

Calculation of the crystal-melt interfacial free energy of succinonitrile from molecular simulation

Xiaobing Feng and Brian B. Laird^{a)}

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

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The crystal-metal interfacial free energy for a six-site model of succinonitrile [$\text{N}\equiv\text{C}-(\text{CH}_2)_2-\text{C}\equiv\text{N}$] has been calculated using molecular-dynamics simulation from the power spectrum of capillary fluctuations in interface position. The orientationally averaged magnitude of the interfacial free energy is determined to be $(7.0\pm 0.4)\times 10^{-3}\text{ J m}^{-2}$. This value is in agreement (within the error bars) with the experimental value $[(7.9\pm 0.8)\times 10^{-3}\text{ J m}^{-2}]$ of Maraşlı *et al.* [*J. Cryst. Growth* **247**, 613 (2003)], but is about 20% lower than the earlier experimental value $[(8.9\pm 0.5)\times 10^{-3}\text{ J m}^{-2}]$ obtained by Schaefer *et al.* [*Philos. Mag.* **32**, 725 (1975)]. In agreement with the experiment, the calculated anisotropy of the interfacial free energy of this body-centered-cubic material is small. In addition, the Turnbull coefficient from our simulation is also in agreement with the experiment. This work demonstrates that the capillary fluctuation method of Hoyt *et al.* [*Phys. Rev. Lett.* **86**, 5530 (2001)] can be successfully applied to determine the crystal-melt interfacial free energy of molecular materials. © 2006 American Institute of Physics. [DOI: 10.1063/1.2149859]

I. INTRODUCTION

The crystal-melt interfacial free energy, γ , is defined as the reversible work required to create an interface of unit area between a crystal and its coexisting melt. Both the magnitude and anisotropy (orientation dependence) of γ are crucial parameters in determining the kinetics and morphology of crystal nucleation and crystal growth.^{1,2} For example, the anisotropy of γ has a profound effect on dendritic growth, even small anisotropies on the order of 1%–4%, which are typical in metals, are significant in determining dendrite shapes.^{3,4} In addition, the nucleation rates of crystals^{5,6} and colloids⁷ exhibit a strong dependence on γ . Direct methods to measure γ experimentally are difficult and have been applied to relatively few materials.⁸ Such direct experiments often involve contact angle measurements and are often not of sufficient precision to determine the anisotropy in γ . However, the anisotropy of γ has been measured directly for a small number of transparent materials, such as succinonitrile and pivalic acid,^{9,10} water,¹¹ ammonium bromide,¹² and hexaoctyloxytriphenylene.¹³ For the majority of materials, the value of the interfacial free energy is extracted indirectly from nucleation data.^{1,14,15} Such indirect measurements are only accurate to 10%–20%, on average, due to the approximations inherent in classical nucleation theory, which is used to extract γ from nucleation rates. In addition, values so obtained represent averages over orientation, so all information as to anisotropy is lost. The difficulty in obtaining reliable experimental measurements has motivated the recent development of two complementary methods to determine γ via molecular simulation—the cleaving method^{16,17} and the fluctuation method.¹⁸ These methods have had success in determining both the magnitude and anisotropy of γ for simple

systems, such as hard spheres,^{17,19} inverse-power potentials,¹⁹ and Lennard-Jones particles,^{16,20,21} as well as for metals^{18,22,23} and metal alloys.²⁴ In this work, we apply the fluctuation method to calculate the interfacial free energy for a molecular system, namely, the organic compound succinonitrile.

In recent years, succinonitrile (SCN)



has become a material of interest in the study of solidification kinetics. SCN, like many metals of technological interest (for example, Fe), freezes into a body-centered-cubic (bcc) crystal structure.²⁵ Unlike face-centered-cubic (fcc) metals, however, SCN is low melting ($T_m=331\text{ K}$) and transparent, making it far easier to study experimentally. As a result, SCN is used as a model material for the study of the solidification kinetics of bcc-forming systems. Also, the succinonitrile-acetone alloy is used as a model material for the study of crystal growth and solidification of metal alloy systems.^{26,27} The importance of SCN in solidification studies has been underscored recently by its use in a series of experiments of bcc dendritic growth kinetics in microgravity.²⁸

