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Self-diffusion across the liquid–crystal interface

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We report a theoretical study of the variation of the self-diffusion coefficient across a liquid–crystal interface at equilibrium. The study is based on the assumption that the interface is broad compared to the molecular diameter of the diffusing particle. The structure at the interface is described by a set of position-dependent order parameters which change smoothly across the interface from zero in the pure liquid to nonzero constant values in the pure solid phase. The effective potential experienced by a particle at the interface is expressed in terms of these order parameters. A Smoluchowski equation is used to describe the dynamics in the presence of this effective potential. The calculated self-diffusion coefficient changes sharply over a length of 4–5 molecular layers in the interface and reproduces the essential features observed in recent computer simulations. We find that significant topological ordering takes place on the liquid side of the interface before the self-diffusion coefficient shows any detectable change from its liquid phase value. We discuss the limitations of the present approach and propose future applications of the model.

I. INTRODUCTION

In this paper we present a theoretical calculation of the self-diffusion coefficient of a particle in the liquid–crystal interface of a one-component system. The calculation is based on the assumption that the interface is broad compared to the molecular diameter of the diffusing particle and that the macroscopic properties, like the average density, change smoothly across the interface.

The self-diffusion coefficient of a liquid is several orders of magnitude larger than that of the crystalline solid. On a macroscopic scale, the liquid–crystal interface is quite narrow, typically 6–10 molecular layers wide. Thus, the self-diffusion coefficient must change sharply across the interface.

Despite its importance in the dynamical processes at the interface, our knowledge of the self-diffusion coefficient in the liquid–crystal interface is rather limited. Most of the quantitative information on this quantity comes from computer simulations. Recently, Cape and Woodcock[1] reported the results of their calculations of the isotropic part of the self-diffusion coefficient D across a planar crystal (100)–liquid interface. They simulated a system of 7680 atoms interacting via the inverse-twelfth soft-sphere potential. They estimated D from the long time limit of the mean-square displacement of the atoms and obtained the values of D as a function of the distance z_0 from the crystal surface. The computed $D(z_0)$ changes smoothly from a small solid-like value to a large liquid-like value over a length of 5–7 molecular layers, measured from the solid surface.

Another interesting observation of Cape and Woodcock[1] is that there exists a region on the liquid side of the interface which shows much greater solid-like topological order than could be deduced from the value of D alone. This implies that the variation of $D(z_0)$ across the interface may be sharper than the build-up of the topological order.

Broughton et al.[2] also reported calculations of the self-diffusion coefficient for the Lennard-Jones fcc(111) and (100) crystal–melt interface. They obtained the values of a (quasi) two-dimensional diffusion coefficient $D_{xy}(z_0)$ by monitoring the mean-square displacement of the particles that remained in one layer throughout the simulation. These authors concluded that $D_{xy}(z_0)$ changes from a solid-like to a liquid-like value over a length of 4–5 molecular layers.

So, the results of the computer simulations indicate that it may be meaningful to define a *local* self-diffusion coefficient in the interface. However, such a diffusion coefficient cannot be defined by a true long-time limit of the mean-square displacement of a particle. It must be defined by an average over a time scale which is sufficiently long so that the particle motion is diffusive, and yet, is sufficiently short so that the particle probes essentially the same local environment. The reason that such a time scale may exist for the motion of a particle in the interface is that the mean free path of a particle in a dense liquid is very small compared to the molecular diameter of the particle. So, it is possible to define a region in the interface which is large compared to the mean free path, yet, has approximately the same local environment everywhere within this region. The last statement is consistent with the assumption that the interface is broad on a molecular length scale.

In this work we adopt the following working definition of the local diffusion coefficient. We define the diffusion coefficient by the usual long time limit of the mean square displacement *with* the constraint that the particle probes the same spatial environment at all times. The local environment changes across the interface and so also the diffusion-coefficient. A more precise, mathematical definition is given in Sec. II C.

In order to calculate the self-diffusion coefficient across the interface, we must take into account the gradual build-up of the crystalline order as the solid surface is approached from the liquid phase. In this work we assume that the inhomogeneous density distribution at the interface can be described by a set of position-dependent order parameters.

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Across the interface these order parameters change smoothly from zero in the liquid phase to nonzero constant values in the solid phase. These order parameters can be obtained by a microscopic calculation[3] and, for the present purpose, they can be assumed to be known without any loss of generality.

The position-dependent order parameters *define* the interface in this problem. They contain all the necessary information about the structure at the interface. The boundary conditions of the problem are also contained within these order parameters.

The inhomogeneous density distribution at the interface gives rise to an effective potential which tends to localize the diffusing particle at the lattice sites of the crystalline solid. The effective potential is expressed in terms of the order parameters described above. We model the influence of this localizing potential by a Smoluchowski equation for the time evolution of the number density distribution function. The self-diffusion coefficient is given by the long time limit of the second moment of this distribution function. A simple analytic expression is obtained for the interface of the simple cubic lattice. For the face-centered and the body-centered cubic lattices, we have used a perturbative calculation to obtain the variation of the self-diffusion coefficient across the interface.

Our theoretical calculation reproduces the essential features of the self-diffusion coefficient in the interface. We find that across the interface the variation of the self-diffusion coefficient is sharper than that of the order parameters, which is in agreement with recent computer experiments.

However, one must recognize that the present treatment is based on a mean-field description of the intermolecular interactions. As the liquid phase is approached from the solid side, the diffusion gets dominated[1,2] by the vacancies and the defects that are present on the solid surface.[4] The influence of these factors are included within the present order-parameter description only as an *average* effect giving rise to the gradual lowering of values of the order parameters as the liquid phase is approached. This coarse-grained description can be valid if the self-diffusion process is much slower than the fluctuations in the interatomic potential experienced by the diffusing particle. The theoretical calculation is definitely valid on the liquid side of the interface where the self-diffusion is dominated by molecular collisions.

