Direct calculation of the crystal-melt interfacial free energies for continuous potentials: Application to the Lennard-Jones system

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Extending to continuous potentials a cleaving wall molecular-dynamics simulation method recently developed for the hard-sphere system [Phys.Rev.Lett 85, 4751 (2000)], we calculate the crystal-melt interfacial free energies, $\gamma$, for a Lennard-Jones system as functions of both crystal orientation and temperature. At the triple point, $T^* = 0.617$, the results are consistent with an earlier cleaving potential calculation by Broughton and Gilmer [J. Chem. Phys. 84, 5759 (1986)], however, the greater precision of the current calculation allows us to accurately determine the anisotropy of $\gamma$. From our data we find that, at all temperatures studied, $\gamma_{111} < \gamma_{110} < \gamma_{100}$. Comparison is made to the results from our previous hard-sphere calculation and to recent results for Ni by Asta, Hoyt and Karma [Phys. Rev. B, 66 100101(R) (2002)].

INTRODUCTION

The magnitude and orientational dependence (anisotropy) of the solid-liquid interfacial free energy, $\gamma_{sl}$, is a primary controlling parameter in the kinetics and morphology of crystal growth from the melt, especially in the case of dendritic growth. As a consequence, the ability to accurately measure or predict this quantity for specific materials is of significant technological and scientific importance. For most materials, the only experimental data for $\gamma_{sl}$ is extracted indirectly from nucleation data (assuming some level of classical nucleation theory), especially in the case of dendritic growth. Such indirect measurements tend to underestimate the actual interfacial free energy by 10-20% and represent orientational averages, so all information as to interfacial anisotropy is lost. Direct experimental measurements, usually involving contact angle studies, are quite difficult and relatively few in number, and, with the exception of a small number of studies on transparent organic materials, are not of sufficient precision to resolve anisotropy. This paucity of reliable direct experimental measurements on technologically useful materials (such as metals) has motivated the development of a variety of novel computational methods to determine $\gamma_{sl}$ via molecular simulation.

The interfacial free energy of a crystal-melt interface is defined as the reversible work required to form a unit area of interface. In a simulation this can be accomplished by constructing a continuous thermodynamic path between an initial system consisting of separated bulk crystal and liquid to a final state containing an interface. The value of $\gamma_{sl}$ is then determined by thermodynamic integration along that path. This is a tedious process and care must be taken to ensure that the process is reversible, i.e., integration along the path in both the forward and backward directions yields the same result (no hysteresis). The first such calculation on a crystal-melt interface was performed by Broughton and Gilmer on a system of particles interacting with a Lennard-Jones potential (truncated so that both the potential and the force vanish at 2.5$\sigma$, where $\sigma$ is the usual LJ diameter). To perform the thermodynamic integration they employed external cleaving potentials that were slowly turned on to separate the samples. The precise (rather complex) functional forms of the cleaving potentials were chosen, more or less by trial and error, to minimize hysteresis. The values of $\gamma_{sl}$ were determined to be 0.35(2), 0.34(2) and 0.36(2) (in units of $\varepsilon/\sigma^2$) for the [111], [100], and [110] crystal orientations, respectively. The numbers in parentheses give the uncertainties in the last digit shown. The main source of this error is the small amount of hysteresis in the cleaving of the liquid phase. Unfortunately, the precision of these results was not sufficient to resolve the anisotropy of the interfacial free energy for this system.

Recently, we have developed a modification of the Broughton and Gilmer approach in which planar cleaving walls, as opposed to cleaving potentials, are used to separate the phases. These walls are constructed out of the same type of particles as present in the system, with a 2-d geometry consistent with the symmetry of the interfacial orientation under study. This method was originally applied to the crystal-melt interface of a system of hard spheres and was shown to have sufficient precision to resolve the anisotropy with [111] being the lowest free energy face, followed by [100] and [110]. The cleaving wall method is complementary to
a method due to Hoyt, Asta and Karma[? ] in which the interfacial free energy is extracted from the interfacial stiffness, which is determined from the spectrum of fluctuations in interfacial position. The cleaving-wall method has an advantage in that it requires simulations with an order of magnitude fewer particles than those required for the fluctuation method ($O[10^4]$ vs. $O[10^5]$). The precision in the raw values of the interfacial free energies is greater for the the cleaving wall method than in the fluctuation approach (even considering the far smaller system samples); however, the fluctuation method yield somewhat more precise values of the anisotropy parameters since these are obtained from the anisotropy of the interfacial stiffness, which is far more anisotropic than the interfacial free energy.

