Langevin Formalism for Solidification

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The question of how thermal noise should be incorporated in the continuum equations of solidification in a way which is consistent with both bulk and interfacial equilibrium fluctuations is investigated. The proper Langevin formalism which accomplishes this task is found to consist of the usual bulk forces, which remain unaffected by the presence of a two-phase boundary, and an extra stochastic force on the interface associated with its kinetics. The relevance of this force in the context of pattern formation is examined.

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Perhaps one of the most remarkable results that has emerged from theoretical studies of dendritic growth [1] is the fact that a tiny noise source can potentially give rise to the pronounced sidebranching activity observed experimentally [2,3]. At present, the precise physical origin of this noise or even its relevance remains uncertain. A quantitative calculation by Langer [4] has indicated that thermal noise (i.e., thermodynamic fluctuations) does not seem large enough to account for the observed sidebranch amplitude in the experiment of Huang and Glicksman [2] and, although unlikely, it cannot yet be ruled out that in fully three-dimensional dendrites the observed noisy sidebranching activity [3] is due to a nonlinear feedback of the sidebranches on the tip. In contrast, Warren and Langer [5] have found recently in the context of directional solidification that thermal noise seems to be of about the right magnitude to account for the initial wavelength of a transient cellular structure observed experimentally by Trivedi and Somboonsuk during the formation of dendritic arrays [6].

Despite the potential importance of thermal noise in the above examples, and perhaps others yet unexplored, a rigorous theoretical basis for its incorporation in the basic continuum equations of solidification [1] has remained largely lacking. The purpose of the present Letter is to present a Langevin formalism consistent with both bulk and interfacial equilibrium fluctuations which provides this basis. Details of the calculations together with an investigation of fluctuations in directional solidification will be presented elsewhere [7]. We only summarize here the part of our results which pertain to the Langevin formalism and the physical relevance of its constitutive forces.

The present procedure [4,5] used to incorporate fluctuations was first introduced by Cherepanova [8] and simply consists of adding to the diffusion equations bulk Langevin forces, uncorrelated in space and time, chosen to reproduce the known *bulk* equilibrium fluctuations of temperature and concentration in each phase separately. To present the issues which arise concerning the validity of this procedure it is simpler to consider the solidification of a pure substance. For a pure substance with an atomically rough solid-liquid interface, the equations of solidification with bulk forces take the form [9]

$$\frac{\partial T_v}{\partial t} = D_T^v \Delta T_v - \nabla \cdot \mathbf{q}^v(\mathbf{R},t), \quad v = L,S , \tag{1}$$

$$L v_n = \hat{\mathbf{n}} \cdot [c_S D_T^S \nabla T_S - c_L D_T^L \nabla T_L] + \hat{\mathbf{n}} \cdot [c_L \mathbf{q}^L(\mathbf{p}) - c_S \mathbf{q}^S(\mathbf{p})] , \tag{2}$$

$$T_I(\mathbf{p}) = T_M - \Gamma\kappa - \frac{v_n}{\mu}, \quad v = L,S , \tag{3}$$

where D_T^v and c_v denote, respectively, the thermal diffusivity and specific heat per unit volume of each phase, L is the latent heat of melting per unit volume, $\Gamma = T_M \gamma / L$ is the Gibbs-Thomson coefficient with γ the surface energy, μ is the kinetic coefficient, κ is the interface curvature, v_n is the normal velocity of the interface, and the bulk forces satisfy

$$\langle q_i^v(\mathbf{R},t) q_j^v(\mathbf{R}',t') \rangle = 2 \frac{D_T^v k_B T_v(\mathbf{R},t)^2}{c_v} \times \delta(\mathbf{R}-\mathbf{R}')\delta(t-t')\delta_{ij}, \quad v = L,S . \tag{4}$$