The contents of the paper are as follows. In the next section we present the general theory which includes the Smoluchowski equation (SE), the order parameter expression of the effective potential at the interface, and a formal solution of the SE for the diffusion coefficient. In Sec. III, we present the various approximations that are employed to obtain quantitative results. Section IV concludes with a discussion of the limitations of the present work and of the proposals for future applications of the results obtained here.

II. GENERAL THEORY

This section consists of three parts. In the first part we present and discuss the Smoluchowski equation (SE) used in this work to analyze the self-diffusion at the interface. In the second part we present an order parameter expression for the

potential experienced by a particle in the interface. In the last part we present a formal expression for the self-diffusion coefficient.

A. Smoluchowski equation

The Smoluchowski equation can be derived from the following Enskog–Vlasov type kinetic equation[5] for the single particle μ-space distribution function $f(\mathbf{r},\mathbf{v},t)$:

$$\frac{\partial}{\partial t} f(\mathbf{r},\mathbf{v},t) + \mathbf{v} \cdot \nabla_r f(\mathbf{r},\mathbf{v},t) + \frac{\mathbf{F}}{m} \cdot \nabla_v f(\mathbf{r},\mathbf{v},t) = I[f], \quad (2.1)$$

where $\mathbf{r}$ and $\mathbf{v}$ denote the position and the velocity in μ space, and m is the mass of the particle. $\mathbf{F}$ is a mean-field force term given by

$$\mathbf{F}(\mathbf{r}) = k_B T \nabla_r \int d\mathbf{r}' \int d\mathbf{v}' \, c(\mathbf{r} - \mathbf{r}') f_{eq}(\mathbf{r}', \mathbf{v}'), \quad (2.2)$$

where $c(\mathbf{r} - \mathbf{r}')$ is the two-particle direct correlation function, T is the temperature, k_B is the Boltzmann constant, and $f_{eq}(\mathbf{r},\mathbf{v})$ is the equilibrium μ-space distribution function. The collision operator $I[f]$ is a model kinetic operator that conserves only the number density because for self-diffusion this is the only important conserved variable. $I[f]$ is assumed to be given by

$$I[f] = \gamma_l \nabla_v \left\{ \frac{k_B T}{m} \nabla_v + \mathbf{v} \right\} f, \quad (2.3)$$

where γ_l is a collision frequency of the pure liquid. The number density $n(\mathbf{r},t)$ is defined in the usual manner:

$$n(\mathbf{r},t) = \int d\mathbf{v} \, f(\mathbf{r},\mathbf{v},t). \quad (2.4)$$

In the limit of large γ_l, is is straightforward to derive the following diffusion equation for the number density:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D_l \nabla \cdot [\nabla n(\mathbf{r}, t) - \beta n(\mathbf{r}, t) \mathbf{F}(\mathbf{r})], \quad (2.5)$$

where D_l is the diffusion coefficient of the pure liquid defined by

$$D_l = \frac{k_B T}{m \gamma_l}. \quad (2.6)$$

Equation (2.5) has the following equilibrium solution:

$$n_0(\mathbf{r}) = c' \exp\left[\int d\mathbf{r}' c(\mathbf{r}-\mathbf{r}') n_0(\mathbf{r}') \right], \quad (2.7)$$

where the constant c' is determined by the normalization condition. The potential energy of a particle at $\mathbf{r}$ is given by

$$\beta V(\mathbf{r}) = - \int d\mathbf{r}' c(\mathbf{r}-\mathbf{r}') n_0(\mathbf{r}') \quad (2.8)$$

and the force $\mathbf{F}(\mathbf{r})$ is given by

$$\mathbf{F}(\mathbf{r}) = -\nabla V(\mathbf{r}). \quad (2.9)$$

The validity of the use of a diffusion equation to describe the dynamics of a liquid-crystal interface is discussed at length by Bagchi and Kirkpatrick,[6] who formulated a molecular theory of crystal growth by using an equation similar to Eq. (2.5). The diffusion equation used in Ref. 6 was, however, more general than Eq. (2.5) because the time dependence of the force term was retained and, as a result, the final equa-

tion was nonlinear.[6] In the present problem a linear equation is sufficient because of the long time scales that are involved in the self-diffusion process.

In order to obtain the self-diffusion coefficient, we need the second moment of the distribution function, $n(\mathbf{r}, t)$. A formal expression for this quantity will be presented in Sec. II C. Next we shall express the force field of the lattice in the interface in terms of a set of order parameters.

B. Expression for the force field F(r)

The order parameter expression for $\mathbf{F}(\mathbf{r})$ is based on the assumption that the equilibrium liquid–solid interface is quite broad compared to the average intermolecular distance. Across the interface the macroscopic properties, like the average density, change smoothly from the liquid-like to the solid-like values. It is, therefore, reasonable to expand the inhomogeneous density distribution $n_0(\mathbf{r})$ in terms of the order parameters appropriate for the liquid–solid interface[3]:

$$n_0(\mathbf{r}) = \rho_l [1 + \phi_0(\mathbf{r})] + \rho_l \sum_{\{\mathbf{G}\}} \phi_{\mathbf{G}}(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}}, \qquad (2.10)$$

where ρ_l is the average equilibrium density of the liquid phase and G's are the reciprocal lattice vectors (RLV) of the crystalline solid phase. ϕ_0 and $\phi_{\mathbf{G}}$'s are the order parameters that characterize the liquid–crystal interface. They are zero in the liquid far from the interface and they have constant nonzero values in the pure solid phase. In the interface region they change smoothly between the values characteristic of the two condensed phases.