In this work, we extend our cleaving wall approach to systems of particles interacting with continuous potentials, specifically applying it to the system of truncated Lennard-Jones (LJ) particles considered by Broughton and Gilmer. Our results at the triple point are consistent with Broughton and Gilmer’s calculation, but are of greater precision allowing us to resolve the anisotropy, which is found to differ slightly from that for the hard-sphere system[? ]. In addition, we determine the temperature dependence of $\gamma_{sl}$ along the coexistence curve. The magnitude of $\gamma_{sl}$ is shown to scale roughly linearly with the melting temperature (as predicted by the hard-sphere model[? ]).

THE CLEAVING WALL METHOD

The direct determination of the excess free energy of the crystal-fluid interface of a model system within a computer simulation can be achieved by thermodynamic integration along a reversible path beginning with separate crystal and fluid bulk systems prepared at the coexistence conditions and ending with a system containing a crystal-liquid interface at equilibrium. The interfacial free energy is calculated as the total work required to perform the above steps divided by the area of the constructed interface. In addition to the coexistence conditions, the result will also depend on the orientation of the crystal with respect to the interfacial plane. We will refer to the plane along which the crystal and liquid systems are split as the cleaving plane. The location of the cleaving plane in the crystal system is chosen in the center of the simulation box between two crystal layers, while in the liquid system the precise location is arbitrary.

The reversibility and precision of the thermodynamics integration process are very sensitive to the choice of cleaving potentials. The requirements for the cleaving potential are two-fold: First, the cleaving potential should perturb the system as little as possible. As a consequence, it is desirable that, in step 2, the potential introduces structure into the cleaved liquid that is compatible with the structure of the crystal layers. Second, the cleaving potential must be strong enough to prevent the particles from crossing the cleaving plane. Otherwise, the rearrangement of the boundary conditions in step 3 cannot be performed.

Broughton and Gilmer[? ] carefully designed a set of cleaving potentials for the truncated Lennard-Jones (LJ) system. However, their approach for constructing...
the cleaving potential was optimized specifically for the LJ system and is not easily adaptable to a general case. Here we outline an approach that is easily adaptable to systems with different interparticle interaction potentials and different crystal structures.

As was demonstrated in our recent calculation of the interfacial free energy for the hard-sphere system[?], the appropriate structure in the interfacial region of the fluid can be easily introduced by the potential of a pair of “cleaving walls”, made of properly oriented crystal layers, each interacting only with the particles on the opposite side of the cleaving plane. The wall particles are held fixed at the crystal lattice sites. When the two walls are far away from the cleaving plane, they do not interact with the system. Moving the walls closer to the cleaving plane introduces a cleaving potential whose structure is similar to that outside the crystal layers of the studied system. When a liquid system interacts with such a cleaving wall, it is expected to form an interfacial layer structure similar to that at the crystal-liquid interface. To achieve this, the interaction potential of the wall particles must be similar to that of the system particles.

Since interactions in the crystal are usually dominated by the short-range repulsive part of the potential, it is sufficient to choose the interaction potential of the wall particles as a monotonically decreasing function \( \phi(r) \) with a relatively small cut-off radius \( r_w \), which models the repulsive core of the interparticle potential in the system under investigation. Interaction of the system with each cleaving wall is then given by

\[
\begin{align*}
\Phi_1(r; z) &= \sum_j \phi(|r - R_j^{(1)} + nz|), \\
\Phi_2(r; z) &= \sum_j \phi(|r - R_j^{(2)} - nz|),
\end{align*}
\]

where \( R_j^{(1,2)} \) are the positions of the particles forming the walls, \( n \) is a unit vector normal to the cleaving plane, and \( z \) measures the distance of the walls to the cleaving plane.