We parametrize the interface by the vector $\mathbf{p} \equiv x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + \xi(\mathbf{r},t)\hat{\mathbf{z}}$ where $\mathbf{r} \equiv x\hat{\mathbf{x}} + y\hat{\mathbf{y}}$ is a two-dimensional vector in the (x,y) plane and $\mathbf{R} \equiv x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$ is the three-dimensional position vector. The three- and two-dimensional gradients are denoted, respectively, by $\nabla \equiv \partial_x \hat{\mathbf{x}} + \partial_y \hat{\mathbf{y}} + \partial_z \hat{\mathbf{z}}$ and $\nabla_\perp \equiv \partial_x \hat{\mathbf{x}} + \partial_y \hat{\mathbf{y}}$, and Δ denotes the three-dimensional Laplacian.

There are two somewhat distinct issues regarding the validity of the above procedure for incorporating thermal noise. Both are linked to the presence of a two-phase boundary. The first issue, pointed out recently in Ref. [5], has to do with the fact that this procedure implicitly assumes that the boundary has no effect on bulk forces. While this assumption seems at least intuitively correct for the symmetric case where the two phases have the same thermodynamic properties ($c_L = c_S$ and $D_T^L = D_T^S$) —in this case bulk fluctuations are independent of the boundary which simply adjusts its position via Eq. (3) —it is not *a priori* obvious why it should be correct in the

more general case where the properties of the two phases differ. The second issue has to do with the fact that the interface does not adjust its position *instantaneously* in response to bulk fluctuations but via a first-order kinetics corresponding to the term v_n/μ in Eq. (3). This term is usually included as a "nonequilibrium correction" to the Gibbs-Thomson condition. However, this kinetics is already present in equilibrium and one would strongly expect a stochastic force, separate from bulk forces, to be associated with it.

To resolve these issues it becomes necessary to determine if Eqs. (1)–(4), which, by construction, are consistent with equilibrium bulk fluctuations, are also consistent with equilibrium interfacial fluctuations. We first recall that fluctuations of the solid-liquid interface on wavelengths $\lambda = 2\pi/k$ much larger than some short wavelength cutoff scale Λ of a few molecular diameters are governed by the Gaussian probability distribution

$$p \sim \exp\left[-\frac{\gamma}{k_B T_M} \int d^2 r \tfrac{1}{2} |\nabla_\perp \xi(\mathbf{r})|^2 \right] \tag{5}$$

with the static fluctuation spectrum

$$\langle \xi_{\mathbf{k}} \xi_{-\mathbf{k}} \rangle_{\text{equil}} = \frac{k_B T_M}{\gamma} \frac{1}{k^2} . \tag{6}$$

This spectrum is then to be compared with the spectrum $\langle \xi_{\mathbf{k}} \xi_{-\mathbf{k}} \rangle_{\text{noise}}$ obtained from the Langevin formalism. In general, to calculate the latter, we have recast Eqs. (1)–(3) in integral form using the standard Green's function approach, linearized the resulting integral equations about a planar interface, and calculated the dynamic response function by Fourier transform. The static spectrum was then obtained using the relation

$$\langle \xi_{\mathbf{k}} \xi_{-\mathbf{k}} \rangle_{\text{noise}} = \frac{1}{(2\pi)^4} \int d\omega\, d\omega'\, d^2 k' \langle \xi_{\mathbf{k}\omega} \xi_{\mathbf{k}'\omega'} \rangle_{\text{noise}} , \tag{7}$$

where the Fourier transform is defined by

$$\xi(\mathbf{r},t) = (2\pi)^{-3} \int d\omega\, d^2 k\, e^{i(\mathbf{k}\cdot\mathbf{r}+\omega t)} \xi_{\mathbf{k}\omega} .$$