These position-dependent order parameters are the natural generalization[3] of the constant order parameters traditionally used in the theories of freezing.[7]

Next, we substitute Eq. (2.10) into Eq. (2.8) to obtain an expression for the potential $V(\mathbf{r})$, hence for $\mathbf{F}(\mathbf{r})$. In order to make the final form analytically tractable, we make the following square-gradient approximation for the order parameters[3]:

$$\phi_0(\mathbf{r}') = \phi_0(\mathbf{r}) + (\mathbf{r}' - \mathbf{r}) \cdot \nabla \phi_0(\mathbf{r})$$
$$+ \tfrac{1}{2}[(\mathbf{r}' - \mathbf{r}) \cdot \nabla]^2 \phi_0(\mathbf{r}) \qquad (2.11)$$

and similarly for $\phi_{\mathbf{G}}(\mathbf{r})$. With this approximation, the integral in Eq. (2.8) can be evaluated to obtain

$$\beta V(\mathbf{r}) = -\rho_l \, \tilde{c}_0 (1 + \phi_0) + \tfrac{1}{2}\rho_l \tilde{c}_0'' \nabla^2 \phi_0$$
$$- \rho_l \sum_{\{\mathbf{G}\}} e^{i\mathbf{G}\cdot\mathbf{r}} \left\{ \tilde{c}_{\mathbf{G}} \phi_{\mathbf{G}} - i\tilde{c}_{\mathbf{G}}'(\hat{\mathbf{G}} \cdot \nabla \phi_{\mathbf{G}}) \right.$$
$$\left. - \tfrac{1}{2} \tilde{c}_{\mathbf{G}}''(\hat{\mathbf{G}} \cdot \nabla)^2 \phi_{\mathbf{G}} \right\}, \qquad (2.12)$$

where

$$\tilde{c}(\mathbf{k}) = \int d\mathbf{r} \, e^{-i\mathbf{k}\cdot\mathbf{r}} c(\mathbf{r}), \qquad (2.12a)$$

$$\tilde{c}_0 = \tilde{c}(\mathbf{k} = 0); \quad \tilde{c}_{\mathbf{G}} = \tilde{c}(\mathbf{k} = \mathbf{G}). \qquad (2.12b)$$

Note that the square gradient approximation is consistent with our assumption that the interface is molecularly broad.

Next, we make some simplifying assumptions. We restrict ourselves to a planar interface with the z axis taken perpendicular to the interface which lie in the x–y plane. The

coordinate system is chosen such that we have the pure solid phase in the $z \rightarrow -\infty$ limit and the pure liquid phase in the $z \rightarrow +\infty$ limit. The interface is situated near $z = 0$ plane and is assumed to be approximately 6–8 monolayers thick. With this choice of the coordinate system, the order parameters ϕ_0 and $\phi_{\mathbf{G}}$ are functions of z only. Next, we set $\tilde{c}_{\mathbf{G}}'$ equal to zero. This should be a good approximation because for most simple liquids, the magnitudes of the important RLV's coincide with the peaks in the liquid structure factor. Finally, we neglect the terms with the second derivatives of the order parameters because in the present case they make only a negligible contribution. With the above approximations, the expression of the potential is given by

$$\beta V(\mathbf{r}) = -\rho_l \tilde{c}_0 [1 + \phi_0(z)] - \sum_{\{\mathbf{G}\}} \rho_l \tilde{c}_{\mathbf{G}} \phi_{\mathbf{G}}(z) e^{i\mathbf{G}\cdot\mathbf{r}}. \qquad (2.13)$$

The last approximation can be easily included in the following calculations. Its main effect is to introduce a weak anisotropy between D_{zz} and D_{xx} or D_{yy}.

The potential $V(\mathbf{r})$, as given by Eq. (2.13), has two kinds of spatial dependence. First, there is a rapid oscillatory variation due to the factor $\exp(i\mathbf{G}\cdot\mathbf{r})$. Secondly, the order parameters themselves change across the interface. The second variation is obviously much slower than the first one because the interface is broad compared to the molecular diameter. We exploit this separation of length scales in the spatial dependence of $V(\mathbf{r})$ to define a *locally* periodic potential given by

$$\beta V(\mathbf{r}|z_0) = -\rho_l \tilde{c}_0 [1 + \phi_0(z_0)] - \sum_{\{\mathbf{G}\}} \rho_l \tilde{c}_{\mathbf{G}} \phi_{\mathbf{G}}(z_0) e^{i\mathbf{G}\cdot\mathbf{r}}, \qquad (2.14)$$

where z_0 now specifies a coarse-grained position in the interface in the following sense. Slowly varying macroscopic properties will be expressed as a function of z_0 by averaging over a unit cell (or some other suitably chosen small volume element) centered around z_0. Thus, the diffusion coefficient will be evaluated as a function of z_0 and will be denoted by $D(z_0)$. z_0 ranges from $-\infty$ (pure solid phase) to $+\infty$ (pure liquid phase).

The validity of a local diffusion coefficient defined by an average over a small volume element in the interface is not quite obvious. There are two reasons why we feel that such a definition is meaningful. First, the simulation results of Cape and Woodcock indicate that a *layer-by-layer* diffusion coefficient exists in the interface. Similar conclusions were reached by Broughton *et al.* who, in fact, used $D(z_0)$ to estimate the width of the interface. Our second reason is that the mean free path of a particle in a dense liquid is very small, much smaller than the length of an edge of the unit cell.

Equation (2.14) can now be used to calculate two somewhat different diffusion coefficients. First, we can calculate a two-dimensional diffusion coefficient $D_{xy}(z_0)$ which is already computed by Broughton *et al.* via computer simulations. Alternatively, we can calculate a three-dimensional diffusion tensor $D(z_0)$ by using the values of ϕ_0 and $\phi_{\mathbf{G}}$ at z_0. The former one is theoretically more tractable but obviously less realistic. In this work we shall calculate the latter quantity. Note that Cape and Woodcock computed the isotropic part of the three-dimensional diffusion tensor $D(z_0)$.

The order parameters $\phi_0(z_0)$ and $\phi_G(z_0)$ can be obtained by a separate microscopic calculation.[3] In this paper we shall assume, without any loss of generality, that the order parameters are given as some simple functions of z_0.

Next, we derive a formal expression for the diffusion tensor by exploiting the periodicity of the potential (2.14).