The primary purpose of the current work is to determine whether the interfacial free energy of a molecular material can be accurately calculated by computer simulation. We have chosen SCN as a test candidate because experimental values for both the magnitude and the anisotropy of the interfacial free energy exist for comparison.^{9,10} The first measurement of SCN crystal-melt interfacial free energy by Schaefer *et al.*,²⁹ using a grain-boundary angle method, produced an orientationally averaged value of $(8.9\pm 0.5)\times 10^{-3}\text{ J m}^{-2}$. A recent measurement by Maraşlı *et al.*,³⁰ using a similar technique, obtained a somewhat lower value of $(7.9\pm 0.8)\times 10^{-3}\text{ J m}^{-2}$. In the same paper, Maraşlı *et al.* used their numerical model to reexamine the data of Schaefer

^{a)}Electronic mail: blaird@ku.edu

et al.,²⁹ obtaining a value of $8.02 \times 10^{-3} \text{ J m}^{-2}$. In the experiments, the orientation dependence of γ for a crystal with cubic symmetry is often represented to low order by the expansion,

$$\gamma(\theta) = \gamma_1[1 + \epsilon_4 \cos(4\theta)], \quad (1)$$

where $\gamma_1 = (\gamma_{100} + \gamma_{110})/2$, the average of the interfacial free energies of (100) and (110) interfaces. ϵ_4 is an anisotropy parameter, and θ the angle between the interface normal and the [100] direction in the crystal. The anisotropy parameter ϵ_4 was measured by both Glicksman and Singh⁹ and Muschol *et al.*¹⁰ to be 0.5% and $(0.55 \pm 0.15)\%$, respectively. This anisotropy is an order of magnitude smaller than that of pivalic acid, a model material for the study of the solidification of fcc materials, for which anisotropies of 5% (Ref. 9) and $(2.5 \pm 0.2)\%$ (Ref. 10) have been measured in separate experiments. The lower value of the anisotropy for bcc materials compared with that of fcc materials appears to be a general phenomenon and has been also observed in simulations of soft repulsive spheres¹⁹ and of various model potentials for iron.²³

II. MEASURING γ IN MOLECULAR SIMULATION

Two qualitatively different, but complementary, simulation methods have been proposed for the calculation of γ and its anisotropy. This first technique, the *cleaving method*,^{16,17,19,20} uses external potentials to construct a reversible path between an initial state consisting of separated bulk crystal and melt and a final state in which the crystal and melt coexist in equilibrium separated by an interface. The interfacial free energy is then directly determined for any crystal orientation as the reversible work along constructed path. (For a more complete review of both the cleaving and fluctuation methods see Ref. 31.)

In the *fluctuation method*,^{18,21–24,32} which is used in this work, the interfacial free energy is determined from the power spectrum of the fluctuations of the interfacial position. In this technique, a slab geometry is used for the simulation box, in which the longest direction is perpendicular to the average interfacial plane. Of the two directions parallel to the interfacial plane, one (defining the width W) is about one-half the length of the longest direction, and the other (defining the thickness b) is only a few atomic layers in length, which makes the interfacial position $h(x)$ a quasi-one-dimensional function of the distance along the width of the box. According to the capillary fluctuation method the equilibrium fluctuation spectrum of the crystal-melt interface height of a quasi-one-dimensional interface can be expressed as¹⁸

$$\langle |\tilde{h}(k)|^2 \rangle = \frac{k_B T}{bW\tilde{\gamma}k^2}, \quad (2)$$

where k_B and T are Boltzmann's constant and the melting temperature, respectively. The function $\tilde{h}(k)$ is the one-dimensional Fourier transform of $h(x)$ at wave number k , and b and W are as defined above. In this expression the angular brackets denote ensemble average. The quantity $\tilde{\gamma}$ is called

the interfacial stiffness and is related to the interfacial free energy by

$$\tilde{\gamma} = \gamma + \frac{d^2\gamma}{d\theta^2}, \quad (3)$$

where θ is the angle between the instantaneous interface normal and the average interface normal. Using Eq. (2), a plot of $\ln\langle |\tilde{h}(k)|^2 \rangle$ versus $\ln(k)$ should be linear with a slope of -2 . The value of the interfacial stiffness can be determined from the intercept of this plot. Once $\tilde{\gamma}$ has been measured for several interfacial orientations, the value of γ in each orientation is obtained indirectly by constructing a functional form for the dependence of γ on orientation and fitting $\tilde{\gamma}$ to obtain the best fits for the parameters of the functional form. One such expansion,³³ recently applied in a number of studies,^{20,21,24} is

