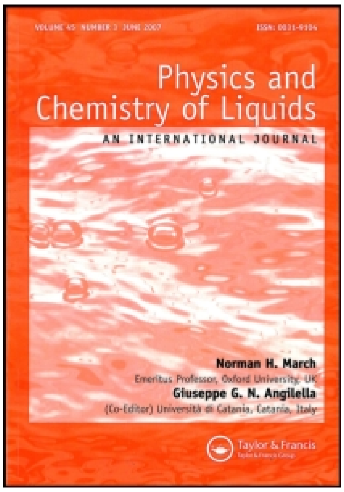

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DENSITY FUNCTIONAL MEAN FIELD THEORY OF CRYSTAL-MELT INTERFACES

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We present a density-functional approach for crystal-melt interface tension of simple metals. The theory is applied to simple bcc metal Na, and simple fcc metals Al and Pb. Comparing with available experimental surface tensions of these elements, the calculated results are in fairly good agreement with the measurements by conjecturing that the 10-90 width of the interfacial transition zone is about ten atomic layers, which is motivated from computer simulation.

KEY WORDS: Density functional, crystal-melt interface, surface tension, Debye Waller factor.

Knowledge of the crystal-melt interfaces is essential for progress in understanding solidification and nucleation from the liquid to crystal. Attention has been focused both on the thermodynamic properties of the crystal-melt interface (especially the surface free energy which plays an important role in determining the equilibrium morphology of crystals) and on the microscopic structure of the interface (such as the density profile width).

Unfortunately, surface tension measurements are extremely difficult to make experimentally for crystal-melt interfaces. Direct measurements of surface tension, which are made by observing the intersection angle of liquid, crystal, and grain boundary surfaces, and using a balance of forces argument, is only available for bismuth[1], water[2], succinonirile[3], cadmium[4], and alkali halides[5]. Indirect measurements[6] according to nucleation theory to estimate surface tension are also available for some metals. However, there remain some questions for the nucleation experiments, such as the problem of puring and homgenity, or the orientation-dependence of the surfaces. Many computer simulations[7-19] have been carried out for studying the interfacial properties. Most works focus on fcc and hcp crystals. Some theoretical studies are also proposed on calculation of surface tension of the crystal-melt interface[20-22]. In this paper, we present a density-functional theory to calculate the interfacial tension of the crystal-melt interface. We apply the theory to simple metals bcc Na and fcc Al and Pb. The calculated results agree fairly well with the experimental measurements.

Our work starts from the following expansion for the free energy functional[23,24], namely, considers the hot solid near melting as a perturbation on the liquid, associated with the one particle density $\rho(\mathbf{r}_1)$:

$$\beta\Omega[\rho] = \beta F_{\mathrm{id}} - \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 C(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho(\mathbf{r}_1) - \rho_0][\rho(\mathbf{r}_2) - \rho_0], \tag{1}$$

where $\beta = 1/(k_B T)$; ρ_0 is the number density of liquid; $C(r)$ is the direct pair correlation function, and F_{id} is the free energy of an ideal gas. Such ideas have done very well on the liquid-solid freezing properties[25]. Then, we expand the solid phase density in its Fourier space:

$$\rho(\mathbf{r}_1) = \rho_0\left(1 + \sum_n U_n^s e^{i\mathbf{K}_n \cdot \mathbf{r}_1}\right), \tag{2}$$

where $\mathbf{K}_n$ is the set of reciprocal lattice vectors of the solid; $U_0^s = (\rho_s - \rho_0)/\rho_0$ is the fractional density change on melting, and ρ_s is the average density of the solid. The amplitudes U_n are taken as the set of order parameters to describe the first-order transition. Since the theory is in the mean-field formalism, the fluctuations in the order parameters are not included. Generalizing Eq. (2) to a nonuniform crystal-melt interface, we have

$$\rho(\mathbf{r}_1) = \rho_0\left[1 + \sum_n U_n(\mathbf{r}_1) e^{i\mathbf{K}_n \cdot \mathbf{r}_1}\right]. \tag{3}$$

