Molecular orientation in crystal formation

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Abstract. A model is proposed for the growth of crystals with molecular orientation from a melt. The proposed free-energy functional depends on a local order parameter ϕ, which may be interpreted as a density, and the orientation of a unit vector $\hat{c}$, which is interpreted as a molecular orientation. Initial studies of the relation between the growth conditions and the growth rate and uniformity of the molecular orientation are reported.

1. Introduction

Despite a long history, the study of how a system moves from a liquid to a solid state remains of great interest from a theoretical point of view. In particular, for technological applications, it is important to understand how the growth conditions of single crystals can be optimized to produce good quality crystals for a specific application.

It has long been recognized that single crystals of solids with a molecular polarization, such as KDP, are valuable as optically active components; however, the structural properties of such solids are determined by a number of factors [1]. In general, one wishes to be able to grow the crystal as quickly as possible; however, optimal conditions for rapid growth of the crystal may be incompatible with the need for good structural properties [2].

Recently, considerable experimental attention has been focused on very thin films of organic molecules, in part because of their potential as electro-optical components and as data storage media [3–8]. These experimental studies reveal that the properties of the crystals formed in these thin films depend on the growth conditions. These properties include the degree of alignment (or more generally the degree of ordering) of the molecular orientations in the film.

Various models based on a Landau–Ginzburg free-energy functional exist for the study of the growth of the condensed phase from a fluid phase. For example, models A and C (in the nomenclature of Hohenberg and Halperin [9]) may be used for this. While such models hide detailed information, such as precise molecular structure, within a small number of model parameters, they enable theoretical studies to focus on general properties. In particular, how growth conditions affect the structure of the condensed phase may be studied. In this spirit, a model is proposed here, which allows us to study the interaction between the growth of the crystal phase and the ordering of the molecular orientations within the resulting crystal.

For the purpose of discussing the physical meaning of the terms in the free-energy functional and making clear the changes relative to standard models (such as model A), we

formulate the model on a continuum in section 2. However, in order to simulate the growth process, this model was replaced by a lattice model and the differential operators in the free energy of section 2 were replaced by finite-difference approximations. Similarly, the time evolution equations were approximated by finite-difference equations using a discrete time variable. Results reported in sections 3 and 4 were obtained from simulations of this discretized model. (As noted below, some care was needed in the choice of model parameters and time step to ensure stability of the discretized model.)

2. The model

2.1. Free-energy functional

A Landau–Ginzburg free-energy functional is proposed:

$$
\mathcal{F} = \int \mathrm{d}x \, \mathrm{d}y \left\{ \frac{\kappa}{2} |\nabla \phi(x, y)|^2 + \frac{k_1}{2} |\nabla \cdot \hat{c}|^2 \phi^2 |\nabla \phi(x, y)|^2 \right.
$$
$$
\left. + \frac{k_2}{2} |\nabla \times \hat{c}|^2 \phi^2 |\nabla \phi(x, y)|^2 + f(\phi(x, y)) \right\} \tag{1}
$$

where

$$
f(\phi) = \phi^2 - 2\phi^4 + \phi^6 + T\phi^2 \tanh(\lambda U).
$$

For the present study we restrict the model to crystal growth in two-dimensional films. The generalization of the model to three dimensions is straightforward.

In this model, ϕ represents an average local density of the material and $\hat{c}$ represents the local molecular orientation. κ determines the width of the solid–liquid interface (throughout, κ is assumed to be non-negative). The potential f was previously used by Kam and Levine [10]. f has a minimum at $\phi = 0$ and near $\phi = 1$ with T a positive constant. The parameter U represents the deviation from the critical temperature. In the case where $k_1 = k_2 = 0$, for $U > 0$, $\phi = 0$, interpreted as the density of the pure liquid phase, is a global minimum and for $U < 0$, the minimum near $\phi = 1$, interpreted as the density of the pure equilibrium solid phase, is a global minimum. λ is a positive constant giving a coupling between the temperature field U and ϕ. Typical graphs of f are shown in figure 1. Non-zero k_1 and k_2 will change the non-zero global and local minimum of $\mathcal{F}(\phi)$ near interfaces. In particular, they will shift the critical temperature from $U = 0$. (See the comments in section 4.)

