Crystalline symmetry and the melt-growth kinetics of solid-liquid interface

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One of the important factors governing the growth morphology of materials is the interface kinetic coefficient \( \mu \), which is the proportionality constant between the velocity of solid-liquid interface and undercooling. We employ Ginzburg-Landau (GL) free energy functional to derive an analytical expression of kinetic coefficients. The anisotropy of kinetic coefficients naturally arise from the broken symmetry at the solid-liquid interface for various crystalline orientations. The analytical expression of kinetic coefficients is compared to Mikheev-Chernov theory [J. Cryst. Growth 112, 591 (1991)] derived from hydrodynamic equations. In addition, we use equilibrium density wave profiles to evaluate kinetic coefficients and compare them with that from MD simulations. Our results are in good agreement with Mikheev-Chernov theory and MD simulations and shed lights on a possible origin of anisotropy of interfacial kinetics.

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I. INTRODUCTION

The growth of crystal phases from the melt occurs in many material processing applications such as zone refinement and epitaxial growth. In the early 20th century, a classical theory by Wilson for the growth of crystals from viscous melt is proposed based on the picture of abrupt interface separating semi-infinite melt and crystal[1]. It assumes that the particles in the liquid phase diffuse over a distance approximately of the order of the particle size before impinging on and later being absorbed by the lattice. Comparing to experiments on crystal growth from viscous melts, this theory shows good agreements in terms of the crystal growth rate[5–7]. However, recent studies on crystal-melt interface of organic crystals[2], simple metals[3], and Lennard-Jones crystals[4] have provided more insights into the growth kinetics and morphology of materials. In contrast to the growth from viscous melts, which consists of large complex molecules, the above-mentioned crystal-melt interface grows at a much higher rate than that predicted by the classical theory. Mikheev and Chernov[13, 14] first offered an analytic treatment of this interface growth kinetic by taking proper account of the crystal ordering at the crystal-melt surface. They propose that as the crystal grows the ordering of atoms occurs simultaneously in many surface layers instead of solely on a sharp crystal-melt interface. With this notion, they derive an analytical expression for kinetic coefficient, which is the proportionality constant between the crystal-melt interface velocity and the interface undercooling, in terms of bulk physical quantities such as relaxation time, structure factor, latent heat of fusion and melting temperature.

In the past few decades, several microscopic theories have been proposed to show that anisotropy of the excess interface energy is a crucial parameter that determines morphology of dendrites during solidification. Ginzburg-Landau (GL) theory with order parameter representing amplitude of density waves has been used to calculate the magnitude of interfacial free energy \( \gamma \) in different systems and also for different crystal structure like fcc and diamond cubic[17] [19, 20]. GL theory is shown to successfully capture capillary anisotropy of crystal-melt interfaces by incorporating underlying crystal symmetries. In this paper, we derive interfacial kinetics using GL theory from a different yet more compact perspective. Firstly we outline the hydrodynamic approach adopted by Mikheev and Chernov in deriving the kinetic coefficient. Then we extend Ginzburg-Landau theory to describe a moving interface of solid-liquid systems under a given undercooling. Based on our previous work on crystalline anisotropy for bcc-liquid interface, we explicitly computed the kinetic coefficients using the equilibrium density wave profiles, which is contrasted with that obtained through the approximation scheme proposed previously[13, 14]. Finally, Comparisons to molecular dynamics(MD) simulation and the physical origin of kinetic anisotropy are discussed.

Outlines of the Hydrodynamic approach: To understand the kinetics of the non-equilibrium solid-liquid interfaces of a given undercooling, it is instructive to consider the number density current \( \vec{j}(\vec{r}, t) \) (i.e. number of particles flowing across an unit area in a given direction per unit time) as well as the quadratic isothermal dissipative function\[11, 13\] constructed accordingly:

\[
R = \int d^3r d^3r' \Gamma_{\alpha\beta}(\vec{r}, \vec{r}' \{ n \}) j_\alpha(\vec{r}) j_\beta(\vec{r}'), \tag{1}
\]

where \( \Gamma_{\alpha\beta} \) is the (generally nonlocal and density dependent) dissipated kernel. The dissipated function \( R \) represents the amount of (free) energy dissipated per unit time. Assuming that the heat transfer at the relevant length scale is much faster than the structure rearrangement under consideration[22, 23], the generalized hydrodynamic equations are\[11\]:
\[ \frac{\partial n(\vec{r})}{\partial t} + \nabla \cdot \vec{j}(\vec{r}, t) = 0 \]  
(2)

\[ m \left( \frac{\partial j_{\alpha} (\vec{r})}{\partial t} + \frac{\partial}{\partial x_{\beta}} n^{-1}(\vec{r}) j_{\beta}(\vec{r}) j_{\alpha}(\vec{r}) \right) = -n(\vec{r}) \frac{\partial}{\partial x_{\alpha}} \tilde{F}(\{n(\vec{r})\}) - n(\vec{r}) \int d^{3}\mathbf{r}' \Gamma_{\alpha\beta}(\vec{r}, \vec{r}') j_{\beta}(\vec{r}') \]  
(3)

