obtained the entire equilibrium phase diagram of a Lennard-Jones fluid using a version of the theory proposed by Tarazona.[9] Sachdev and Nelson[10] have used the DF theory, in its Debye-Waller form, to treat the relative stability of quasicrystalline phases and of models for the structure of metallic glasses.

Thus the DF theory seems indeed to be suitable for studying transitions from the liquid to the solid state in simple, and perhaps even rather complex, systems. To date, however, it appears that only Oxtoby and Haymet[11] and Klubsch[12] used a DF formalism to study the liquid-solid interface. Oxtoby and Haymet have included a relatively small number of Fourier components in this formalism to calculate τ as a function of orientation for several bcc metals. Klubsch[12] has developed a DF theory based on the Percus-Yevick equation for an inhomogeneous fluid, and formally solved it in the case of a crystal-liquid interface of a Lennard-Jones fluid.

The present work is an investigation of a particularly simple DF theory for the interfacial tension between simple solids and their coexisting liquids. Our approach is, in fact, only a slight generalization of the simplest of all such theories, the Ginzburg-Landau formalism. Although oversimplified, the present approach has the advantage that the parameters entering the theory can all be deduced in a simple fashion from bulk properties, which may then be used to predict surface properties. The theory can also be used to compare states of different symmetry, and behavior along different crystalline interfaces. While quantitative reliability is not to be expected, the qualitative predictions may be useful guides in condi-

tions where experiments are difficult to carry out, as well as in developing more elaborate theories. Our results are similar, where comparable, to those of Oxtoby and Haymet (except for our surface widths, which are narrower than theirs).

We turn now to the body of the paper. Section II describes our density functional for the liquid-solid interface. Section III describes its application to several interfaces between liquid and bcc solid, and Sec. IV presents a brief discussion.

II. FORMALISM

According to the density-functional formalism,[4-10] the Helmholtz free energy F of an inhomogeneous system can be expressed as a functional of the singlet atomic number density $n(\mathbf{x})$ by the relation

$$F = F[n(\mathbf{x})] . \tag{2.1}$$

Here F may also depend on other thermodynamic variables, such as the absolute temperature T, which for compactness we have not explicitly indicated.

We consider first how Eq. (2.1) may be applied to a bulk crystalline solid. In this case, $n(\mathbf{x})$ can always be expressed in the form

$$n(\mathbf{x}) = n_0 \left[1 + \sum_{\mathbf{K}} u_{\mathbf{K}} \exp(i\mathbf{K} \cdot \mathbf{x}) \right] , \tag{2.2}$$

where n_0 is some constant density, and $\mathbf{K}$ is a reciprocal-lattice vector of the solid. The sum may be assumed to run over all $\mathbf{K}$, including $\mathbf{K} = 0$. The free energy F is then a function of the variables $u_{\mathbf{K}}$. It is sometimes useful to express this function as a power series in the coefficients $u_{\mathbf{K}}$.

$$\frac{F(\{u_{\mathbf{K}}\})}{V}$$

$$= \frac{F_0}{V} + \tfrac{1}{2} n_0 k_B T \left[\sum_{\mathbf{K}} a_{\mathbf{K}} u_{\mathbf{K}} u_{-\mathbf{K}} \right.$$

$$\left. + \sum_{\mathbf{K}} a_{\mathbf{K}, \mathbf{K}', \mathbf{K}''} u_{\mathbf{K}} u_{\mathbf{K}'} u_{\mathbf{K}''} + \cdots \right] , \tag{2.3}$$

where V is the volume of the system. In the third-order term, only those reciprocal-lattice vectors enter which satisfy the condition $\mathbf{K} + \mathbf{K}' + \mathbf{K}'' = 0$, and, in general, for the nth-order term, the condition is that $\mathbf{K} + \mathbf{K}' + \mathbf{K}'' + \cdots + \mathbf{K}^{(n)} = 0$.[13] (This well-known condition is a result of the symmetry requirement that the total free energy of the system be invariant under a uniform translation. We have automatically used this condition in omitting terms linear in the coefficients $u_{\mathbf{K}}$.[14]) F_0 is the free energy of a uniform liquid of density n_0. Henceforth, we take n_0 to be the density at which the liquid is at zero pressure.