Next, we need to ensure that the system on the one side of the cleaving plane interacts only with the wall on the other side of the plane. To achieve this, we use the monotonic character of the potential \( \phi(r) \) and define the cleaving potential as the minimum of the two wall potentials, namely

\[
\Phi(r; z) = \min(\Phi_1, \Phi_2),
\]

which decays to zero away from the cleaving plane, as long as the potential \( \phi(r) \) is chosen to be a positive monotonically decreasing function. To remove discontinuity of the gradient of \( \Phi \) at the points where \( \Phi_1 = \Phi_2 \), we slightly modify the minimum function as follows:

\[
m(x, y) = \begin{cases} 
  x, & x \leq y - \delta(x + y) \\
  y, & x \geq y + \delta(x + y) \\
  p(x, y), & \text{otherwise}
\end{cases}
\]

with

\[
p(x, y) = \frac{x + y}{4} (2 - \delta) - \frac{(x - y)^2}{4\delta(x + y)},
\]

and parameter \( \delta \) characterising the relative width of the interpolation region. We set \( \delta = 0.25 \) for the present study. The cleaving potential is defined as

\[
\Phi(r; z) = m(\Phi_1, \Phi_2).
\]

Even though the crystal system does not require additional ordering and, as proposed by Broughton and Gilmer, can be cleaved with a short-range repulsive potential centered at the cleaving plane, we have found that using the same cleaving potential for both crystal and liquid systems results minimizes the error during the thermodynamic integration in step 3.

To calculate the reversible work in steps 1, 2, and 4, we can use the wall position \( z \) as the integration coordinate. The reversible work is thus determined by evaluating the integral

\[
w_{1,2,4} = \int_{z_i}^{z_f} \left( \frac{\partial \Phi}{\partial z} \right) dz,
\]

where the angle brackets denote averaging over a simulation run at a fixed cleaving wall position. In steps 1 and 2, the initial position of the cleaving walls, \( z_i \), is just outside the range of the interaction potential determined by the cut-off radius \( r_w \). The final wall position \( z_f \) is determined by the requirement that the cleaving potential is sufficiently strong to prevent the particles from crossing the cleaving plane. In step 4, the initial and final positions of the walls are reversed. Because of the repulsive character of the cleaving potential, the work in steps 1 and 2 is expected to be positive, while in step 4 it is negative.

In step 3, the boundary conditions are gradually rearranged using a coupling parameter \( \lambda \). The total interaction energy in step 3 is given by

\[
U(\lambda) = (1 - \lambda) \sum_{i < j, AB} u(r_{ij}) + \lambda \sum_{i < j, AA} u(r_{ij}) = \sum_i \Phi(r_i; z_f),
\]

where the letters \( AB \) refer to the boundary conditions with crystal-crystal and liquid-liquid interactions across the cleaving planes, and \( AA \) refer to
the boundary conditions with crystal-liquid interactions (see the diagram). The last term represents the cleaving potential at the final wall positions in steps 1 and 2. The work done during step 3 is determined from the integral

\[ w_3 = \int_0^1 \left( \frac{\partial U}{\partial \lambda} \right) d\lambda, \]  

where

\[ \frac{\partial U}{\partial \lambda} = \sum_{i<j, AA} u(r_{ij}) - \sum_{i<j, AB} u(r_{ij}). \]  

RESULTS FOR TRUNCATED LENNARD-JONES POTENTIAL

In order to have direct comparison with the results of Broughton and Gilmer [7], we have used the same modification of the Lennard-Jones potential, namely [7]

\[ u(r) = \begin{cases} 4\epsilon \left( \phi(r) \right)^{12} - \left( \phi(r) \right)^{6} + C_1 & r \leq 2.3\sigma \\ C_2 \left( \phi(r) \right)^{12} + C_3 \left( \phi(r) \right)^{6} + C_4 \left( \phi(r) \right)^2 + C_5 & 2.3\sigma < r < 2.5\sigma \\ 0, & 2.5\sigma \leq r. \end{cases} \]

where \( C_1 = 0.016132\epsilon, C_2 = 3136.6\epsilon, C_3 = -68.069\epsilon, C_4 = -0.083312\epsilon, \) and \( C_5 = 0.74689\epsilon. \) (Note: the sign of \( C_4 \) was incorrectly reported as positive in Broughton and Gilmer’s original publication.) This potential has a continuous first derivative and a small discontinuity in its second derivative at \( r = 2.3\sigma. \)