Here, $U_n(\mathbf{r}_1)$ is smoothly changed from zero on the liquid side to U_n^s on the solid side. Therefore we can use the gradient expansion on the order parameters,

$$U_n(\mathbf{r}_2) = U_n(\mathbf{r}_1) + (\mathbf{r}_2 - \mathbf{r}_1)\cdot\nabla U_n(\mathbf{r}_1) + \tfrac{1}{2}[(\mathbf{r}_2 - \mathbf{r}_1)\cdot\nabla]^2 U_n(\mathbf{r}_1). \tag{4}$$

With Eqs (2), (3) and (4), Eq. (1) can be reduced to

$$\beta\Omega[\rho] = \beta\int f(\rho(\mathbf{r}_1))d\mathbf{r}_1 - \frac{1}{4}\int d\mathbf{r}_1[C''(0)(\nabla U_0)^2 + \sum_{n\neq 0} C''(K_n)(\hat{K}_n\cdot\hat{r}_1)^2(\nabla U_n)^2], \tag{5}$$

where

$$\beta\int f(\rho(\mathbf{r}_1))d\mathbf{r}_1 = \beta F_{\mathrm{id}} + \frac{1}{2}\rho_0\iint d\mathbf{r}_1 d\mathbf{r}_2 C(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho(\mathbf{r}_1) - \rho_0]\left[\sum_n U_n(\mathbf{r}_1)e^{i\mathbf{K}_n\cdot\mathbf{r}_2}\right] \tag{6}$$

is the free energy for an uniform phase, and $C''(k) = d^2C(k)/dk^2$, $C''(0) = d^2C(k)/dk^2|_{k=0}$. Considering a planar interface perpendicular to the z-direction at pressure p and melting temperature T_m, the surface tension takes the form

$$\begin{aligned}\tau_{sl} = {} & \int_{-\infty}^{+\infty} dz[f(\rho(z)) - \mu\rho(z) + p] - \frac{\rho_0 k_B T_m}{4} \\ & \times \int dz\left[C''(0)\left(\frac{dU_0}{dz}\right)^2 + \sum_{n\neq 0} C''(K_n)(\hat{K}_n\cdot\hat{z})^2\left(\frac{dU_n}{dz}\right)^2\right].\end{aligned} \tag{7}$$

Here μ is the chemical potential. In order to calculate the surface tension, it is required to minimize Eq. (7) with respect to the order parameter profiles. We make the ansatz that the profiles are given by

$$U_n(z) = \frac{U_n^s}{2}[1 + \tanh(\alpha z)], \tag{8}$$

where the U_n^s are the values of the order-parameters on the solid side, and α is the variational parameter. The final results are as follows: the surface tension

$$\tau_{sl} = 2(I_A I_B)^{1/2}, \tag{9}$$

and

$$w = 2.2/\alpha \tag{10}$$

with

$$\alpha = (I_A/I_B)^{1/2}, \tag{11}$$

$$I_A = \int_{-\infty}^{+\infty} \omega(\rho(z))d(\alpha z), \tag{12}$$

$$I_B = -\frac{\rho_0 k_B T_m}{12}\left[C''(0)U_0^{s2} + \sum_{n\neq 0}(\hat{K}_n\cdot\hat{z})^2 C''(K_n)U_n^{s2}\right], \tag{13}$$

where $\omega(\rho(z)) = f(\rho(z)) - \mu\rho(z) + p$, and w is the 10-90 width for the order parameter profile, which is a reasonable estimate of the interface width. From the above equations, we can calculate the surface tension by evaluating quantities I_A and I_B.