Note that \( \tilde{F}(\{n(\vec{r})\}) \) refers to the free energy for the (inhomogeneous) equilibrium fluid minus its kinetic energy contribution, which is different from the free energy in the GL theory used later.

For small undercoolings, the density profile for the solid-liquid interface can be described by the constant velocity wave of the form:

\[ n(\vec{r}) = \sum_{\vec{K}} u(z - Vt) e^{i\vec{K} \cdot \vec{r}}, \]  
(4)

where the sum is taken over principal reciprocal lattice vectors of the crystal. Note that we align the interface normal in \( \hat{z} \), and denote the steady-state velocity as \( V \). By solving Eqs. (2)-(4) one immediately gets the free energy balance relation between dissipation and crystallization:

\[ \frac{1}{2} \sum_{\vec{K}} \int d\tau \Gamma_{\vec{K}} |\tilde{J}_{\vec{K}}|^2 = \frac{L}{T_m} \Delta T n_0 V \]  
(5)

with the dissipated kernel given by:

\[ \Gamma_{\vec{K}} = \left( \frac{\tau(\vec{K}) k_B T_m |\tilde{K}|^2}{n_0 S(\hat{K})} \right)^2 \]  
(6)

Here \( n_0 \) represents the density of liquid, \( T_m \) the melting temperature, and \( \Delta T \equiv T - T_m \) the undercooling with reference to the melt. Note that the dissipated kernel is related to the relaxation time \( \tau(\vec{K}) \) measured as the inverse half-width of the dynamical structure factor \( S(k, \omega) \) at given \( k = K \). Inserting the longitudinal part of the traveling density wave Eq. (4) into the energy balance equation Eq. (5), one arrives at the expression for interface velocity:

\[ V = \frac{L(T - T_m) S(\hat{K})}{k_B T_m^2 \tau(\hat{K})} \left[ \int d\tau \sum_{\vec{K}} \left( \frac{du_z}{dz} \right)^2 \right]^{-1} \]  
(7)

As will be shown latter, Eq. (7) can be derived from the GL theory by including a linear temperature dependence.

**Extension of Ginzburg-Landau Theory:** Different from the Ginzburg-Landau theory for the solid-liquid interface at equilibrium developed by Shih et al. [18] and Wu et al. [17], we extend the discussion to a solid-liquid system that is out of equilibrium where the system is undercooled and the solid-liquid interface moves at a constant velocity. Near the melting point \( T_m \), the free energy difference between solid and liquid phase is related to latent heat of fusion \( L \),

\[ F_s(T) - F_L(T) = (S_s - S_L)(T - T_m) = L \frac{T - T_m}{T_m}, \]  
(8)

where we have used the thermodynamic relation \( dF = -SdT \). Since we are to deal with the dynamics close to the melting temperature, we should incorporate a term linear in \( u \) (i.e. the amplitude of density waves corresponding to a specific principal lattice vector of the reciprocal lattice of the solid) with the equilibrium free energy so as to recover Eq. (8). Thus, one can write

\[ \Delta F' = \Delta F + \frac{n_0 k_B T_m}{2} \int d\vec{r} \sum_i \frac{1}{6} u_i - u_s L \frac{T - T_m}{T_m}, \]  
(9)

where \( \Delta F' \) is the excess free energy for the solid-liquid system in equilibrium, which, under the assumption that the density wave amplitude varies slowly over a scale \( 1/K_{\text{max}} \) where \( K_{\text{max}} \) represents the wave vector at which the peak of structure factor is located, takes the form:

\[ \Delta F' = \frac{n_0 k_B T_m}{2} \int d\vec{r} \left( \sum_{i,j} \frac{1}{S(\vec{K}_i)} u_i u_j \delta_0 \hat{K}_0 + \hat{K}_i \right) \]  
\[ - \frac{1}{2} C''(|\vec{K}|) \times (\vec{K} \cdot \vec{n})^2 \left( \frac{du_z}{dz} \right)^2 \]  
(10)

Note that \( C(K) \) refers to the Fourier transform of the direct correlation function \( C(|\vec{r} - \vec{r}'|) \) and \( C''(K) \equiv d^2 C(K)/dK^2 \), \( n_0 \) is the atomic density in the liquid phase, and \( u_s \) is the equilibrium amplitude of the principal reciprocal lattice vectors in the solid which corresponds to one minimum of \( \Delta F'(u, T_m) \). One can check that this is point where \( \Delta F'(u, T_m) = 0 \). Note that for convenience in subsequent comparisons we include a
normalization factor $1/6$ to account for the slope of the linear tilt potential of the bcc-liquid interface\cite{17}.