$$\begin{aligned} \gamma(\hat{\mathbf{n}})/\gamma_0 = & 1 + \epsilon_1 \left(\sum_{i=1}^3 n_i^4 - \frac{3}{5} \right) \\ & + \epsilon_2 \left(3 \sum_{i=1}^3 n_i^4 + 66n_1^2n_2^2n_3^2 - \frac{17}{7} \right), \end{aligned} \quad (4)$$

where $\{n_1, n_2, n_3\}$ are the Cartesian components of the interface normal $\hat{\mathbf{n}}$, γ_0 is the orientationally averaged interfacial free energy, and ϵ_1 and ϵ_2 are expansion coefficients that quantify the anisotropy. Because the interfacial stiffness is an order of magnitude more anisotropic than γ itself,¹⁸ the interface fluctuation method, which directly measures $\gamma + \gamma''$, is very sensitive to small anisotropies in γ . This method thus gives very precise values of the anisotropy values (ϵ_1 and ϵ_2) in Eq. (4). However, because γ itself is not measured directly, but instead is indirectly fitted to the stiffness data using Eq. (4), the precision in the magnitude of γ is lowered.

The two methods can be viewed as complementary, in that the cleaving method gives a more precise value for the magnitude of γ (because γ is measured directly), whereas the anisotropy of γ is better resolved by the fluctuation method. The two methods have been shown to produce identical results (within numerical uncertainty) for a truncated Lennard-Jones system.^{20,21} Both methods indicate that $\gamma_{100} > \gamma_{110} > \gamma_{111}$ for all fcc materials studied. In addition, both methods have also shown that bcc systems have smaller magnitude and anisotropy in interfacial free energy than for fcc systems.^{19,23} These studies also have shown that the amplitude and anisotropy of the interfacial free energy is sensitive to the potential.^{19,23} For bcc soft spheres, the relationship $\gamma_{100} > \gamma_{111} > \gamma_{110}$ is found with the cleaving method.¹⁹ The calculation on Fe with the fluctuation method gives different ordering for different potentials of Fe.

It is our eventual goal to determine the interfacial free energy of succinonitrile using both the cleaving and fluctuation techniques. We have chosen the fluctuation method for this first study because there remain some technical issues with respect to optimal manner in which to construct cleaving walls for systems with Coulomb interactions.

TABLE I. The interface orientations and system sizes. The notation of Ref. 21 is used to label interface orientation, that is, the square brackets denote the “short” direction of the simulation box. The lattice constant of plastic SCN is 6.4095 Å at 332 K, which is the simulation temperature.

Orientation	Size (in Å)	Molecules
(100) [001]	25.64 × 192.28 × 388.37	14 400
(110) [001]	25.64 × 182.28 × 366.16	12 800
(111)[1 $\bar{1}$ 0]	27.19 × 157.00 × 403.61	12 960

III. THE INTERFACIAL FREE ENERGY OF SUCCINONITRILE

Before beginning simulations on succinonitrile, it is necessary to define a molecular interaction potential. We use a recently developed six-site force field for SCN.³⁴ This force field was chosen because it gives a melting temperature (332 K at 1 bar) that is very close to the experiment (331 K) and it has been shown that the interfacial free energy for fcc metals is strongly correlated with the melting temperature.³⁵ This six-site interaction potential was shown to produce a more well-defined crystalline state and better melting point than an earlier four-site force field.³⁶ In addition, the proportion of *trans* conformers (20%) in the crystalline state is in good agreement with the experiment (23%).³⁷

The molecular-dynamics (MD) simulations were performed using the DLPOLY package³⁸ at constant N , V , and T using a Berendsen thermostat to hold the temperature constant at the melting temperature (332 K). A 1 fs time step was used in all simulations. To create the equilibrium interface we use the following procedure.