We treat the *uniform* solid by a simple, truncated version of the expansion (2.3). Namely, we assume that *one* set of nonzero reciprocal-lattice vectors of equal length, denoted $\{\mathbf{K}\}$, is dominant in the solid phase, and that the coefficients of other reciprocal-lattice vectors can be ade-

quately included to lower order in their amplitudes $u_{\mathbf{K}}$ than the dominant coefficients. In general, the dominant set of reciprocal-lattice vectors is the smallest nonzero set, for example, the 12 [110] reciprocal-lattice vectors in a bcc crystal.

We now focus specifically on bcc crystals. In this case, the coefficients $u_{\mathbf{K}}$ of all the [110] reciprocal-lattice vectors must be of equal magnitude in the bulk solid, in order for the resulting solid to have the proper cubic point-group symmetry. We denote this coefficient u_{110}, and assume initially that this is the *only* nonvanishing coefficient. The free energy expansion (2.3) can then be concisely written

$$\frac{F_{110}}{V} = \frac{F_0}{V} + \frac{n_0 k_B T}{2} (a_2 u_{110}^2 - a_3 u_{110}^3 + a_4 u_{110}^4 + \cdots) , \tag{2.4}$$

where we assume the amplitudes u_{110} to be real. The coefficient a_3 is nonzero because there exist triangles of [110] reciprocal-lattice vectors which add up to zero.[13] This is not the case in fcc crystals, and the cubic term would be absent in this simple approximation, seemingly leading to a second-order freezing transition in the fcc crystal. This unphysical feature means only that the single-set approximation is too crude to treat freezing of fcc crystals.

We can readily include other coefficients in (2.4) as follows. Suppose there is a reciprocal-lattice vector, say $\mathbf{K}_i$, such that $\mathbf{K}_i + \mathbf{K}_1 + \mathbf{K}_2 = 0$, where $\mathbf{K}_1$ and $\mathbf{K}_2$ are both members of the dominant [110] set, while $\mathbf{K}_i$ is not. Then for any such vector, we add to (2.4) a term of the form

$$\Delta F_i / V = [c_i u_i (u_{110})^2 + d_i u_i^2] \frac{n_0 k_B T}{2} . \tag{2.5}$$

The second term in (2.5) (quadratic in the u_i's) will always be present, since for any $\mathbf{K}_i$ there always exists another reciprocal-lattice vector $-\mathbf{K}_i$ with the same amplitude $u_{\mathbf{K}_i}$. One of the K_i's that may be included as in (2.5) is $\mathbf{K}_i = 0$, corresponding to a nonzero *density* difference between solid and liquid. Since the coefficients u_i are assumed smaller than u_{110}, we do not include terms of order u_i^3.

The total free energy of the uniform solid phase, in this approximation, is

$$F = F_{110} + \sum_i \Delta F_i . \tag{2.6}$$

F may be minimized with respect to the u_i's at fixed u_{110} with the result

$$u_i = -(c_i / 2d_i) u_{110}^2 . \tag{2.7}$$

Substitution of this form back into F yields a one-parameter expansion of F in terms of u_{110}, including second-, third-, and fourth-order coefficients; the quartic coefficient is, however, renormalized relative to that in (2.3):

$$\frac{F}{V} = \frac{F_0}{V} + \frac{n_0 k_B T}{2} (a_2 u_{110}^2 - a_3 u_{110}^3 + a_4' u_{110}^4) , \tag{2.4a}$$

$$a_4' = a_4 - \sum_i \frac{c_i}{4d_i} . \tag{2.4b}$$

Thus the fourth-order Ginzburg-Landau expansion in *one* order parameter automatically includes several *additional* order parameters to a lower power. One of these additional order parameters is the density difference between solid and liquid. A similar treatment has been recently used by Mermin and Troian in their discussion of the stability of quasicrystalline phases.[15]

The treatment so far is confined to a uniform solid phase. In order to extend this approach to nonuniform solids, one must include terms in the free energy which involve gradients of the u_K's. If the coefficients u_K are slowly varying in space, it will usually be sufficient to include only terms involving first spatial derivatives of the u_K's. These additional terms take the form

$$\Delta F_{gr} = \frac{n_0 k_B T}{2} \oint_{K,\alpha\beta} d^3x \, b_{K,\alpha\beta} \frac{\partial u_K(\mathbf{x})}{\partial x_\alpha} \frac{\partial u_K(\mathbf{x})}{\partial x_\beta} , \tag{2.8}$$

where the sum is over all reciprocal-lattice vectors, and over all Cartesian components x_α and x_β of the position variable $\mathbf{x}$. The coefficients $b_{K,\alpha\beta}$ satisfy various conditions imposed by the point group symmetry of the system under consideration.