To achieve optimal performance of the simulation at all stages of the cleaving process, we use a cell-assisted force evaluation method [7]. The simulation region is subdivided into cells with edge sizes just exceeding the interatomic interaction range. When atoms are assigned to cells according to their current position, only interactions between atoms in the same cell or in immediately adjacent cells needs to be considered. Such a method is particularly useful in step 3, where interaction forces must be computed for two different boundary conditions [see Eq. (4)]. With the cell-assisted method the additional computational effort is limited to the cell layers immediately adjacent to the cleaving planes. (Note, the cell subdivision is carried out in such a way that the cell boundary coincides with the cleaving plane.)

The insertion of the external cleaving potentials ("walls") breaks the translational symmetry of the system Hamiltonian, linear momentum is no longer strictly conserved. This leads to a problem for long runs in that the crystal, taken as a whole, can drift relative to the cleaving plane. To prevent this, we immobilize the innermost 2 crystal layers by assigning them an infinite mass. In the data-collection runs these fixed planes were 20 crystal layers away from the nearest crystal-melt interface, and should not have a significant effect on the interfacial properties. To check this, we have performed smaller simulations with identical cross-sectional area, but fewer crystal layers (where the interface is about 12-14 crystal layers distant from the fixed planes) and obtain results identical, within simulation error, to the larger systems.

For the present study, we calculate \( \gamma \) at both the triple point temperature of \( T^*=k_BT/\epsilon = 0.617 \) (as determined by Broughton and Gilmer [7]), and at higher temperatures \( k_BT/\epsilon = 1.0 \) and \( 1.5. \) The crystal-liquid coexistence parameters at these temperatures are summarized in Table I (Note the slightly negative pressure at \( k_BT/\epsilon = 0.617 \). We have found that \( k_BT/\epsilon = 0.618 \) is a better estimate of the triple point temperature for the modified LJ potential used here. However, to have a direct comparison with the results of [7], we have calculated interfacial free energy at the lower temperature.) The parameters are obtained by monitoring long simulation runs of the crystal-liquid interfacial systems. If the initial conditions are shifted from those at coexistence, such a system equilibrates itself through melting/freezing at the interfaces. During the runs, the pressure tensor profiles are monitored and the simulation box rescaled, if necessary, to remove any stress in the bulk crystal.

| \( T, k_B\epsilon^{-1} \) | \( \rho_c, \sigma^{-3} \) | \( \rho_l, \sigma^{-3} \) | \( P, \epsilon\sigma^{-2} \) |
|------------------------|-----------------|-----------------|-----------------|
| 0.617                  | 0.945           | 0.828           | -0.02           |
| 1.0                    | 1.005           | 0.923           | 4.95            |
| 1.5                    | 1.074           | 1.003           | 12.9            |

At each of the three temperatures, we calculate the interfacial free energy for three crystal orientations: [100], [110], and [111]. The cleaving wall is constructed from a single crystal layer for the [100] and [111] orientations and from two layers for the [110] orientation (this was necessary to prevent atoms from crossing through this non-close-packed face). As discussed in the previous section, the cleaving potential \( \phi(r) \) is constructed from the repulsive core of the LJ potential:

\[ \phi(r) = \begin{cases} 4\epsilon \left( \phi(r) \right)^{12} - \left( \phi(r) \right)^{6} + \epsilon, & r < r_w = 2^{1/6}\sigma \\ 0, & r_w \leq r. \end{cases} \]  

(10)
The results are summarized in Table II. For illustration of the method we show in Fig. 2 the thermodynamic integration integrand (Eq. 6) for steps 1, 2 and 4 for the [111] interface at $T^* = 0.617$. For that same interface and temperature, the integrand for step 3 (Eq. 7) is shown in Fig. 3 with an inset highlighting the region of maximum hysteresis error.

Even though the relative statistical accuracy that can be achieved for a given duration of the simulation run is about the same for all temperatures and orientations (approximately 0.5%), we see that the relative error range in Table II increases with the temperature, especially for the [111] orientation. This may be due to a particular choice of the cleaving potential. More research is necessary to elucidate the origin of the hysteresis and ways to eliminate it.