- Slab-shaped crystal and melt samples were prepared separately.
- The crystal and melt slabs were joined together to form an interface. A gap is created at the interface to avoid overlapping, and the melt was scaled to maintain the correct density.
- Solid atoms were held fixed and melt molecules were allowed to fill the gap and come to equilibrium in contact with the frozen crystal. The total time for this step in each run was between 60 and 80 ps.
- The entire system was equilibrated for 50–60 ps.
- To generate data for analysis a total of between 3800 and 4200 system configurations were stored. The interval between each stored configuration was 100 fs.

A minimum of three interface orientations are needed to extract ϵ_1 , ϵ_2 , and γ_0 using Eq. (4). The orientations and system sizes used in this work are summarized in Table I. The accuracy of the fitting process is improved by using more than the minimum number of three orientations; however, because of the large number of molecules necessary in these simulations (14 000 molecules=84 000 atomic interaction sites) we were restricted to only three orientations for the present calculation. For the slab geometry used in the fluctuation model, both the interface normal and the “short” direction must be specified for a given orientation. The three

box orientations used here are (100)[001], (110)[001], and (111)[1 $\bar{1}$ 0] where the numbers in parentheses are Miller indices for the interface normal and the numbers in square brackets are those for the short direction of the simulation box. In terms of the Fehner-Vosko coefficients, the stiffnesses for these three orientations are

$$\tilde{\gamma}_{(100)[001]} = \gamma_0 \left(1 - \frac{18}{5} \epsilon_1 - \frac{80}{7} \epsilon_2 \right),$$

$$\tilde{\gamma}_{(110)[001]} = \gamma_0 \left(1 + \frac{39}{10} \epsilon_1 + \frac{155}{14} \epsilon_2 \right),$$

$$\tilde{\gamma}_{(111)[1\bar{1}0]} = \gamma_0 \left(1 + \frac{12}{5} \epsilon_1 - \frac{1280}{63} \epsilon_2 \right).$$

The simulations are analyzed using Eq. (2) to obtain the raw stiffness values, which are used to obtain ϵ_1 , ϵ_2 , and γ_0 . The free energies for the (100), (110), and (111) interfaces can be obtained,

$$\gamma_{100} = \gamma_0 \left(1 + \frac{2}{5} \epsilon_1 + \frac{4}{7} \epsilon_2 \right),$$

$$\gamma_{110} = \gamma_0 \left(1 - \frac{1}{10} \epsilon_1 - \frac{13}{14} \epsilon_2 \right),$$

$$\gamma_{111} = \gamma_0 \left(1 - \frac{4}{15} \epsilon_1 + \frac{64}{63} \epsilon_2 \right).$$

In order to determine the interface height $h(x)$, it is necessary to distinguish between “crystal” and “melt” atoms. To do this, we define an order parameter for a molecule of the form,²²

$$\phi = \left| \frac{1}{N_q Z} \sum_{\mathbf{r}, \mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \right|^2, \quad (5)$$

where Z is the number of nearest neighbors of the molecule and N_q the number of reciprocal vectors \mathbf{q} that satisfy $\exp(i\mathbf{q} \cdot \mathbf{r}) = 1$ for an ideal bcc crystal. Six reciprocal vectors with modulus equal to $2\sqrt{2}\pi/a$ (a is the lattice constant) were used. The vectors \mathbf{r} are the vectors between the center of mass of a molecule and each of its Z nearest neighbors. In the calculation this local order parameter is further averaged over its neighbors. The order parameter so defined should be unity for a molecule in an ideal crystal and take on a small value for a liquid molecule. The order parameters of all the molecules of a typical configuration are shown in Fig. 1. We employ a cutoff value of $\phi_c = 0.12$ to distinguish between crystal ($\phi > \phi_c$) and melt ($\phi < \phi_c$) molecules. Shown in the inset of Fig. 1 are the height functions for each of the two interfaces in the same configuration.