In principle, a density-functional expansion of this kind can be used to calculate the free energy of *any* inhomogeneous system, provided the Fourier amplitudes $u_K(\mathbf{x})$ are sufficiently slowly varying in space. For the liquid-solid interface, one minimizes the free energy of an inhomogeneous system, subject to the boundary conditions that the system should approach a pure liquid at sufficiently large distances on one side of the interface, and a pure solid on the other. The surface tension is extracted as the difference between the free energies of the inhomogeneous system and the suitably volume-averaged free energies of the corresponding uniform system.

To carry out this program, one needs the various coefficients entering the free energy expansion. The coefficients a_K [Eq. (2.3)] and $b_{K,\alpha\beta}$ [Eq. (2.8)] are related to the two-body correlation functions of the uniform liquid. The relations are[4-6]

$$a_K = 1/S(|K|) \tag{2.9}$$

and

$$b_{K,\alpha\beta} = -\tfrac{1}{4} C''(|K|) \frac{K_\alpha K_\beta}{K^2} , \tag{2.10}$$

where $S(K)$ is the liquid structure factor, and $C(K)$ is the direct correlation function of the liquid, related to $S(K)$ by

$$S(K) = 1/[1 - C(K)] . \tag{2.11}$$

$C''(K)$ denotes the second derivative $d^2C(K)/dK^2$. As has been noted by other workers,[4,8,13] relation (2.9) shows that a_K is smallest for solid reciprocal-lattice vectors which lie closest to the maximum in the liquid structure factor. Thus the energy barrier to formation of a solid with many such reciprocal-lattice vectors near this maximum tends to be relatively small.

The remaining coefficients are related to higher-order correlation functions of the uniform liquid, and cannot be determined easily from fundamental theory. We choose to obtain them by fitting to appropriate empirical quantities, as described below.

To be explicit, we now specialize to a bcc crystal in the single-set approximation mentioned earlier. The free energy of the uniform solid can be written

$$(F_s - F_l)/V = (n_0 k_B T/2)(a_2 u^2 - a_3 u^3 + a_4' u^4) , \tag{2.12}$$

where we have for convenience abbreviated the amplitudes (equal in the bulk solid) of all the [110] reciprocal-lattice vectors by u. The coefficient a_2 is given by

$$a_2 = 12/S(K) \tag{2.13}$$

where $S(K)$ is the value of the liquid structure factor at the value of K corresponding to the 12 [110] reciprocal-lattice vectors of the solid. Assuming this coefficient is known, we require two conditions to determine a_3 and a_4' empirically. (a_4' is the renormalized quartic coefficient incorporating the effects of several other sets of reciprocal lattice vectors.) We choose the following two conditions.

(i) The Helmholtz free energy difference per atom between solid and liquid shall vanish at the melting temperature, and

(ii) the density-functional expansion shall correctly yield the empirical heat of fusion.

We also have the requirement that, in the solid phase, the amplitude u is determined by minimizing $(F_s - F_l)/V$ with respect to it. From the two conditions

$$F_s - F_l = 0 , \tag{2.14}$$

$$\left[\frac{\partial}{\partial u}(F_s - F_l) \right]_{N,V,T} = 0 , \tag{2.15}$$

we obtain

$$a_3 = (2a_2 a_4')^{1/2} \tag{2.16}$$

and

$$u = (a_2/a_4')^{1/2} . \tag{2.17}$$

The condition (ii) on the heat of fusion is equivalent to

$$\Delta = (1/Nk_B) \left[\frac{\partial(F_s - F_l)}{\partial T} \right]_{T=T_m}$$

$$= T_m u^2/2(da_2/dT)_{T=T_m} . \tag{2.18}$$

Equations (2.17) and (2.18) together determine a_4' in terms of a_2 and its constant-volume temperature derivative da_2/dT at melting. (Δ is the increase in entropy on melting; N is the number of molecules in the system.)

III. SOLID-LIQUID INTERFACIAL TENSION

A. Isotropic approximation

To apply this formalism to the calculation of interfacial tension, we must include in the free energy functional all

the terms involving gradients of the coefficients u. In principle, there are 12 independent coefficients u, corresponding to the amplitudes of the 12 [110] reciprocal-lattice vectors of the bcc lattice. Although these amplitudes are equal in the bulk, they need not be equal in the vicinity of the interface. If we assume that they remain equal in the interface we will obtain an isotropic surface tension, i.e., one that is independent of crystal face. This isotropic tension can be calculated analytically, and we therefore consider the isotropic approximation first.