The first issue raised above can be considered essentially independently from the second by neglecting in a first step the kinetic term [i.e., by setting $\mu^{-1} = 0$ in Eq. (3)]. In this case, lengthy calculations [7] for the two-sided model yield the required fluctuation-dissipation theorem $\langle \xi_{\mathbf{k}} \xi_{-\mathbf{k}} \rangle_{\text{noise}} = \langle \xi_{\mathbf{k}} \xi_{-\mathbf{k}} \rangle_{\text{equil}}$. Implicit in this result is the fact that the boundary has no net effect on the bulk forces of each phase and that Eqs. (1)–(4) provide the proper incorporation of thermal noise in the *absence* of interfacial kinetics. To address the second issue related to interfacial kinetics it is simpler to present our results for the symmetric case where the two phases have the same thermodynamic properties (with no loss of generality for the general nonsymmetric case). With the definitions $c_S = c_L = c$, $D_T^S = D_T^L = D_T$, and $\mu^{-1} \neq 0$, the integral equation describing the linear response of the interface takes the form [10]

$$\Gamma \nabla_\perp^2 \xi(\mathbf{r},t) - \frac{1}{\mu} \frac{\partial \xi(\mathbf{r},t)}{\partial t} = \int_{-\infty}^{t} \frac{dt'}{[4\pi D_T (t-t')]^{3/2}} \left\{ \int d^2 r' \exp\left(-\frac{|\mathbf{r}-\mathbf{r}'|^2}{4D_T(t-t')} \right) \left[\frac{L}{c} \frac{\partial \xi(\mathbf{r}',t')}{\partial t'} + q_z^S(\mathbf{p}) - q_z^L(\mathbf{p}) \right] \right.$$
$$\left. - \int d^2 r' \exp\left(-\frac{|\mathbf{r}-\mathbf{r}'|^2 + z'^2}{4D_T(t-t')} \right) \left[\int_{-\infty}^{0} dz' \nabla' \cdot \mathbf{q}^S(\mathbf{R}',t') + \int_0^{\infty} dz' \nabla' \cdot \mathbf{q}^L(\mathbf{R}',t') \right] \right\} . \tag{8}$$

Fourier transforming Eqs. (4) and (8) and using Eq. (7) we obtain, after lengthy manipulations, the result

$$\langle \xi_{\mathbf{k}} \xi_{-\mathbf{k}} \rangle_{\text{noise}} = \langle \xi_{\mathbf{k}} \xi_{-\mathbf{k}} \rangle_{\text{equil}} F_B(d_0 k; \bar{\mu}) , \tag{9}$$

where $d_0 = \Gamma c/L$ is the capillary length, $\bar{\mu} \equiv \mu\Gamma/D_T$ is a dimensionless kinetic coefficient, and

$$F_B(d_0 k; \bar{\mu}) = \int_{-\infty}^{+\infty} \frac{d\Omega}{\pi} \frac{1}{h(\Omega)} \operatorname{Re}[1/g(\Omega)] , \tag{10}$$

$$g(\Omega) = 2 d_0 k (1 + i\Omega/\bar{\mu})(1 + i\Omega)^{1/2} + i\Omega , \tag{11}$$

$$h(\Omega) = 1 - [(1+\Omega^2)^{1/2} - 1]/\bar{\mu} . \tag{12}$$

In the physically relevant limit where $\bar{\mu} \ll 1$, the wavelength $\lambda^* = 2\pi/k^*$ at which the noise-averaged spectrum is half the equilibrium one [i.e., $F_B(d_0 k^*; \bar{\mu}) = \frac{1}{2}$] can be shown to take the simple form $\lambda^* \cong 4\pi d_0/\bar{\mu} = 4\pi c D_T/(\mu L)$. To illustrate these results, we have shown in Fig. 1 a plot of $F_B(d_0 k; \bar{\mu})$ calculated by evaluating numerically the integral in Eq. (10) with $\bar{\mu} = 5 \times 10^{-3}$. The main point here is that Eqs. (1)–(4) generate interfacial fluctuations which are consistent with equilibrium fluctua-