The values of the stiffnesses for each of the three slab orientations are obtained from the intercepts of plots of $\ln(|\tilde{h}(k)|^2)$ versus $\ln(k)$, shown in Fig. 2. The lines are weighted fittings to Eq. (2). The stiffnesses obtained by these fittings together with the free energies are shown in Table II. The orientationally averaged free energy is $\gamma_0 = (7.0 \pm 0.4) \times 10^{-3} \text{ J m}^{-2}$. The anisotropy parameters are $\epsilon_1 = (1.2 \pm 2.0)$

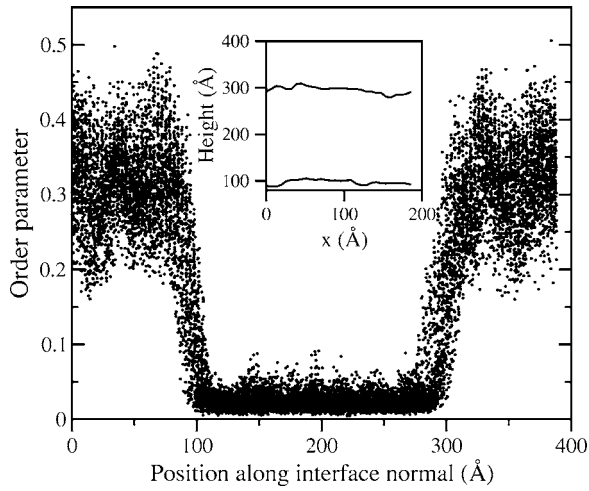


FIG. 1. The averaged order parameters for all molecules of a snapshot. The inset shows the interface heights for the same snapshot.

$\times 10^{-2}$ and $\epsilon_2 = (1.4 \pm 4.6) \times 10^{-3}$. The results show that $\gamma_{100} > \gamma_{110} \approx \gamma_{111}$, but the errors in the interfacial free energy and other related quantities are larger than the differences. The errors could be reduced further by longer runs, but given the small anisotropy in this system, it would require runs that are at least ten times longer simply to determine the signs of ϵ_1 and ϵ_2 . Although the interfacial free energies themselves have large errors, the errors in the differences between γ for different orientations are smaller. From the values of ϵ_1 , ϵ_2 , and γ_0 , we have

$$\gamma_{100} - \gamma_{110} = (5.8 \pm 8.6) \times 10^{-5} \text{ J m}^{-2},$$

$$\gamma_{100} - \gamma_{111} = (5.3 \pm 9.5) \times 10^{-5} \text{ J m}^{-2},$$

$$\gamma_{110} - \gamma_{111} = (-1 \pm 7) \times 10^{-5} \text{ J m}^{-2}.$$

The orientationally averaged interfacial free energy (γ_0) for succinonitrile determined from our simulation is about 20% lower than the experimental result of Schaefer *et al.*²⁹ $[(8.9 \pm 0.5) \times 10^{-3} \text{ J m}^{-2}]$, but within the error bars of the

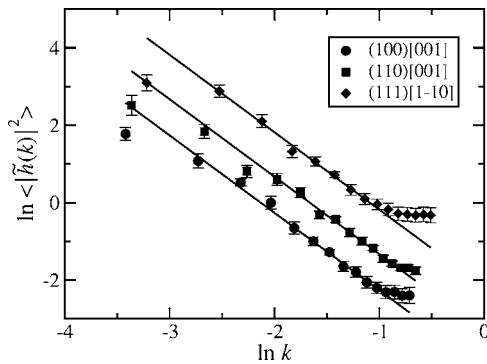


FIG. 2. The fluctuation spectrum of the quasi-one-dimensional interface height. The solid lines, which have slopes of -2 , are fits to the simulation results. The solid circles, squares, and diamonds are for (100)[001], (110)[001], and (111)[1 $\bar{1}$ 0] interfaces, respectively. The indices in the parentheses indicate interface Miller indices, and the indices in the square brackets denote the “short” directions of the simulation box, which is of slab geometry. To be clear, the (110)[001] data have been moved along Y axis by 1, and (111)[1 $\bar{1}$ 0] moved by 2.

TABLE II. The interfacial stiffness ($\tilde{\gamma}$) and free energy (γ) for each interfacial orientation studied. $\tilde{\gamma}$ and γ are in the unit of 10^{-3} J m^{-2} .