In the isotropic approximation, the free energy functional takes the form

$$\Delta F = \frac{n_0 k_B T}{2} \int d^3x [a_2 u(\mathbf{x})^2 - a_3 u(\mathbf{x})^3$$

$$+ a_4' u(\mathbf{x})^4 + b \mid \nabla u \mid^2] , \quad (3.1)$$

where ΔF represents the free energy difference between the inhomogeneous system containing the liquid-solid interface and the same volume of uniform solid or liquid. The coefficient b can be worked out from Eq. (2.10) if we assume that $u(\mathbf{x})$ is real, and that it represents the amplitude of any one of the 12 [110] amplitudes, all of which are locally equal. The result is

$$b = -\tfrac{1}{4} \sum_{\mathbf{K}_{110}} C''(K_{110})(\hat{\mathbf{K}}_{110} \cdot \hat{\mathbf{z}})^2 = -C''(K_{110}) , \quad (3.2)$$

where the sum runs over the 12 [110] reciprocal-lattice vectors. and $\hat{\mathbf{K}}_{110}$ denotes a unit vector in the direction of $\mathbf{K}_{110}$.

To obtain the liquid-solid interfacial tension for a planar interface, in this isotropic approximation, we assume that u varies only in the z direction. At melting, the relations (2.14) through (2.18) determine the coefficients a_2, a_3, and a_4', and the amplitude u in the solid phase. The interfacial tension is determined by minimizing ΔF with respect to $u(z)$, subject to the boundary conditions that $u(z) \rightarrow 0$ deep in the liquid ($z \rightarrow +\infty$) and that $u(z)$ approach its solid value (2.18) deep in the solid ($z \rightarrow -\infty$). The appropriate Euler-Lagrange equation can be solved analytically, and the corresponding surface free energy $\tau = \Delta F / A$ (where A is the surface area) and surface profile are given by

$$\tau = (n_0 k_B T / 6) u^2 (a_2 b)^{1/2} , \quad (3.3)$$

$$u(z) = (u_0/2)[1 + \tanh(\alpha z)] , \quad (3.4)$$

$$\alpha = [a_2/(4b)]^{1/2} . \quad (3.5)$$

We have applied this simple approximation to two bcc metals, the simple metal Na, and the transition metal Fe. The calculation requires knowledge of the structure factor of the liquid, $S(k)$ and the direct correlation function $C(k)$, as well as their temperature derivatives at the melting point. Rather than obtain these from experiment, we have carried out the following procedure. For Na, we use a hard-sphere structure factor, which is available analytically in the Percus-Yevick approximation, and which provides an adequate fit to the experimental structure factor of Na near its melting point, especially in the vicinity of the principal peak. The effective hard-sphere diameter is determined as a function of temperature by means of a variational principle based on a hard-sphere reference system; this procedure is described in detail elsewhere.[16] The resulting values for the hard-sphere packing fraction, as well as the coefficients a_2, da_2/dT, and b, are listed in Table I.

For Fe, which is not a simple metal like Na, and which therefore does not have easily calculated pairwise interactions in the liquid state which can be treated by the hard-sphere variational principle, we obtain a_2 and b by assuming a hard-sphere packing fraction equal to that obtained variationally for Na at melting. We determine da_2/dT by making the assumption that the derivatives $T(da_2/dT)$ at melting are equal for Na and for Fe; this assumption seems reasonable if we imagine that the structure factors $S(k)$ of both metals change by the same amount at fixed k for the same *fractional* change in temperature. The other parameters for the Fe calculation are also listed in Table I.

The calculated interfacial tensions and surface width parameters for Na and Fe, in the isotropic approximation, are also listed in Table I, along with the measured values quoted by Taylor[17] and Turnbull.[18] The agreement is quite reasonable, especially considering the simplicity of our assumptions.

B. Corrections due to anisotropy

The approximation just described can be generalized to allow for the variation of interfacial tension (and interfacial density profile) with crystalline direction. In the isotropic approximation, the parameters u_{110}, representing the amplitudes of the 12 [110] Fourier density coefficients, are assumed all equal, not only in the bulk, but also

TABLE I. Input parameters and calculated results for Na and Fe. Columns are the coefficients a_2, $(da_2/dT)_{T=T_m}$, and b, all as defined in the text (in cgs units); the increase Δ in entropy per atom on melting; the theoretical and experimental liquid-solid interfacial tensions (in erg/cm^2); and the width w (in $\mathring{A}$), defined as twice the length appearing in the hyperbolic tangent density profile of the surface.