The second source of hysteresis is the fluctuation in the interface position at the end of step 4. When the cleaving potential is removed from the interfacial system in step 4, the position of the interface is no longer tied to the cleaving plane. Because the system contains two interfaces, they can change their position without disturbing system equilibrium by the process of melting at one interface and simultaneous freezing at the other interface. The difficulty in verifying the reversibility of step 4 is that the mobility of the interfaces causes the reverse process to follow a slightly different thermodynamic integration path. To deal with this problem, we try the reverse step 4 process on the interfacial systems after several equilibration runs of various duration and select the one with the path closest to the forward process. The difference in the calculated work during the forward and reverse processes is accounted for in the estimate of the error range given in Table II.

**TABLE II: Interfacial free energy (in units of $\epsilon \sigma^{-2}$) for the truncated Lennard-Jones potential for selected temperatures and crystal orientations. Numbers in parentheses indicate two standard deviation error bars (plus an estimate of the hysteresis error on the last digit(s) shown).**

|       | $T^* = 0.617$ | 1.0 | 1.5 |
|-------|--------------|-----|-----|
| $\gamma_{100}$ | 0.371(3) | 0.562(6) | 0.84(2) |
| $\gamma_{110}$ | 0.360(3) | 0.543(6) | 0.82(2) |
| $\gamma_{111}$ | 0.347(3) | 0.508(8) | 0.75(3) |

**ANALYSIS AND SUMMARY**

The error bars on the calculations described above are small enough to resolve the anisotropy in the interfacial free energy for the Lennard-Jones system. While we have determined $\gamma_{sl}$ only for the [100], [110] and
[111] directions, it is possible to extract from these data some information as to the full angular dependence of the free energy. Defining the orientation unit vector $\mathbf{n}$ as the unit vector perpendicular to the interfacial plane, one defines an orientation dependent interfacial free energy $\gamma(\mathbf{n})$, which can be parameterized by an expansion in terms of cubic harmonics. One such expansion, due to Fehlner and Vosko, has been recently applied to the interfacial free energy of Ni/Cu alloys by Asta, et al.\[? \] In terms of the Cartesian components of $\mathbf{n} = \{n_1, n_2, n_3\}$, this expansion (truncated at sixth-order) is

$$\gamma(\mathbf{n}) = \gamma_0 \left[ 1 + \epsilon_1 \left( \sum_{i=1}^{3} n_i^4 - \frac{3}{5} \right) + \epsilon_2 \left( \sum_{i=1}^{3} n_i^4 + 66 n_1^2 n_2^2 n_3^2 - \frac{17 \gamma^2}{7} \right) \right],$$

where $\gamma_0$ is the orientationally averaged interfacial free energy and $\epsilon_1$ and $\epsilon_2$ are expansion coefficients. This parameterization has an advantage over the so-called "Kubic Harmonic" expansion\[? \] that has been used recently to parameterize free energy anisotropy in metals\[? \] in that the expansion terms are orthogonal\[? \]. For the orientations studied here this expansion becomes

$$\gamma_{100} = \gamma_0 \left[ 1 + \frac{2}{5} \epsilon_1 + \frac{4}{7} \epsilon_2 \right]$$
$$\gamma_{110} = \gamma_0 \left[ 1 - \frac{1}{10} \epsilon_1 - \frac{13}{14} \epsilon_2 \right]$$
$$\gamma_{111} = \gamma_0 \left[ 1 - \frac{4}{15} \epsilon_1 + \frac{64}{63} \epsilon_2 \right]$$

Using our values for $\gamma$ for the [100], [110] and [111] orientations one can solve for the three parameters $\gamma_0$, $\epsilon_1$ and $\epsilon_2$:

$$\gamma_0 = \frac{10 \gamma_{100} + 16 \gamma_{110} + 9 \gamma_{111}}{35}$$
$$\epsilon_1 = \frac{35 \gamma_{100} - 8 \gamma_{110} - 27 \gamma_{111}}{22 \gamma_0}$$
$$\epsilon_2 = \frac{3}{22 \gamma_0} (\gamma_{100} - 4 \gamma_{110} + 3 \gamma_{111})$$