Interface	Short direction	$\tilde{\gamma}$	γ
(100)	[001]	6.60 ± 0.7	7.06 ± 0.4
(110)	[001]	7.47 ± 0.5	7.00 ± 0.4
(111)	[1 $\bar{1}$ 0]	7.02 ± 0.8	7.01 ± 0.4

more recent value of $[(7.9 \pm 0.8) \times 10^{-3} \text{ J m}^{-2}]$ of Maraşlı *et al.*³⁰ However, even given the large experimental uncertainty, it is reasonable to conclude that our value is at least 10% lower than the true experimental value. Our simulation indicates that the anisotropy in the interfacial free energy is very small. The nearly isotropic character of SCN interfacial free energy is also observed in the experiments. To make contact with the experiments we determine the anisotropy coefficient ϵ_4 . Using Eq. (1), ϵ_4 can be expressed in terms of $\tilde{\gamma}$ differences,

$$\epsilon_4 = \frac{\tilde{\gamma}_{(110)[001]} - \tilde{\gamma}_{(100)[001]}}{15(\tilde{\gamma}_{(110)[001]} + \tilde{\gamma}_{(100)[001]})}. \quad (6)$$

Using our values we obtain $\epsilon_4 = (0.4 \pm 0.6)\%$, which is within the error bars of the values obtained by both Muschol *et al.*¹⁰ $[(0.55 \pm 0.15)\%]$ and Glicksman and Singh⁹ (0.5%).

Using interfacial free energies obtained indirectly from nucleation rate experiments, Turnbull reported an empirical correlation between the interfacial free energy per surface particle $\hat{\gamma} = \rho^{-2/3} \gamma$ (where ρ is the number density of the crystal) and the latent heat of fusion, $\Delta_{\text{fus}} H$,

$$\hat{\gamma} = C_T \Delta_{\text{fus}} H / N_A, \quad (7)$$

where N_A is Avogadro’s number and C_T the Turnbull coefficient, which was found by Turnbull to be about 0.45 for most metals and 0.32 for semimetals and water. For succinonitrile, the experimental crystal density and latent heat are determined to be 1.0158 g cm^{-3} and $3.704 \text{ kJ mol}^{-1}$, respectively.³⁹ Using these values, C_T for SCN is found to be 0.33 ± 0.03 from the results of Maraşlı *et al.*³⁰ and 0.38 ± 0.02 from the results of Schaefer *et al.*²⁹ The six-site model for succinonitrile gives $1.0108 \pm 0.0008 \text{ g cm}^{-3}$ for the equilibrium crystal density and a latent heat of $3.11 \pm 0.19 \text{ kJ mol}^{-1}$, which results in a C_T of 0.35 ± 0.02 . So the value of the Turnbull coefficient from the simulation is in agreement (within the error bars) with both experimental measurements, as well as being close to Turnbull’s predictions for semimetals and water (0.32). The good agreement of our results for the Turnbull coefficient is due largely to the fact that both the latent heat and interfacial free energy are underestimated in the six-site model, and, because the Turnbull coefficient is a ratio of these two quantities, a partial cancellation of errors occurs. It is possible that an improved force field, with a more accurate latent heat, might also produce better interfacial free energies. Recently, Hoyt *et al.*⁴⁰ reported values of the Turnbull coefficient of 0.29 from fluctuation method simulations on a variety of bcc metals (Fe, V, and Mo). In contrast, Turnbull coefficients for bcc soft-sphere systems were found, using the interfacial free energies from the cleaving method, to be larger (0.45).¹⁹ These and the current

results indicate that, unlike fcc materials, the Turnbull coefficients of bcc materials depend rather sensitively on the potential.

IV. CONCLUSION

Using the capillary fluctuation method¹⁸ and a six-site molecular force field,³⁴ we have calculated the crystal-melt interfacial free energy, γ , and its anisotropy for the model bcc-forming material succinonitrile. The magnitude of γ is found to be about 20% lower than the experimental value obtained by Schaefer *et al.*,²⁹ but within the error bars of the more recent experimental result of Maraşlı *et al.*³⁰ The interfacial free energy is found to be very nearly isotropic, in agreement with experiment.^{9,10} In addition, the Turnbull coefficient for succinonitrile from our simulation (0.35 ± 0.02) is in agreement with the experiments within the error bars.

These results show that the capillary fluctuation method can be used to accurately determinate crystal-melt interfacial free energies for molecular systems.

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