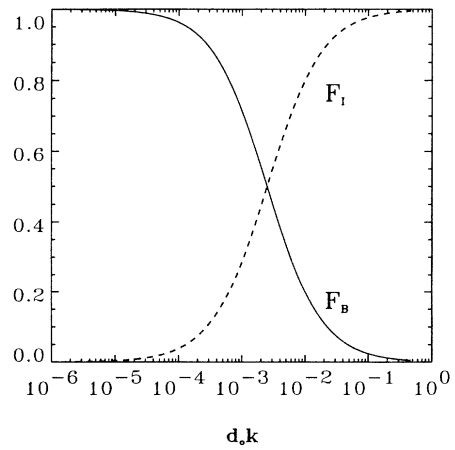

FIG. 1. Plot of $F_B(d_0 k; \bar{\mu})$ (solid line) and $F_I(d_0 k; \bar{\mu})$ (dashed line) for the symmetric model of the solidification of a pure substance with $\bar{\mu} = \mu\Gamma/D_T = 5 \times 10^{-3}$.

tions on scales larger than λ^* but are strongly in error (drop to zero) on scales smaller than λ^*. Since situations can arise where fluctuations on scales smaller than λ^* can become selectively amplified by morphological instabilities, it becomes crucial to determine how the Langevin formalism should be modified in order to reproduce the correct equilibrium interfacial fluctuations on all scales (i.e., all $k \ll \Lambda^{-1}$).

The necessary modification of the Langevin formalism consists in adding a stochastic force $\eta(\mathbf{r},t)$ with variance

$$\langle \eta(\mathbf{r},t)\eta(\mathbf{r}',t')\rangle = 2\frac{k_B T_I(\mathbf{p})^2}{\mu L}\frac{\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')}{[1+|\nabla_\perp \xi(\mathbf{r},t)|^2]^{1/2}} \quad (13)$$

to the right-hand side of Eq. (3) which, using the definition of v_n, can be rewritten in the form

$$\frac{\hat{\mathbf{n}}\cdot\hat{\mathbf{z}}}{\mu}\frac{\partial \xi(\mathbf{r},t)}{\partial t} = T_M - T_I(\mathbf{p}) - \Gamma\kappa + \eta(\mathbf{r},t)\,. \quad (14)$$

The factor of $[1+|\nabla_\perp \xi(\mathbf{r},t)|^2]^{1/2}$ in the denominator of Eq. (13) is necessary to ensure that the net force on a small area dS of the interface is independent of its orientation with respect to the (x,y) plane. Note that our present parametrization requires $\xi(\mathbf{r},t)$ to be single valued [the generalization to the more general case where $\xi(\mathbf{r},t)$ is multivalued is straightforward]. In an analogous way that bulk forces originate microscopically from fluctuations in the kinetic energy of molecules inside a small volume, the interface force $\eta(\mathbf{r},t)$ can be interpreted as originating from fluctuations associated with the exchange of molecules between the two phases across a small area of the interface. In particular, this exchange results from the balance of two activated processes (corresponding to adding and withdrawing a molecule to and from the solid) whose average rates are strongly temperature dependent and equal when $T_I(\mathbf{p}) = T_M$. The interface force describes fluctuations in the difference of these rates.

The consistency of the Langevin formalism now defined by Eqs. (1), (2), and (4) together with Eqs. (13) and (14) is then straightforwardly verified by calculating the static fluctuation spectrum with $\eta(\mathbf{r},t)$ added to the left-hand side of Eq. (8). The analog of Eq. (9) becomes $\langle \xi_{\mathbf{k}}\xi_{-\mathbf{k}}\rangle_{\text{noise}} = \langle \xi_{\mathbf{k}}\xi_{-\mathbf{k}}\rangle_{\text{equil}}[F_B(d_0k;\bar{\mu}) + F_I(d_0k;\bar{\mu})]$, where