Element	a_2	da_2/dT	$10^{16}b$	Δ/k_B	τ_{th}	τ_{exp}	w
Na	4.87	0.0067	13.8	0.85	11.7	20[a]	6.65
Fe	4.88	0.00137	7.27	0.99	151	204[b]	4.88

[a]J. W. Taylor, Philos. Mag. **46**, 857 (1955).
[b]D. Turnbull, J. Appl. Phys. **21**, 1022 (1950).

in the surface region. Actually, these coefficients need not all be equal near the surface, but divide into several classes, each with a different amplitude in the surface region, depending on the direction cosine between the particular [110] vector and the surface normal. This difference gives rise to a surface tension which depends on surface orientation.

To be specific, we consider a [111] surface of a bcc crystal. The 12 [110] reciprocal-lattice vectors divide into two classes, each containing six vectors. Within each class, all vectors must have equal amplitude in the surface region, because they have the same direction cosine with respect to the surface normal. Calling these amplitudes u and v, and assuming that these vary only in the z direction (defined to be perpendicular to the interface), we obtain the following form for the free energy functional:

$$\Delta F = \frac{n_0 k_B T}{2} \int \left[a_2(\tfrac{1}{2}u^2 + \tfrac{1}{2}v^2) - a_3(\tfrac{3}{4}u^2 v + \tfrac{1}{4}v^3) \right.$$
$$+ a_4'(\tfrac{2}{9}u^4 + \tfrac{2}{9}v^4 + \tfrac{5}{9}u^2 v^2)$$
$$\left. + b\left[\frac{du}{dz}\right]^2 \right] d^3x \ . \tag{3.6}$$

This functional form is constructed according to the following principles. At any power (say the nth power) of the order parameters u and v, there exist several symmetry classes of polygons with n sides, each side consisting of a [110] reciprocal-lattice vector. All the polygons in a given symmetry class can be transformed into one another by an operation of the cubic point group. We make the ansatz that all polygons with the same number of sides have the *same* coefficient. This is not necessarily guaranteed by symmetry [at fourth order, for example, as can be seen from Eq. (3.6), there are three sets of quadrilaterals, each of which may have a different coefficient], but if different coefficients are assumed for each set, there is no convenient way to fix these coefficients empirically.

The free energy functional is fully determined by (3.6), given the coefficients from Sec. III, and the ansatz just mentioned, and one may calculate the surface tension in the [111] direction by minimizing the functional with

respect to the two variables u and v. This minimization leads to two Euler-Lagrange equations

$$\frac{d^2 u}{dz^2} = \frac{u}{36b}[18a_2 - 27va_3 + (16u^2 + 20v^2)a_4'] \ , \tag{3.7a}$$

$$a_2 v - \tfrac{3}{4}(u^2 + v^2)a_3 + (8v^3 + 10u^2 v)\frac{a_4'}{9} = 0 \ , \tag{3.7b}$$

which may be solved numerically, subject to the boundary conditions $u = v = (a_2/a_4')^{1/2}$ at $(z \to -\infty,)$, i.e., deep within the solid. The resulting surface tension and surface profile are given in Table II and in Fig. 1.

A similar procedure may be used to calculate the surface tensions and surface profiles in other symmetry directions. In the [100] direction, for example, the set of 12 [110] reciprocal lattice vectors breaks up into two sets, containing eight and four vectors respectively, with amplitudes u and v, the members of each set having the same direction cosine to the surface normal. The free energy functional is found to take the form

$$\Delta F = \frac{n_0 k_B T}{2} \int d^3x \left[a_2(\tfrac{2}{3}u^2 + \tfrac{1}{3}v^2) - a_3 u^2 v \right.$$
$$\left. + a_4'(\tfrac{2}{3}u^2 + \tfrac{1}{3}v^2)^2 + b\left[\frac{du}{dz}\right]^2 \right] \ , \tag{3.7c}$$

where the various quartic coefficients have been assumed equal as in Eq. (3.6). For a [110] face, the set of 12 [110] reciprocal lattice vectors can be divided into *three* sets with different amplitudes, containing eight, two, and two vectors, respectively, having amplitudes u, v, and w. The free energy functional in this case is

$$\Delta F = \frac{n_0 k_B T}{2} \int \left[a_2(\tfrac{2}{3}u^2 + \tfrac{1}{6}v^2 + \tfrac{1}{6}w^2) - a_3(\tfrac{1}{2}u^2 v + \tfrac{1}{2}u^2 w) \right.$$
$$\left. + a_4'(\tfrac{12}{27}u^4 + \tfrac{1}{27}v^4 + \tfrac{1}{27}w^4 + \tfrac{4}{27}u^2 v^2 + \tfrac{4}{27}u^2 w^2 + \tfrac{1}{27}w^2 v^2 + \tfrac{4}{27}u^2 vw) + \tfrac{4}{5}b\left[\frac{du}{dz}\right]^2 + \tfrac{1}{5}b\left[\frac{dv}{dz}\right]^2 \right] d^3x \ . \tag{3.8}$$