The second and third terms in $\mathcal{F}$ are introduced here to represent the coupling between the local density and the local molecular orientation. It can be seen that $\mathcal{F}$ is reduced by lowering the divergence or the curl of the orientation. Thus, for sufficiently large k_1 or k_2 the molecules in the solid phase will tend towards some uniform orientation. (Throughout, we take k_1 and k_2 to be non-negative.) The powers of ϕ and $|\nabla \phi|$ in the divergence and curl terms ensure that these terms do not contribute to the dynamics in the melt or away from interfaces. This reflects our assumption that in the liquid the molecules are sufficiently far apart that their orientations do not affect one another and that when they are packed into the solid they cannot rotate to any great extent. Thus, most of the changes in alignment of the molecular orientations should occur at the interface between the liquid and solid phases. (The divergence and curl terms are similar to the distortion energy terms which occur in theories of liquid crystals [11]; however, in the case of liquid crystals the coefficients are constant through the system—i.e. independent of ϕ.)

(a)

(b)
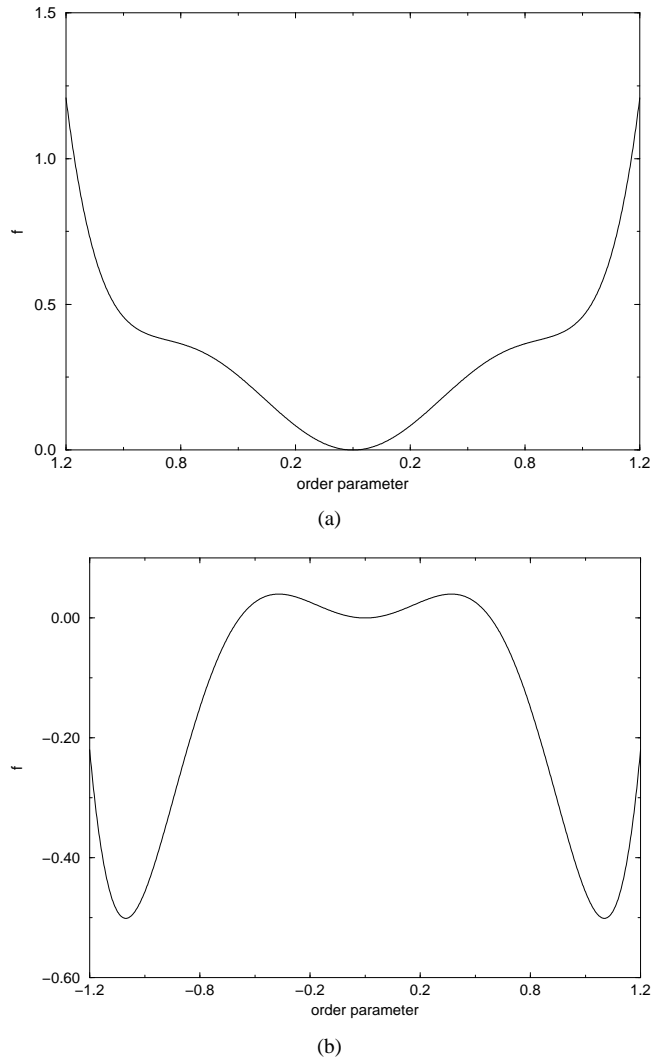
Figure 1. Typical free-energy curves with $T = 0.6$, $\lambda = 10.0$ and for reduced temperatures $U = 0.1$ (a) and $U = -0.1$ (b).

2.2. Time evolution

The time evolution of ϕ is given by

$$\frac{\partial \phi}{\partial t} = -\Gamma_\phi \frac{\delta \mathcal{F}}{\delta \phi}.$$

In order to obtain the time evolution of $\hat{c}$, we let $\hat{c} = \cos\theta \hat{i} + \sin\theta \hat{j}$ and consider the time evolution of θ:

$$\frac{\partial \theta}{\partial t} = -\Gamma_\theta \frac{\delta \mathcal{F}}{\delta \theta}.$$

Given these equations, one can see that the ratio $\Gamma_\theta / \Gamma_\phi$ determines the ability of the molecules to align on the timescale of the growth process. If Γ_ϕ is large enough, the crystal can grow very

quickly in comparison to the rate at which θ can change. Once the interface has passed a point in the system, then θ is essentially fixed at that point. Thus, the orientations will tend to be frozen in the interior of the grown crystal. On the other hand, if Γ_θ is large in comparison to Γ_ϕ, the orientations have a chance to change before the interface goes past and they become locked in. The larger the ratio, the more the molecular orientations in the crystal will be aligned.