C. Formal expression for the diffusion coefficient

The diffusion tensor is defined by the following expression:

$$D(z_0) = \frac{1}{2} \lim_{t \to \infty} \frac{\partial}{\partial t} \langle (\mathbf{r} - \langle \mathbf{r} \rangle)(\mathbf{r} - \langle \mathbf{r} \rangle) \rangle (t, z_0) \qquad (2.15)$$

or, for the present problem, by

$$D(z_0) = \frac{1}{2} \lim_{t \to \infty} \frac{\partial}{\partial t} \langle \mathbf{r}, \mathbf{r} \rangle (t, z_0) \qquad (2.16)$$

with

$$\langle \mathbf{r}, \mathbf{r} \rangle (t, z_0) = \int d\mathbf{r} \, \mathbf{r} \mathbf{r} n(\mathbf{r}, t \,| z_0). \qquad (2.17)$$

We shall express $D(z_0)$ in terms of the eigenvalues of a modified Smoluchowski operator. In the following, we shall drop the index z_0 for convenience. In Eq. (2.5), we set

$$\tilde{n}(\mathbf{r}, t) = e^{(\beta/2)V(\mathbf{r})} n(\mathbf{r}, t) \qquad (2.18)$$

to obtain

$$\frac{\partial \tilde{n}}{\partial t} = - \mathcal{L} \tilde{n} \qquad (2.19)$$

with

$$\mathcal{L} = D_l(\nabla + \tfrac{1}{2}\beta \, \mathbf{F}) \cdot (-\nabla + \tfrac{1}{2}\beta \, \mathbf{F}). \qquad (2.20)$$

The operator $\mathcal{L}$ has the following characteristics. First, it is self-joint. Secondly, it is periodically dependent on $\mathbf{r}$, with the same periodicity as $V(\mathbf{r})$. So according to Bloch's theorem, the eigenfunctions of $\mathcal{L}$ have the following form:

$$\psi_{\mathbf{k}}^{(j)}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \chi_{\mathbf{k}}(\mathbf{r}), \qquad (2.21)$$

where $\psi_{\mathbf{k}}^{(j)}(\mathbf{r})$ satisfies the following eigenvalue equation:

$$\mathcal{L} \psi_{\mathbf{k}}^{(j)}(\mathbf{r}) = \lambda(\mathbf{k}, j) \psi_{\mathbf{k}}^{(j)}(\mathbf{r}). \qquad (2.22)$$

In Eq. (2.21), χ's are periodic functions of $\mathbf{r}$, $\mathbf{k}$ is a generic vector in the reciprocal space ranging in the first Brillouin zone, and $j = 1, 2, 3 \dots$ denotes the band index. $\tilde{n}(\mathbf{r}, t)$ and $\langle \mathbf{rr} \rangle(t)$ are now given by[8]

$$\tilde{n}(\mathbf{r}, t) = \sum_j \int_{Bz} d\mathbf{k} \, b(\mathbf{k}, j) e^{-t\lambda(\mathbf{k}, j)} \psi_{\mathbf{k}}^{(j)}, \qquad (2.23)$$

$$\langle \mathbf{rr} \rangle(t) = \sum_j \int_{Bz} d\mathbf{k} \, b(\mathbf{k}, j) e^{-t\lambda(\mathbf{k}, j)} \mathbf{m}(\mathbf{k}, j) \qquad (2.24)$$

with

$$b(\mathbf{k}, j) = \int d\mathbf{r} \, [\psi_{\mathbf{k}}^{(j)}(\mathbf{r})]^* \tilde{n}(\mathbf{r}, 0), \qquad (2.25)$$

$$\mathbf{m}(\mathbf{k}, j) = \int d\mathbf{r} \, \mathbf{rr} e^{-1/2\beta V(\mathbf{r})} \psi_{\mathbf{k}}^{(j)}(\mathbf{r}). \qquad (2.26)$$

Since we are interested in the asymptotic behavior of the second moment, we need only the lowest nonzero eigenvalue, $\lambda(\mathbf{k}, 1)$. After some straightforward manipulations,

one obtains the following formal expression[8] for the diffusion tensor:

$$D = \tfrac{1}{2} [\nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \lambda(\mathbf{k}, 1)]_{\mathbf{k} = 0}. \qquad (2.27)$$

Equation (2.27) can be reduced to a simpler form by a perturbation calculation of $\lambda(\mathbf{k}, 1)$ for small values of $\mathbf{k}$. The final expression is[8]

$$\lambda(\mathbf{k}, 1) = D_l k^2 - iD_l \mathbf{k} \cdot \frac{\int d\mathbf{r} \exp[-\beta V(\mathbf{r})] \nabla \xi_{\mathbf{k}}(\mathbf{r})}{\int d\mathbf{r} \exp[-\beta V(\mathbf{r})]}, \qquad (2.28)$$

where $\xi_{\mathbf{k}}(\mathbf{r})$ is found by solving the following partial differential equation:

$$-\nabla \cdot \exp[-\beta V(\mathbf{r})] \cdot \nabla \xi_{\mathbf{k}}(\mathbf{r}) = i\mathbf{k} \cdot \nabla \exp[-\beta V(\mathbf{r})], \qquad (2.29)$$

$\xi_{\mathbf{k}}$ is a periodic function of $\mathbf{r}$ with the same periodicity as $V(\mathbf{r})$.

Equations (2.27)–(2.29) constitute the formal expression for the diffusion coefficient. It is nontrivial to solve these equations to obtain quantitative information on D. In the next section, we consider several different ways of solving the above equations.

III. SELF-DIFFUSION COEFFICIENT: APPROXIMATIONS AND RESULTS

In this section we obtain solutions of Eqs. (2.28) and (2.29) for several lattice geometries. First we consider a case when the potential separates in three coordinates so that the problem is one dimensional and hence exactly solvable. This happens for the simple cubic lattice geometry. Next, we construct perturbation solutions of Eqs. (2.28) and (2.29). Two separate perturbation solutions, one for small values of the order parameters (valid on the liquid side of the interface) and the other for large values of the order parameters (valid near the solid surface) are developed.