The coupled Euler-Lagrange equations corresponding to (3.7) and (3.8) can be solved numerically; the resulting surface tensions are given in Table II along with those of Oxtoby and Haymet; the surface profile for the [100] and [111] cases are shown in Fig. 2. The anisotropy is evidently quite small. Also, the difference in amplitudes between u and v as they cross the interface is not very large, either between different amplitudes on the same face, or among different faces. (The same is true for the [110] profile, which we have not shown.)

TABLE II. Orientation dependence of surface tension of Na (in erg/cm²)

	[111]	[110]	[100]
Present results	11.0	11.6	11.5
Oxtoby and Haymet[a]	11.0		11.4

[a]Reference 11.

C. Effect of density difference between solid and liquid

The density difference between solid and liquid does not appear explicitly in the theory just described. Nonetheless, it is not assumed to vanish, but is present *implicitly*, via terms of the form (2.5). Consider, for example, the [111] interface. In the absence of a density difference, but including only the 12 [110] reciprocal-lattice vectors, we obtain a free energy functional of the form (3.6). We may include the solid-liquid density difference to lowest order
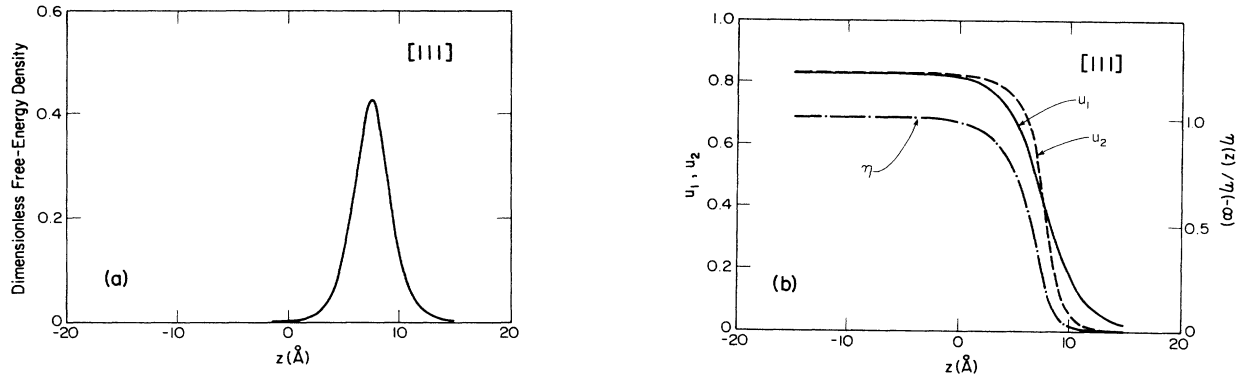
FIG. 1. (a) Excess Helmholtz free energy density per unit area for the [111] surface of Na. Plotted is the dimensionless integrand of Eq. (3.6) as a function of distance z into the liquid (in A). (b) Order parameter amplitudes u, v, and η as a function of z for the [111] interface of Na, plotted as in (a). Because of the fitting procedure described in the text, η is guaranteed to reduce to the experimental fractional liquid-solid density difference deep within the solid.

by adding to (3.6) a term of the form

$$\Delta F' = \frac{n_0 k_B T}{2} \int d^3x \left[c\eta^2 + \tfrac{1}{2}d(u^2\eta + v^2\eta) + e \left[\frac{d\eta}{dz} \right]^2 \right],$$ (3.9)

where $\eta \equiv u_{K=0}$ is the fractional density change on freezing.

We now argue that the term involving $e(d\eta/dz)^2$ can be neglected. First, the amplitude η is typically much smaller than the amplitude u of the [110] Fourier components of density in the solid. Secondly, the coefficient e of $(d\eta/dz)^2$ is $-\tfrac{1}{4}C''(K=0)$, which is typically much smaller than the value of $C''(K)$ for K in the vicinity of a [110] reciprocal-lattice vector.