In this initial study we have assumed that the constants k_1 and k_2 are equal. Also for this initial study, we have assumed that heat diffusion is extremely rapid on the scale of the crystal growth rate; consequently the local value of U is treated as a constant throughout the simulations. We consider two cases for U: that in which the temperature has the same value everywhere in the growth cell; and that in which there is a temperature gradient between the seed crystal and the walls of the growth cell.

3. Growth from seed crystals

3.1. Growth in a uniform temperature field

For the present study, a number of simulation runs were performed using a discretized version of the model defined in section 2. Associated with each point i on a square grid are two continuous variables ϕ_i and θ_i, representing the local density and local molecular orientation respectively. The initial system consists of a seed crystal ($\phi_i \approx 1$) at the centre of the system, with all of the molecular orientations aligned at $\theta_i = 0$, surrounded by fluid ($\phi_i = 0$). In the fluid, the molecular orientations are each initially randomly assigned from a distribution corresponding to a vector mean of zero for the orientations of molecules in the fluid. (As the simulations randomly sample the configurations of molecular orientations in the fluid, where appropriate, we indicate error bars corresponding to the statistical variation over different simulations for a given set of model parameters.)

For all of the simulation runs described in this section, the parameters were set with $k_1 = k_2 = 1$, $T = 0.6$, $\lambda = 10.0$ and $\kappa = 0.5$. We chose a (reduced) temperature $U = -0.1$. Under these conditions the equilibrium phase has a density $\phi = 1.086$. The crystal grew to fill the entire system. Intermediate growth stages for two values of $\Gamma_\theta/\Gamma_\phi$ are shown in figure 2.
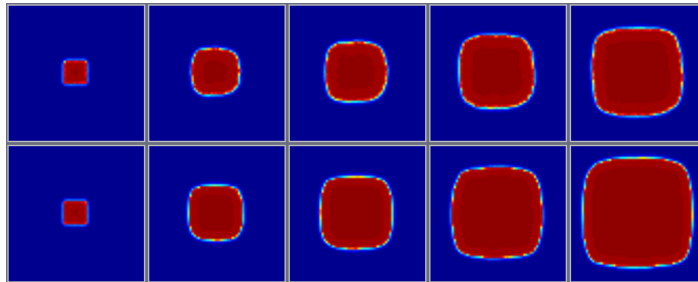

Figure 2. Typical growth stages of the simulated growth from seed of two-dimensional crystallites for ratio = 0 and ratio = 1500 and $\kappa = 0.5$. The outer dark region represents fluid, $\phi \approx 0$, and the inner dark region represents the seed and surrounding crystal growth, $\phi \approx 1$. The white regions represent the interface in which intermediate values of ϕ occur. (The parameters for the simulation are described in subsection 3.1.)

The intermediate-time crystallites show some dependence of the crystal shape and boundary roughness on the ratio $\Gamma_\theta/\Gamma_\phi$; however, it is clear from figure 2 that one of the primary effects of the ratio $\Gamma_\theta/\Gamma_\phi$ is that intermediate crystallites are smaller for the smaller ratio at equal times.

The interior of the crystallites exhibited a near-homogeneous value of ϕ close to the equilibrium value. This indicates that the simulations correspond to growth conditions resulting in structurally good crystals with few defects such as inclusions.

Figure 3 shows the change in the total value of ϕ_i during the growth process. The flattening of the curves at long times is an artifact of the finite system size and corresponds to filling of the system. The growth rates indicated by the curves prior to the onset of these finite-size effects show that some increase in the growth rate is observed as $\Gamma_\theta / \Gamma_\phi$ is increased from zero to 600. This behaviour is understood, as the higher values of Γ_θ mean that the molecular orientations are better able to align during a given time interval, and this increased alignment of the molecular orientations enhances growth of the crystal through the terms with coefficients k_1 and k_2 in F. As discussed below, as $\Gamma_\theta / \Gamma_\phi$ is increased, the degree of molecular alignment saturates and we therefore expect increasing $\Gamma_\theta / \Gamma_\phi$ to have a diminishing effect on the crystal growth rate. This is observed. (Note: our early simulations revealed that care must be taken to chose a sufficiently small time step for larger values of $\Gamma_\theta / \Gamma_\phi$ in order to avoid unphysical results such as the growth rate decreasing with increasing values of this ratio. For improved computational efficiency, future studies of systems with large values of $\Gamma_\theta / \Gamma_\phi$ should use a multiple-time-step method [12].)
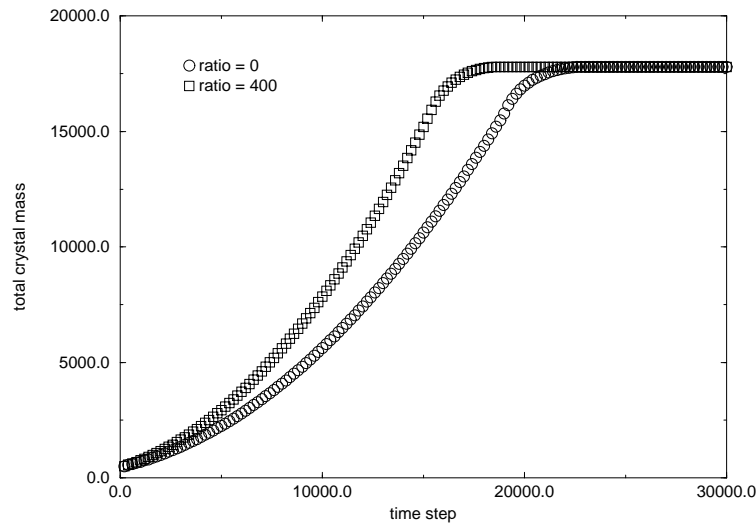
Figure 3. The change in crystal mass with time for two values of the ratio $\Gamma_\theta / \Gamma_\phi$ with $\kappa = 0.5$.