A. Separable potential: Simple cubic lattice

For the simple cubic lattice, the first set of RLV contains six members, given by $(\pm 1, 0, 0) 2\pi/a$, $(0, \pm 1, 0) 2\pi/a$, and $(0, 0, \pm 1) 2\pi/a$, where a is the length of an edge of the unit cell of the lattice. So, the potential (2.14) becomes

$$\beta V(\mathbf{r}) = \rho_l \tilde{c}_0 [1 + \phi_0(z_0)] - 2\phi_G(z_0)\rho_l \tilde{c}_G$$
$$\times \left(\cos \frac{2\pi}{a} x + \cos \frac{2\pi}{a} y + \cos \frac{2\pi}{a} z \right) \qquad (3.1)$$

with

$$|\mathbf{G}| = (2\pi)/a. \qquad (3.1a)$$

The first term in Eq. (3.1) is a constant and does not contribute to $D(z_0)$. Due to the separable form of the potential, Eqs. (2.28) and (2.29) can be solved to obtain

$$\lambda(\mathbf{k}, 1) = D_l k^2 - D_l k^2$$
$$\times \left[\left(\frac{1}{a} \int_0^a dx \, e^{-\beta V(x)} \right) \left(\frac{1}{a} \int_0^a dx \, e^{\beta V(x)} \right) \right]^{-1}. \qquad (3.2)$$

The self-diffusion coefficient is isotropic and is given by

$$\frac{D(z_0)}{D_l} = \left[\left(\frac{1}{a} \int_0^a dx \, e^{2A \cos(2\pi/a)x} \right) \right.$$
$$\left. \times \left(\frac{1}{a} \int_0^a dx \, e^{-2A \cos(2\pi/a)x} \right) \right]^{-1} \quad (3.3)$$

with

$$A = \rho_l \, \tilde{c}_G \, \phi_G(z_0). \quad (3.3a)$$

Equation (3.3) is our final expression for the self-diffusion coefficient in the SC crystal-melt interface. Several comments about this expression are in order:

(1) The microscopic structure of the crystal–melt interface is given by the order parameters ϕ_0 and ϕ_G and also by the direct correlation function $\tilde{c}_G$. The order parameters are usually different for different crystal planes and so is the diffusion coefficient. The order parameters can be obtained by a first principle microscopic calculation. So, Eq. (3.3) is a purely theoretical expression of $D(z_0)$.

(2) $D(z_0)$ changes more rapidly in the interface than the order parameters. Thus, there may exist a region on the liquid side of the interface where the values of the order parameters may indicate significant ordering, but the diffusion coefficient may not change significantly from its liquid phase value.

(3) Since no one component system is known to freeze into a SC lattice, the expression (3.3) is not directly applicable to any realistic system. However, this system is unique in that it can be solved exactly within the present theoretical framework and many qualitative features can be obtained directly. Figure 1 depicts the variation of $D(z_0)$ in the interface, as given by Eq. (3.3). We have used the following functional form for $\phi_G(z_0)$:

$$\phi_G(z_0) = \tfrac{1}{2}\phi_G(\text{solid})[1 - \tanh(\alpha z_0)] \quad (3.4)$$

with $\alpha = 0.375$, ϕ_G (solid) $= 0.95$, and $\rho_l \tilde{c}_G = 0.65$. The last two values are taken from the equilibrium order parameter theories of freezing.[7] z_0 is measured in units of the lattice
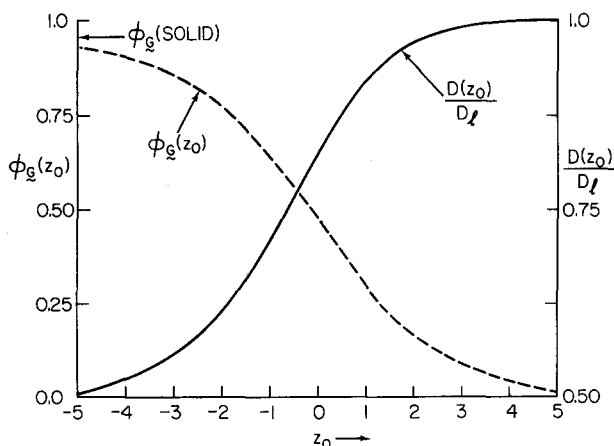

FIG. 1. The variation of the self-diffusion coefficient $D(z_0)$ (solid line, right axis) across the simple cubic crystal–melt interface. The dashed line gives the variation of the order parameter $\phi_G(z_0)$ (left axis), used as an input. The distance is measured in the units of the lattice parameter a. The coordinate system is such that the pure solid phase is at $z \to -\infty$ and the pure liquid phase is at $z \to +\infty$.

parameter a. Note that $D(z_0)$ does not attain the small value characteristic of a solid phase. This is because the localizing potential $V(\mathbf{r})$ is rather small in the solid phase. This is also the main reason why a one-component system does not freeze into a SC lattice.[7]

Next we present perturbative calculations of $D(z_0)$.

B. Perturbative calculations

Here we present two different perturbative calculations[9] of $D(z_0)$ valid at two different regions of the interface. The first calculation is for small values of the order parameters whereas the second one is for large values.

Due to the periodicity of $\xi_k(\mathbf{r})$ and of $n_0(\mathbf{r})$, it is convenient to work in the reciprocal space. We, therefore, define the following quantities:

$$E_Q = \frac{1}{\Delta} \int d\mathbf{r} \, e^{-\beta V(\mathbf{r})} e^{-i\mathbf{Q} \cdot \mathbf{r}}, \quad (3.5)$$

$$F_Q = \frac{1}{\Delta} \int d\mathbf{r} \, \xi_k(\mathbf{r}) e^{-i\mathbf{Q} \cdot \mathbf{r}}, \quad (3.6)$$

where the integration is over a unit cell of volume Δ and $\mathbf{Q}$ is a reciprocal lattice vector. The dependence of F_Q on k is suppressed for convenience. The inverse transforms are given by

$$e^{-\beta V(\mathbf{r})} = \sum_Q E_Q e^{i\mathbf{Q} \cdot \mathbf{r}}, \quad (3.7)$$

$$\xi_k(\mathbf{r}) = \sum_Q F_Q e^{i\mathbf{Q} \cdot \mathbf{r}}. \quad (3.8)$$

We introduce a further quantity, $(E^{-1})_Q$, by the following relation:

$$(E^{-1})_Q = \frac{1}{\Delta} \int_\Delta d\mathbf{r} \, e^{\beta V(\mathbf{r})} e^{-i\mathbf{Q} \cdot \mathbf{r}}, \quad (3.9)$$

$$e^{\beta V(\mathbf{r})} = \sum_Q (E^{-1})_Q e^{i\mathbf{Q} \cdot \mathbf{r}}, \quad (3.10)$$