If the term in $(d\eta/dz)^2$ can be neglected in the free energy functional, the Euler-Lagrange equation corresponding to $\eta(z)$ reduces to a purely algebraic equation, namely,

$$\eta = -\frac{d}{4c}(u^2 + v^2)$$ (3.10)

which is plotted in Fig. 1. The parameter d/c can be fitted to the experimental density difference between solid and liquid densities. The coefficient c can be obtained from the experimental compressibility, via the relation $c = 1/S(0) = (n_0 k_B T K_T)^{-1}$ where K_T is the isothermal compressibility. Thus d can be deduced from experiment also. This fitting procedure has been followed in Fig. 1, where the calculated $\eta(z)$ is therefore *guaranteed* to reduce to the experimental liquid-solid density difference deep within the solid.

The corresponding procedure for the [100] interface leads to the Euler-Lagrange equation

$$\eta = -\frac{d}{2c} \left[\frac{2}{3}u^2 + \frac{1}{3}v^2 \right]$$ (3.11)

the solution to which is shown in Fig. 2; and for the [110] interface
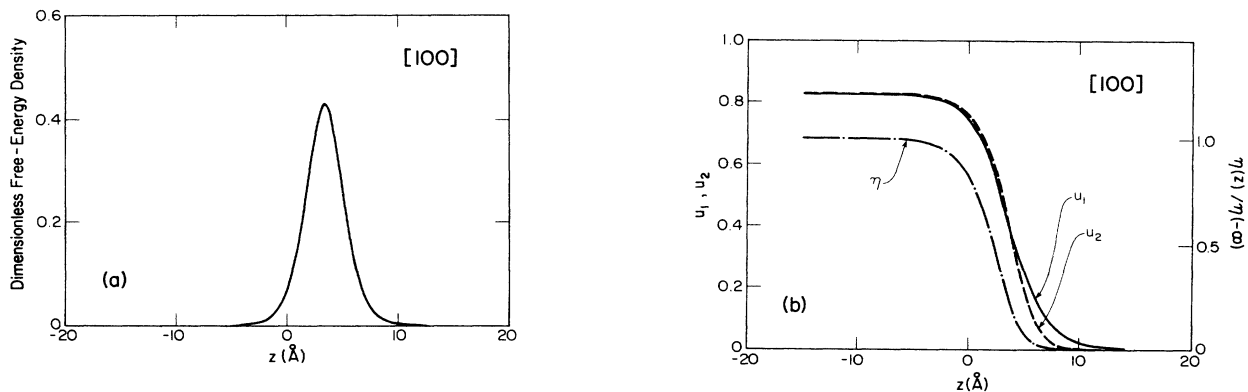
$$\eta = -\frac{d}{12c}(4u^2 + v^2 + w^2) .$$

FIG. 2. (a) and (b) excess Helmholtz free energy density and order parameters u, v, and η for the [100] interface, plotted as in Fig. 1.

As noted earlier, when the density difference between the solid and liquid is included in the manner just described, the quartic coefficient a_4 is renormalized relative to its value when the density change is taken as zero. If we call the renormalized coefficient a_4', then a_4' is related to a_4 by the equation

$$a_4' = a_4 - d^2/(4c) .$$ (3.12)

Note that it is a_4' rather than a_4 which is fitted empirically to the heat of fusion. Thus the calculated free energy functional automatically includes the effects of the solid-liquid density difference.

D. Empirical law for liquid-solid surface tension

If one is willing to make the isotropic approximation, the formalism just described permits one to construct a simple empirical formula for the liquid-solid interfacial tension of any bcc element. From Eqs. (2.14)—(2.18) and the relationship (3.3), we may deduce for the interfacial tension

$$\tau = \frac{n_0 \Delta}{3(da_2/dT)} (a_2 b)^{1/2} ,$$ (3.13)

where Δ is the increase in entropy per atom on melting, and the other quantities are evaluated at their melting point. Substituting (2.13) and (3.2) for a_2 and b gives

$$\tau = \frac{n_0 \Delta \dfrac{12}{S(K)} [-C''(K)]^{1/2}}{3 \dfrac{d}{dT} \left[\dfrac{12}{S(K)} \right]}$$ (3.14)

which may in principle be used to compute the surface tension of any bcc metal at melting, given measurements of the relevant bulk quantities and their temperature derivatives. We can, however, make further assumptions to simplify this formula. As in Sec. III A, we assume that $S(K)$ has a universal value at the melting temperature (computer simulation typically gives around 2.85).[19] We also assume that the temperature derivative in the denominator varies as A/T_m where A is a universal constant and T_m is the melting temperature. Finally, we write