Of primary interest in this study is the effect of the growth conditions on the degree of molecular alignment in the resulting crystal. A measure m of alignment relative to the seed

$$m = \left(\sum \phi_i \cos(\theta_i) \right) \Big/ \left(\sum \phi_i \right)$$

was calculated for different ratios $\Gamma_\theta / \Gamma_\phi$ (figure 4). As expected, the molecular alignment is small at low values of $\Gamma_\theta / \Gamma_\phi$ and increases as this ratio increases. (m is non-zero even when the ratio approaches zero in figure 4, as the seed is included in the sum defining m.) The alignment approaches saturation at a finite value of this ratio.

In addition, the variation in the effect of the seed with distance from the seed was studied by calculating the correlation function

$$\langle \hat{c}(0) \cdot \hat{c}(r) \rangle$$
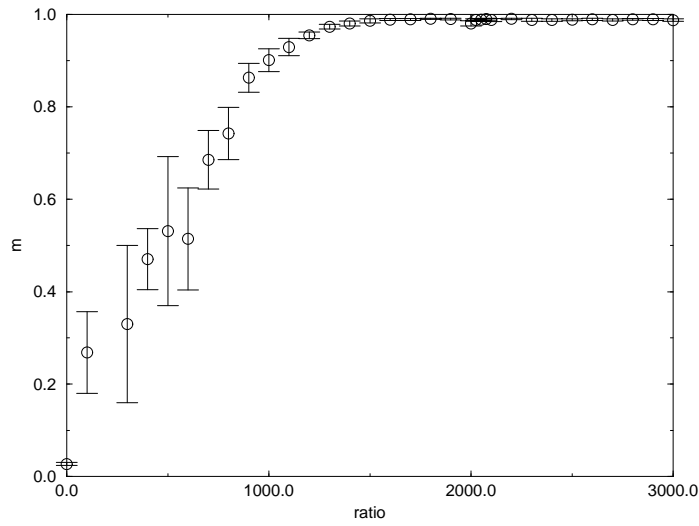
Figure 4. Variation of the global alignment of the molecular orientation for various values of the ratio $\Gamma_\theta / \Gamma_\phi$ with $\kappa = 0.5$.
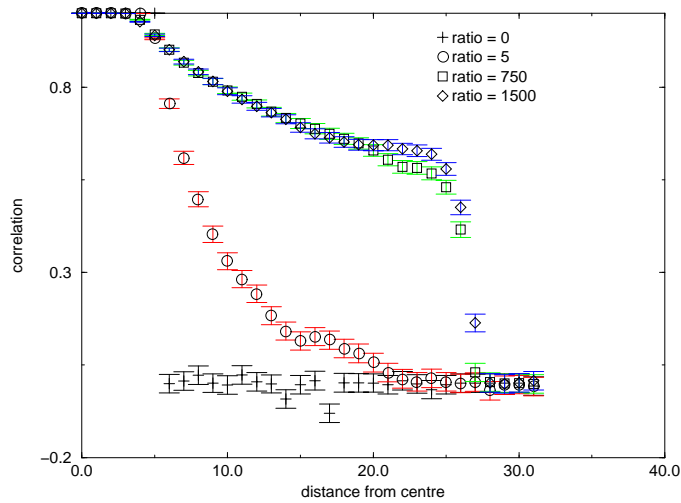

Figure 5. Variation of the molecular orientation correlation function with distance from the centre of the seed for $\kappa = 0.5$.

for different radii, r, from the centre of the system for different ratios $\Gamma_\theta / \Gamma_\phi$. It is seen that for small ratios the correlation falls off rapidly with distance while for large ratios the correlation decays relatively slowly (figure 5).