The anisotropy parameters for the Lennard-Jones system studied here, as well as those for the hard-sphere system calculated from the data from our earlier calculation\[? \], are summarized in Table III. Also included in Table III are the values of $\frac{\gamma_{110} - \gamma_{111}}{\gamma_0}$, which also serve to quantify the anisotropy. The error bars in $\gamma_0$ are smaller than those for the raw interfacial free energies since $\gamma_0$ represents a weighted average of similar numbers - a process that decreases statistical error. The anisotropy parameters represent differential quantities involving differences between similar numbers (which magnifies relative error) so the relative error bars for those quantities are larger than in the raw data. This is in contrast to the fluctuation method\[? \] where the relative error in the interfacial free energy is larger than in the current study (despite the much larger systems), but the anisotropy parameters are more precisely determined due to the fact that in that method the anisotropy is determined from the anisotropy in the interfacial stiffness, which is far greater than that of the interfacial free energy itself. From the anisotropy parameters given in Table III the trend is observed that the anisotropy parameters increase in magnitude with increasing temperature, with $\epsilon_1$ becoming more positive and $\epsilon_2$ becoming more negative. In comparison with the hard-sphere values, the value of $\epsilon_2$ approaches the hard-sphere value as $T$ gets larger, but the value of $\epsilon_1$, which is at $T^* = 0.617$ quite close to the hard-sphere value, diverges away from the hard-sphere value as $T$ increases. Of course, in the limit of high temperatures, the Lennard-Jones system approaches an inverse twelth-power repulsive potential, not the hard-sphere potential, so one would expect the high temperature behavior of the anisotropy to approach that of the former potential. This implies that any perturbation theory for the interfacial free energy with a hard-sphere reference potential will not be adequate to predict anisotropy, and that a study of the anisotropy for a variety of different possible repulsive potentials would be very useful.

In recent work\[? \], we have pointed out that the interfacial free energy for simple systems with face-centered cubic (fcc) crystal structures can be quantitatively described by a hard-sphere model. It is useful to check this hypothesis here, since the LJ system is a standard molecular model that freezes to an fcc crystal,
and since the interfacial free energy was determined in this study directly and not indirectly from nucleation data. The hard-sphere model predicts

\[ \gamma_0(HS) = 0.617kT/\sigma^2. \tag{14} \]

where \( \sigma^2 \) is the hard-sphere diameter. For our Lennard-Jones system we can define an effective (temperature dependent) hard-sphere diameter using the Barker-Henderson criterion\[? \] from liquid-state perturbation theory

\[ \sigma_{\text{eff}} = \int_0^\infty \{1 - \exp[-u_r(r)/kT]\}dr, \]

where \( u_r(r) \) is the repulsive part of the potential, which we define in the Week-Chandler-Anderson sense\[? \] as the full potential truncated (and shifted) to zero beyond the minimum of the attractive well. This procedure yields values of \( \sigma_{\text{eff}} \) of 1.032\( \sigma \), 1.016\( \sigma \) and 1.000\( \sigma \), for \( T^* = 0.617, 1.0 \) and 1.5, respectively. Inserting these values into Eq. 14 yields predicted values of \( \gamma_0 \) (in units of \( \epsilon/\sigma^2 \)) of 0.36, 0.60 and 0.93, for \( T^* = 0.617, 1.0 \) and 1.5, respectively. The agreement with the values listed for LJ in Table III is excellent at the lower temperature, but overestimates the actual value by several percent at the higher temperatures. This agreement gives more evidence to support the general hypothesis\[? \] that the interfacial free energy of close packed systems is largely determined by packing considerations, not energy.

It is interesting to note that the anisotropy parameters \( \epsilon_1 \) and \( \epsilon_2 \) for the truncated LJ potential at the triple point (\( T^* = 0.617 \) and essentially zero pressure) are identical to those calculated\[? \] for Ni at 1.00 atm (also essentially zero pressure). The fact that the parameters are exactly the same for these two (essentially) zero pressure systems is, given the error bars, probably coincidental; however, the data does show that the anisotropy for Ni is better modelled by a LJ potential than by a hard-sphere potential. More study is required to determine the exact role that details of the potential play in determining interfacial anisotropy.

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