$$F_I(d_0k;\bar{\mu}) = \frac{2d_0k}{\bar{\mu}}\int_{-\infty}^{+\infty}\frac{d\Omega}{\pi}\frac{1}{h(\Omega)}\frac{\mathrm{Re}[1/g(\Omega)]}{\mathrm{Re}[1/(1+i\Omega)^{1/2}]} \quad (15)$$

represents the additional contribution of the interface force $\eta(\mathbf{r},t)$ to the fluctuations. The two functions can be shown to satisfy the conditions $F_B(d_0k;\bar{\mu}) + F_I(d_0k;\bar{\mu}) = 1$ for all k and $\bar{\mu}$ which verifies the consistency of the formalism.

The most relevant question which arises from the present results is under what growth condition the interface force should affect the formation of solidification patterns. Without embarking on a detailed calculation along the line of Ref. [4], a crude estimate of the growth rate at which this force should become relevant can be obtained by noting that only interfacial fluctuations of wavelength larger than the stability length $\lambda_S \sim \sqrt{D_T d_0/v}$ are amplified by morphological instabilities (e.g., on the side of needle crystal in the case of sidebranching). Since the interface force only affects fluctuations of wavelengths shorter than λ^*, the growth rate at which it should become relevant (obtained by setting $\lambda_S \sim \lambda^*$) is then given by $v^* \sim \mu^2 \gamma T_M / c D_T$. The value of μ is usually not precisely known. However, for monoatomic metals we can use the theoretical estimate of Ref. [11], consistent with a large body of rapid solidification experiment, given by $\mu = V_S L/RT_M^2$, where L is the latent heat per mole, R the gas constant, and V_S is the speed of sound in the bulk (typically of order 2000 m/sec in metals). This estimate, together with typical material parameters for monoatomic metals, yields values of λ^* in the range of a few hundred nm to 1 μm and v^* in the range of several cm/sec to a few m/sec. For these materials, we therefore expect the interface force to be relevant at large solidification rates. For materials like succinonitrile [2] or ammonium bromide [3] where sidebranching has been well characterized, values of μ are not precisely known but are probably smaller since larger molecules tend to yield slower interfacial kinetics, in which case v^* will also be smaller (note in particular the μ^2 dependence of v^*). However, we do not expect v^* to be small enough for the interface force to play a significant role in the low velocity experiment of Huang and Glicksman [2] to which Langer's calculation [4] applies.

In summary, we have presented a self-consistent Langevin formalism which provides a rigorous theoretical basis to incorporate thermal noise in the basic continuum equations of solidification. It differs from that originally proposed by Cherepanova (which is generally not consistent with equilibrium interfacial fluctuations) in that (i) bulk Langevin forces need also to be included in the interface conservation conditions and (ii) an extra stochastic interface force associated with the relaxational kinetics of the interface needs to be included in the Gibbs-Thomson condition. In connection to experiment, there are a number of alleys of investigation which seem worth exploring in the future. For example, it would be useful to perform using the present formalism a detailed calculation of noise amplification during *rapid* dendritic solidification where a pronounced sidebranching activity is still observed [12] and one could expect the considerably finer dendrite tips to be more susceptible to thermal noise. This might help decide if the present inadequacy of this noise to account for the observed sidebranch amplitude is peculiar to slow solidification rates or a general feature of dendritic growth, in which case the effect of other *extrinsic* noise sources such as the heterogeneous nucleation of microbubbles of dissolved gases at the

solid-liquid interface, for which there is experimental evidence [13], may have to be considered. In the context of directional solidification, it would also be useful to perform an analysis of the effect of thermal noise close to the onset of morphological instability. There, the noise level can be directly inferred experimentally by measuring the time necessary for fluctuations to become macroscopically amplified [14]. An analysis of this type for the one-sided model of directional solidification [7] indicates that such noise measurements should be possible for extremely dilute alloys or liquid crystal systems [15] where a direct comparison of theory and experiment could be made.

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