Generally it is not trivial to calculate integral I_A. Curtin[21] uses a weighted-density approximation to account for this nonlocal part of the Helmholtz free energy, and McMullen *et al.*[22] obtain this integral by numerical integration. However the interfacial widths calculated from both approaches are too narrow in comparison with the results of computer simulation, and the surface tension is quite sensitive to the form of the trial density. Therefore, to eliminate the effect of the uncertainties from different conjectures in calculating I_A, it is more reasonable to examine the product of surface tension and the width of the interface, which is related to the quantity I_B. This can be seen from the paper I and paper II[22] by McMullen and Oxtoby. Although they obtain significantly different results of surface tensions and surface widths with different assumptions of density profile, the products τw calculated from their one order-parameter derivation are very close. To evaluate I_B, we need the direct correlation function of the liquid $C(k)$ and order parameters U_n^s on the solid side. It is known that the hard-sphere correlation function is a good approximation of $C(k)$ for simple metals. Thus we use the hard-sphere model reference system to calculate $C''(k)$. It has been claimed by Ramakrishnan and Yussouff[24] that U_n^s is related to the Debey-Waller factor e^{-2W_n} by $\bar{U}_n^{s2} = e^{-2W_n}$, where $\bar{U}_n^s = U_n^s/(1 + U_0^s)$. From the Debye phonon theory of solids, we know that the Debye-Waller factor is related to the Debye temperature θ_D. Near melting, the Debye-Waller factor can be expressed as $W_n = (3\hbar^2 K_n^2 T_m)/(2Mk_B\theta_D^2)$, where T_m is the melting temperature, and M is the atomic mass of the element. Motivated from the computer simulation of the solid-liquid

Table 1 Input experimental data of bcc Na and fcc Al, Pb near melting. a_0 is the lattice constant of the crystal; T_m is the melting temperature; θ_D is the Debye temperature; ρ_0 is the number density of liquid; U_0^s is the fractional density increase at melting; and η is the hard-sphere packing fraction of the elements in the liquid state.

Element	a_0 (Å)	T_m (K)	θ_D (K)	ρ_0 (Å^{-3})	U_0^s	η
Na	4.313	371	158	0.0243	0.026	0.435
Al	4.13	933	428	0.0529	0.073	0.471
Pb	5.0	600	105	0.0310	0.032	0.455

interface[7–19], we conjecture that the interfacial width takes about ten atomic layers universally for the simple liquid elements, which means that the thickness of the surface is about 3 cubic lattice constant for fcc crystal elements and 3.7 cubic lattice constant for bcc crystal elements. In Table 1, we list the input experimental data for bcc element Na and fcc elements Al, Pb. Calculated results of the interfacial tensions and widths with the experimental surface tensions[6,26] of these simple metals are listed in Table 2.

We use only one order parameter for bcc Na, since it has been shown[25] that this is sufficient to describe the melting transition of solid to liquid and the contributions from the other order parameters are two orders of magnitude smaller than that of the first order parameter. For fcc metals, only some leading order parameters (we take twenty order parameters) are required to evaluate the solid-liquid surface tensions. This is because $U_n(z)$ for large K_n must decay to zero much faster than those of the small K_n, and $|C''(K_n)|$ also goes to zero very quickly as K_n becomes larger. We ignore the term $C''(0)U_0^{s2}$ since it is three orders smaller than the main term. Comparing the theoretical calculation with the indirect measurements quoted by Turnbull[6], we find that the agreement is fairly reasonable, considering the simplicity of our assumption and taking into account the uncertainty of the nucleation experiments.

In conclusion, we have presented a mean-field theory to carry out the calculation of the crystal-melt interfacial properties for simple metals. The estimated interfacial tensions of three simple metals are very reasonable upon comparison with available measurements. However calculation from first principles on general elements still remains a challenging problem.

Table 2 The calculated results of the interfacial tension τ_{th}, and the experimental interfacial tension τ_{ex}[6,26]; w is the 10–90 width of the interface.

Element	τ_{th} (erg/cm^2)	τ_{ex} (erg/cm^2)	w (Å)
Na	11	20	16
Al	88	93	12.4
Pb	35	33.3	15

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