$$C''(K) \equiv \sigma^2 \frac{d^2 C}{d(\sigma K)^2} ,$$ (3.15)

where σ is the effective, variationally determined hard-sphere diameter at melting. Since the effective hard-sphere *packing fraction* at melting is typically[20]

$$\eta \equiv \frac{\pi}{6} \sigma^3 n_0 \sim 0.45 ,$$

we see that $\sigma \sim n_0^{-1/3}$ at melting. Furthermore, the derivative $d^2 C/d(\sigma K)^2$ has a *universal* value at melting for K equal to a [110] reciprocal-lattice vector, then, combining all these empirical assumptions, we obtain

$$\tau = K n_0^{2/3} T_m \Delta ,$$ (3.16)

where K is a universal constant. Equation (3.16) states that the *liquid-solid interfacial tension is proportional to*

TABLE III. Surface tension τ of some bcc elements, from the empirical law (3.16). The constant K is fitted so as to give a surface tension of 11.7 erg/cm^2 for Na. Experimental values, where available, are in brackets.

Element	n_0 (10^{22}/cm^3)	H_f (cal/g-mol)	τ (erg/cm^2)
Na	2.44	630	11.7 [20][a]
K	1.27	574	6.89
Rb	1.04	525	5.52
Cs	0.837	500	4.55
Li	4.48	1100	30.6 [30][a]
Ba	1.48	1830	24.4
V	6.58	4200	151.0
Nb	5.07	6500	195.0
Ta	5.07	7500	225.0
Cr	7.48	3600	141.0
Mo	5.87	6600	220.0
W	5.76	8420	277.0
Fe	7.65	3560	142 [204][b]
Eu	1.99	2500	41.0

[a]J. W. Taylor, Philos. Mag. **46**, 857 (1955).
[b]Turnbull, J. Appl. Phys. **21**, 1022 (1950).

the heat of fusion per surface atom, a very reasonable empirical hypothesis which we have now "derived," in a simple but plausible way. Equation (3.16) is identical to the formula proposed by Turnbull[18] many years ago to account for some of his measurements on the solid-liquid interfacial tensions of simple metals.

Table III shows the predictions of Eq. (3.16) for the liquid-solid interfacial tension of a number of bcc metals at melting. The unknown constant K is fitted to give $\tau = 11.7$ erg/cm^2 for Na at melting. Agreements with experimental data is quite reasonable where comparison is possible.

E. Discussion

The model presented here, although very simple, certainly suggests that the density-functional approach is a reasonable way to calculate the surface energies and surface profiles of the solid-liquid interface. More elaborate calculations, involving more Fourier components of the density and an expansion of the free energy to higher powers of these Fourier components, are undoubtedly necessary if quantitative accuracy is to be achieved. It may also be necessary to go beyond the gradient approximation, since, the widths we obtain are quite narrow of (of the order of two or three atomic layers). However, the present scheme has two advantages: It allows surface properties to be obtained quickly and easily from bulk ones; and it permits a rapid survey of many surface properties for a wide variety of materials (possibly even alloys) which can then be studied by more accurate approaches. The density-functional approach certainly seems to be one of the most promising available at present; the principal other contender is probably numerical simulation, which requires a major effort for each calculation, especially for surfaces.

It is of interest to contemplate the possible application of this method to other structures. For the fcc structure, the use of a single set of reciprocal lattice vectors leads to an unphysical second-order liquid-solid transition, as noted earlier. One must include at least the [111] and the [200] vectors to obtain a first-order transition. This makes the fitting of the relevant coefficients to experimental bulk properties more complicated than in the bcc case, though not impossible.

The diamond structure presents other possibilities. The principal peak in the structure factor corresponds roughly to the [220] reciprocal-lattice vector in the solid (there is a considerable decrease in density on freezing). The amplitude of this [220] vector is presumably the most appropriate order parameter for a density-functional theory of the freezing of diamond structures. Even though the [220] vectors form only the third shortest set of reciprocal-lattice vectors in the diamond structure, they are more numerous, and their atomic structure factor in the solid phase is much larger, than the [111] and [200] sets. Thus this order parameter is not unreasonable. We may speculate that the reason for the big decrease in density of Si and Ge on freezing is to allow the structure to take advantage of the lowering of energy made possible by lining up the [220] reciprocal-lattice vectors with the peak of the liquid structure factor.

ACKNOWLEDGMENTS

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