E_Q and $(E^{-1})_Q$ are orthogonal to each other:

$$\sum_{Q''} (E^{-1})_{Q-Q''} E_{Q''-Q'} = \delta_{Q, Q'}. \quad (3.11)$$

Use of Eqs. (3.5)–(3.8) in Eqs. (2.28) and (2.29) gives

$$\lambda(\mathbf{k}, 1) = D_l k^2 + D_l \mathbf{k} \cdot \sum_Q \mathbf{Q} F_Q E_{-Q}/E_0, \quad (3.12)$$

$$\sum_{Q'} (\mathbf{Q} \cdot \mathbf{Q}') E_{Q-Q'} F_{Q'} = -\mathbf{k} \cdot \mathbf{Q} E_Q. \quad (3.13)$$

In the next step we apply the orthogonality condition to Eq. (3.12) to obtain

$$Q^2 F_Q - \sum_{Q'} \mathbf{Q}' \cdot (\mathbf{Q} - \mathbf{Q}') F_{Q'} \beta \tilde{V}(\mathbf{Q} - \mathbf{Q}')$$
$$= \mathbf{k} \cdot \mathbf{Q} \, \beta \tilde{V}(\mathbf{Q}), \quad (3.14)$$

where

$$\beta \tilde{V}(\mathbf{Q}) = \frac{1}{\Delta} \int_\Delta d\mathbf{r} \, \beta V(\mathbf{r}) e^{-i\mathbf{Q} \cdot \mathbf{r}}. \quad (3.15)$$

Equation (3.14) serves as a basis for our first perturbative solution[9] for F_Q. We now define an operator I_Q by

$$I_Q f_Q = \sum_{Q'} Q' \cdot (Q - Q') f_{Q'} \beta \widetilde{V}(Q - Q'). \tag{3.16}$$

Then Eq. (3.14) can be written in the following form:

$$F_Q = \frac{1}{Q^2 - I_Q} \, k \cdot Q \, \beta \widetilde{V}(Q). \tag{3.17}$$

We now use the standard operator expansion

$$\frac{1}{Q^2 - I_Q} = \frac{1}{Q^2} + \frac{1}{Q^2} I_Q \frac{1}{Q^2}$$
$$+ \frac{1}{Q^2} I_Q \frac{1}{Q^2} I_Q \frac{1}{Q^2} + \cdots . \tag{3.18}$$

The first and the second order terms in the perturbation expansion for F_Q are now given by

$$F_Q^{(1)} = \frac{1}{Q^2} \, k \cdot Q \beta \widetilde{V}(Q), \tag{3.19}$$

$$F_Q^{(2)} = \frac{1}{Q^2} \sum_{Q'} \frac{1}{Q'^2} [Q' \cdot (Q - Q')] k \cdot Q'$$
$$\otimes \beta \widetilde{V}(Q') \beta \widetilde{V}(Q - Q'). \tag{3.20}$$

Since the potential $V(r)$ is given by Eq. (2.14), the perturbation is actually in the powers of the order parameters. Thus the perturbation series, given by Eqs. (3.17) and (3.18), will be rapidly convergent for small values of the order parameters.

Substitution of Eqs. (3.17)–(3.20) in Eq. (3.12) gives the required expression for λ (k, 1) which, together with Eq. (2.27), gives the self-diffusion coefficient. The resulting calculation is straightforward but tedious. The details of the calculation for the face-centered cubic lattice geometry are given in the Appendix. In the following we present the final expressions for the self-diffusion coefficient in the interface for both the face-centered cubic lattice (fcc) and the body-centered cubic lattice (bcc).

1. Face-centered cubic lattice

$$D_{xx}(z_0) = D_{yy}(z_0) = D_{zz}(z_0)$$
$$= D_l (1 - \tfrac{8}{3} A^2 - \tfrac{1}{3} A^4 \dots) \tag{3.21}$$

and

$$D_{xz}(z_0) = D_{yz}(z_0) = D_{xy}(z_0) = 0. \tag{3.21a}$$

2. Body-centered cubic lattice

$$D_{xx}(z_0) = D_{yy}(z_0) = D_{zz}(z_0)$$
$$= D_l (1 - 4A^2 + \tfrac{2}{3} A^4 \dots) \tag{3.22}$$

and

$$D_{xz}(z_0) = D_{yz}(z_0) = D_{xy}(z_0) = 0, \tag{3.22a}$$

where

$$A = \rho_l \bar{c}_G \phi_G(z_0). \tag{3.23}$$

In deriving Eqs. (3.21) and (3.22), we have used a truncated set of RLV's for both the two lattices. For fcc lattice, we have used $G = 2\pi/a(\pm 1, \pm 1, \pm 1)$. For bcc lattice, we have used $G = 2\pi/a(\pm 1, 0, \pm 1)$, $2\pi/a(\pm 1, \pm 1, 0)$, $2\pi/a(0, \pm 1, \pm 1)$. This truncated description is only a minor approximation for the bcc lattice where the 12 members of the first set are known to provide a fairly accurate descrip-

tion of freezing.[7] It is, however, a more serious approximation for the fcc lattice. It is, of course, straightforward to include the higher-order parameters, but that involves rather lengthy (and tedious) calculations. There are, however, two reasons why we feel that Eq. (3.21) provides a semiquantitatively reliable description of $D(z_0)$. First, we use for ϕ_G (solid) a value given by the multi-order parameter calculation of freezing.[7] So, the error incurred will be less than that in the study of the freezing itself. Secondly, the dominant term in the series (3.21) is $(\rho_l \bar{c}_G \phi_G)^2$ so the contribution from higher order parameters, which will have smaller values of $\rho_l \bar{c}_G \, \phi_G$, will rapidly diminish.