As usual, one can obtain the kinetic coefficient $v$ by looking for the steady-state propagating solutions of the following equation of motion (assuming the interface normal $\hat{n} = \hat{z}$)

$$\tau \frac{\partial \tilde{u}_i}{\partial t} = -\tau V \frac{\partial \tilde{u}_i}{\partial z} - \delta \frac{\Delta F'}{\delta \tilde{u}_i}, \quad (11)$$

where $\tau = \tau(G)/S(G)$ is the relaxation time measured as the inverse half-width of the dynamic structure factor\cite{24}. An analytic expression for $V$ and hence $\mu$, the kinetic coefficient, can be obtained by using a solvability condition as outlined in all phase-field review papers\cite{25-27}, which relates $V$ and $T - T_m$. For anisotropic cases, the interface profiles for different sets of density wave amplitudes are coupled but $\mu$ can still be computed analytically from a similar solvability condition whose procedure is shown below.

Using the equation of motions Eq. (11) we have

$$\frac{\partial u}{\partial t} = -\left( \frac{1}{8} \frac{\delta F}{\delta u} + \alpha \right),$$

$$\frac{\partial v}{\partial t} = -\left( \frac{1}{2} \frac{\delta F}{\delta v} + \alpha \right),$$

$$\frac{\partial w}{\partial t} = -\left( \frac{1}{2} \frac{\delta F}{\delta w} + \alpha \right), \quad (12)$$

where $\alpha$ is the linear tilt appended to the the free energy of the equilibrium case

$$\alpha = \frac{L}{6k_BT_m} \frac{T - T_m}{T_m} \frac{1}{u_s}. \quad (13)$$

To obtain a steady-state solution of propagating wave with velocity $V$ along the interface normal $\hat{z}$, we cast Eq. (12) into the moving frame and expand the density wave amplitude around the melting point. After using the stationarity of the equilibrium density and simplifying, one arrives at the following matrix equation:

$$LU = F, \quad (14)$$

where

$$L = \begin{pmatrix}
  f_{uu} + 8\mathcal{D}_u & f_{uv} & f_{uw} \\
  f_{vu} & f_{vv} + 2\mathcal{D}_v & f_{vw} \\
  f_{wu} & f_{wv} & f_{ww} + 2\mathcal{D}_w
\end{pmatrix}, \quad (15)$$

and

$$\mathcal{D}_i = C''(\langle |\tilde{K}_{110}| \rangle \langle \tilde{K}_i \cdot \hat{n} \rangle^2) \frac{d^2}{dz^2},$$

$$U = \begin{pmatrix}
  u_1 \\
  v_1 \\
  w_1
\end{pmatrix}, \quad F = \begin{pmatrix}
  8V\tau \frac{\partial u_0}{\partial z} - 4\alpha \\
  2V\tau \frac{\partial v_0}{\partial z} - \alpha \\
  2V\tau \frac{\partial w_0}{\partial z} - \alpha
\end{pmatrix}. \quad (16)$$

Here we denote $u_0, v_0$ and $w_0$ as the equilibrium density wave amplitudes specific to the $\{110\}$ interface. Note that $\Delta F = \int df/(u, v, w)$, $f_u = \partial f/\partial u$. Employing again the stationarity of equilibrium density profile, we have $L'V = 0$ with $V = (\frac{\partial u_0}{\partial z}, \frac{\partial v_0}{\partial z}, \frac{\partial w_0}{\partial z})^T$. Combining this with Eq. (14) one arrives at

$$\langle \tilde{V}|F \rangle = 0 \quad \int_{-\infty}^{\infty} dz \left\{ 4 \left( \frac{d\tilde{u}_0}{dz} \right)^2 + \left( \frac{d\tilde{v}_0}{dz} \right)^2 + \left( \frac{d\tilde{w}_0}{dz} \right)^2 \right\}$$

$$- \left( \alpha \left( \frac{4d\tilde{u}_0}{dz} + \frac{d\tilde{v}_0}{dz} + \frac{d\tilde{w}_0}{dz} \right) \right). \quad (18)$$