Several observations on Eqs. (3.21)–(3.26) are in order:

(1). These equations provide a fairly accurate description of $D(z_0)$ in the interface because for both the two lattices, the values of A will be significantly less than unity for the most part of the interface except near the solid surface, where A will be, approximately, 0.6 and 0.5 for fcc and bcc lattices, respectively.

(2). The rate of decrease of $D(z_0)$ from the liquid phase value D_l is less than the rate of increase of $\phi_G(z_0)$ as the interface is traversed from the liquid side. Significant ordering takes place even before $D(z_0)$ shows any appreciable change. This result is in agreement with the computer simulations of Cape and Woodcock.[1]

(3) Since $\phi_G(z_0)$ is different for different crystal planes, the variation of $D(z_0)$ will also be different.

(4) Equations (3.21)–(3.26) are sort of "high-temperature" expansions for the diffusion coefficient. Note that the predicted behavior is non-Arrhenius. This is similar to the behavior observed by Festa and d'Agliano for the one-dimensional case.

An alternative perturbation expansion for F_Q can be derived directly from Eq. (3.13) by writing it in the following form:

$$Q^2 E_0 F_Q + \sum_{Q' \neq Q} (Q \cdot Q') E_{Q - Q'} F_{Q'} = - k \cdot Q E_Q. \tag{3.24}$$

Then, following a procedure similar to the one described by Eqs. (3.16)–(3.18), we can derive a perturbative expansion for F_Q. The first order term is simply given by

$$F_Q^{(1)} = - \frac{k \cdot Q}{Q^2 E_0} E_Q. \tag{3.25}$$

Substitution of Eq. (3.25) into Eqs. (2.28) and (2.27) gives the first order correction to the self-diffusion coefficient in the following form:

$$D_{xx}(z_0) = D_{yy}(z_0) = D_{zz}(z_0)$$
$$= D_l \left[1 - B \left(\frac{E_G}{E_0} \right)^2 \right] \tag{3.26}$$

with

$$B = 8/3 \quad \text{for the fcc lattice}$$

and

$$= 4 \text{ for the bcc lattice.} \tag{3.27}$$

E_G is given by Eq. (3.5) with $Q = G$, where G is any member of the first set of RLV.

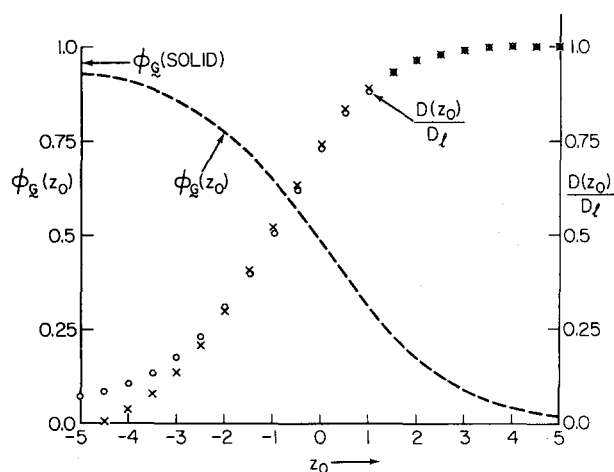The second order terms from Eq. (3.24) are more com-

FIG. 2. The variation of $D(z_0)$ across the fcc crystal–melt interface. The results of Eq. (3.21) are given by crosses ($\times$) and the results of Eq. (3.26) are denoted by circles (O). The rest is the same as in Fig. 1.

plicated. We have not calculated them here. For many purposes, the first order correction is sufficient.

3. Numerical results

We have calculated $D(z_0)$ by using Eqs. (3.21)–(3.23) and Eqs. (3.26) and (3.27), with $\phi_G(z_0)$ given by the parametric form (3.4). For the fcc lattice interface, we have used the following values of the parameters:

$$\phi_G(\text{solid}) = 0.95, \quad \rho_l \bar{c}_G = 0.65, \quad \alpha = 0.375. \qquad (3.28)$$

For the bcc lattice interface, we have used

$$\phi_G(\text{solid}) = 0.7, \quad \rho_l \bar{c}_G = 0.68, \quad \alpha = 0.375. \qquad (3.29)$$

The values of $\phi_G(\text{solid})$ and $\rho_l \bar{c}_G$ are consistent with the known facts about these two lattices in equilibrium with their own liquids. We have chosen, rather arbitrarily, the same value of α for both the two lattices. This value of α entails a width, measured by a decrease of $\phi_G(z_0)$ from 95% to 5% of its solid phase value, of $8a$, where a is the lattice parameter.

Figure 2 shows the variation of the isotropic part of the self-diffusion coefficient, $D(z_0)$, across the fcc crystal–melt interface. A similar figure is obtained for the bcc crystal–melt interface. Figure 2 clearly shows the asymmetry between $\phi_G(z_0)$ and $D(z_0)$ in their variation across the interface; the variation of $D(z_0)$ being sharper, especially near the liquid side of the interface. Figure 2 shows the expected decrease of $D(z_0)$ to a very small value at the solid surface. As expected, Eq. (3.21) becomes inadequate in that region, whereas Eq. (3.26) continues to hold.

Figure 2 is the principal result of this paper. The observed variation in $D(z_0)$ suggests that an order parameter description is capable of describing some of the essential features of the crystal–melt interface.

IV. DISCUSSION

Our motivation for the foregoing analysis was twofold. First, we wanted to know if the order parameter description of the liquid–crystal interface is capable of describing the variation of the self-diffusion coefficient across the interface. This is a natural first step towards an order parameter theory of the dynamical processes at the interface. Secondly we wanted to obtain reliable numbers for the self-diffusion coefficient across the interface. Since it is difficult to obtain experimental information on the order parameters themselves, direct experimental verification of the theoretical predictions on these quantities may not be possible. The self diffusion coefficient, on the other hand, is amenable to experimental study, especially by computer simulations, so the predictions of the theory can be tested directly against the experiments.

The present study suggests that an order parameter theory is capable of reproducing the essential features of the self-diffusion at the liquid–crystal interface. Our results appear to be in semiquantitative agreement with the results of the computer experiments. However, a detailed comparison would require reliable numbers for both the order parameters and the self-diffusion coefficient. Such information is not available at the present time.

The most important limitation of the present work is that the interface must be sufficiently broad so that the square-gradient approximation [Eq. (2.11)] is meaningful. In other words, our calculation is exact only in the limit of infinitely broad interface. The results of the computer simulations[1,2] indicate that, for a simple liquid like argon, the interface is 6–8 monolayers wide. Thus the present study may be semiquantitatively reliable. This point deserves further study.

The other limitations of the present study include the neglect of the triplet and the higher order direct correlation functions in the expression (2.2) for the mean field force term and the neglect of the higher order parameters. It is not difficult (though tedious) to rectify the second approximation, but the improvement of the first one, that is the inclusion of the higher direct correlation functions in the above formalism, is nontrivial.

Another important limitation is that the present calculation is based on a mean-field description of the potential experienced by the diffusing particle. On the solid side of the interface, the self-diffusion may be dominated by the defects and vacancies that will be present in that region of the interface. The influence of these factors are included only as an *average* effect. However, the present calculation is expected to be semiquantitatively reliable on the liquid side of the interface where the self-diffusion is dominated by molecular collisions. A more detailed study is needed to obtain reliable results on the solid side of the interface.

The results of the present study should be useful in a number of problems of current interest. First, they can be used in a theory on the dynamics of crystal growth. In the theory developed in Ref. 6, it was found that the variation of the self-diffusion coefficient across the interface plays a crucial role in determining the growth velocity of a crystal from its supercooled melt. Secondly, quantitative information on $D(z_0)$ is essential in the study of the dynamic structure factor $S(k, \omega)$ at large values of the wave vector k. And lastly, the present work may be useful in the study of the elementary kinetic processes of particles undergoing solid–liquid transi-

tion, especially in the estimation of the time needed for a particle to reach the liquid from the solid surface and vice versa.

ACKNOWLEDGMENTS

APPENDIX

Here we sketch a derivation of the perturbation series (3.21). For the first set of RLV of the fcc lattice, we can write the potential $V(\mathbf{r})$ in the following form:

$$\beta V(\mathbf{r}) = -A \sum_{\mathbf{G} = (\pm 1, \pm 1, \pm 1)2\pi/a} \exp(i\mathbf{G} \cdot \mathbf{r}), \qquad (A1)$$

where $A = \rho_l \tilde{c}_G \phi_G$. In Eq. (A1) we have dropped the first term of Eq. (2.14) because it does not contribute to D. The contribution of the first-order term to $\lambda(\mathbf{k}, 1)$ is given by

$$\lambda^{(1)}(\mathbf{k}, 1) = -A \sum_{\{\mathbf{G}\}} \frac{(\mathbf{kk}:\mathbf{GG})}{G^2} \frac{E_{-\mathbf{G}}}{E_0} . \qquad (A2)$$

Expanding $E_{-\mathbf{G}}$ and E_0 in powers of $\beta V(\mathbf{r})$ and substituting the resulting expression in Eq. (2.27), we get the first order correction to the self-diffusion coefficient in the following form:

$$D_{xx}^{(1)} = -A^2 \sum_{\{\mathbf{G}\}} \frac{G_x^2}{G^2} = -\frac{8}{3} A^2. \qquad (A3)$$

The calculation of the second-order term is a bit more complicated. We write $\lambda(\mathbf{k}, 1)$ in the following form:

$$\lambda^{(2)}(\mathbf{k}, 1) = \lambda^{(21)} + \lambda^{(22)} + \lambda^{(23)}. \qquad (A4)$$

The various $\lambda^{(2i)}$ terms on the right-hand side of Eq. (A4) can be found by first substituting Eq. (A1) into Eq. (3.20) and

then using the resulting expression in Eq. (3.12). The final result is

$$\lambda^{(21)} = -\frac{A^4}{6} \sum_{\mathbf{G}} \frac{(\mathbf{kk}:\mathbf{GG})}{G^2} \sum_{\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3} \delta(\mathbf{G} + \mathbf{G}_1 + \mathbf{G}_2 + \mathbf{G}_3), \qquad (A5)$$

$$\lambda^{(22)} = \frac{A^4}{2} \sum_{\mathbf{G}, \mathbf{G}', \mathbf{G}_1, \mathbf{G}_2} \frac{[\mathbf{kk}:\mathbf{G}(\mathbf{G} + \mathbf{G}')]}{(\mathbf{G} + \mathbf{G}')^2} \frac{(\mathbf{G} \cdot \mathbf{G}')}{G^2}$$
$$\otimes \delta(\mathbf{G} + \mathbf{G}' + \mathbf{G}_1 + \mathbf{G}_2), \qquad (A6)$$

and the last term is

$$\lambda^{(23)} = 4A^4 \sum_{\mathbf{G}} \frac{(\mathbf{kk}:\mathbf{GG})}{G^2} . \qquad (A7)$$

The use of Eqs. (A4)–(A7) in Eq. (2.27) gives the following second-order correction to the self-diffusion coefficient:

$$D_{xx}^{(2)} = D_{xx}^{(21)} + D_{xx}^{(22)} + D_{xx}^{(23)}$$
$$= -12A^4 + A^4 + \frac{32}{3} A^4$$
$$= -\tfrac{1}{3} A^4. \qquad (A8)$$

Combining Eqs. (A3) and (A8), we obtain the expression (3.21) of the text.

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