Setting the boundary conditions $u_0(-\infty) = v_0(-\infty) = w_0(-\infty) = 0$ and $u_0(\infty) = v_0(\infty) = w_0(\infty) = u_s$, the density wave velocity $V$ can be further simplified into (here the subscript of $V$ indicates the crystal face normal $\{110\}$ specific to this case)

$$V_{110} = \frac{6\omega u_s}{\tau} \left\{ \int_{-\infty}^{\infty} dz 8 \left( \frac{d\tilde{u}_0}{dz} \right)^2 + 2 \left( \frac{d\tilde{v}_0}{dz} \right)^2 + 2 \left( \frac{d\tilde{w}_0}{dz} \right)^2 \right\}^{-1} \quad (19)$$

| Different orientation of crystal faces | 100 | 110 | 111 |
|-------------------------------------|-----|-----|-----|
| $(K_i \cdot \hat{n})^2$            | 0   | 1/2 | 1/4 |
| Number of $\tilde{K}_i$'s          | 4   | 8   | 8   |
| Square gradient term $c_i = (\tilde{K}_i \cdot \hat{n})^2/4$ | 0   | 1/8 | 1/16|

TABLE I: Classifications and the values of square gradient $c_i$ of different orientations of bcc crystal interfaces.
FIG. 2: (Color online) Velocity versus dimensionless undercooling $\Delta T = \frac{(T - T_m)}{L/k_BT_m^2}$ for different crystal faces.

We can also apply the same analysis to different crystal faces with references to different sets of density wave amplitudes and square gradients listed in TABLE I. In any case, we can re-write the kinetic coefficient ($\mu$) in a more compact form by noting that $V = \mu \Delta T$ and $\Delta T = (T - T_m)$:

$$\mu = \frac{6\alpha u_s}{\tau \Delta T} \left[ \int dz \sum_{\vec{K}_i} \left( \frac{du_i}{dz} \right)^2 \right]^{-1} = \frac{L}{k_BT_m^2 \tau(\vec{K}_i)} \left[ \int dz \sum_{\vec{K}_i} \left( \frac{du_i}{dz} \right)^2 \right]^{-1}$$

As one can see, this is the same as that derived by Mikheev et al [13] (see Eq.7). We plotted the dependence of velocity $V$ with reference to different crystal faces on the dimensionless undercooling $\Delta T = (T - T_m)L/k_BT_m^2$ explicitly in FIG 2 and contrasted the numerical value of $\mu$ obtained here with that in MC theory in TABLE II. Although both theories predict similar kinetic anisotropy ordering[28], $\mu_{100} > \mu_{110} > \mu_{111}$, we would like to emphasize that MC theory (i.e. the second row in TABLE II) computed the kinetic coefficient with $u_i$ estimated from a linear theory, which is different from the exact profiles we used here (i.e. the first column in the same table). The good agreement of our calculation with both MD and MC theory reveals that by taking into consideration the anisotropy of crystalline orientations the broken symmetry of interfacial kinetics is automatic regardless of (i) the details of atomistic dynamics within or outside of the interface as well as (ii) the hydrodynamical properties of the melt.

| GL Theory | Mikheev-Chernov | MD |
|-----------|-----------------|----|
| $\mu_{100}/\mu_{110}$ | 1.06 | 1.14 | 1.37 ± 0.07 |
| $\mu_{100}/\mu_{111}$ | 1.27 | 1.23 | 1.44 ± 0.07 |

TABLE II: The anisotropy of the kinetic coefficient for bcc lattices calculated by GL theory derived in this work, Mikheev-Chernov model[13], and MD simulation with MH(SA) potential[16, 17].

Conclusions: We have computed the kinetic coefficient $\mu$, which is the proportionality constant between interface velocity and undercooling, by incorporating a temperature dependence term into the Ginzburg-Landau (GL) free energy functional. Though different from the Mikheev-Chernov (MC)[13] theory based on the hydrodynamic equations of conservation of momentum and particle number, our intuitive and more compact extension of Ginzburg-Landau calculation predicts the same ordering for kinetic coefficients in different crystal faces. In addition, we have contrasted both theories with MD simulations and find good accuracy. This reveals that not only is our method quantitatively precise in dealing with non-equilibrium interfacial kinetics problems but also provides an explanation to the anisotropy of interfacial kinetics – the broken symmetry at the interface for various crystalline orientations.

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