3.2. Growth in a temperature gradient

In figure 6 the change in the total crystal mass with time is shown for typical crystals grown in a temperature gradient. The temperature at the centre of the seed crystal was $U = -0.1$ and the temperature increased linearly to the edge of the system where it was $U = -0.01$.
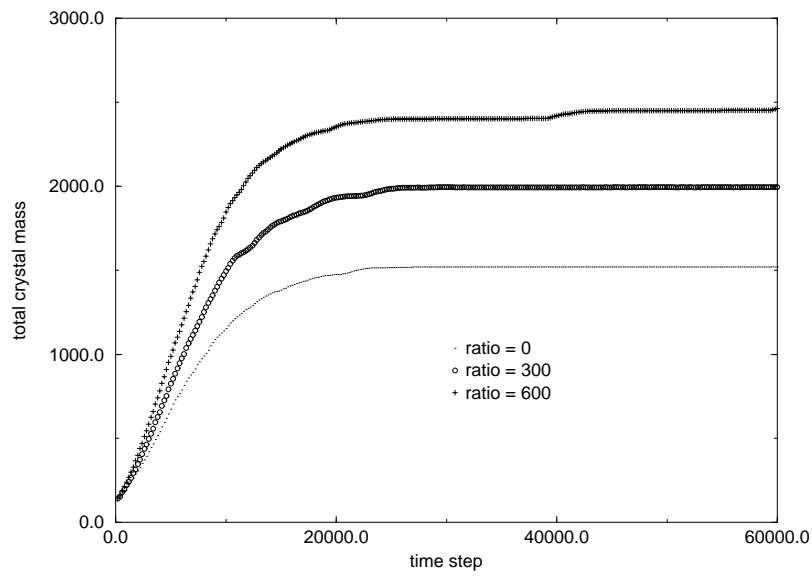
Figure 6. Crystal mass versus time in a temperature gradient for various values of $\Gamma_\theta / \Gamma_\phi$ for $\kappa = 0.5$. (The parameters for the simulation are described in subsection 3.2.)
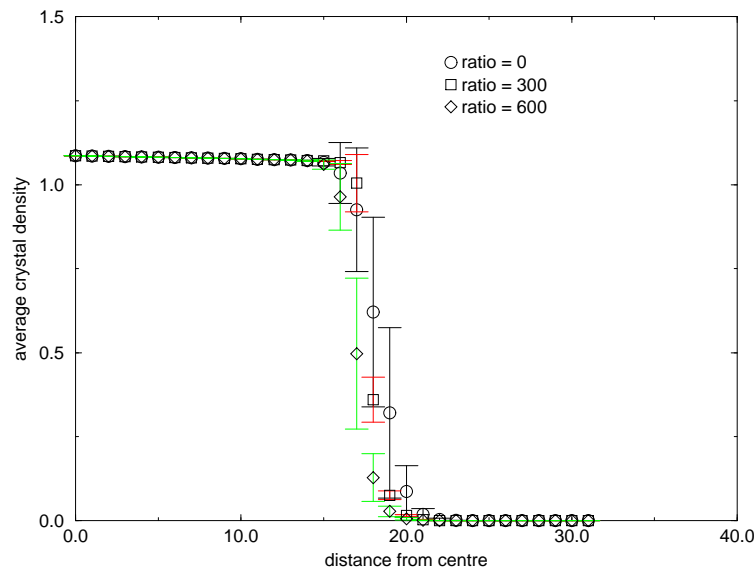

Figure 7. Variation of the density with distance from the centre of the seed after growth has been stopped for crystals grown in a temperature gradient for various values of $\Gamma_\theta / \Gamma_\phi$.

Figure 7 shows the variation in crystal density (ϕ) with distance from the seed centre once the growth process has been stopped. As is clear from the figures, the principal role of the temperature gradient is to slow and eventually halt crystal growth; however (at least for the parameter values given above), the structure of the grown crystal remains very good (i.e. with the density close to saturation) for seeds grown in a temperature gradient. The correlation

of the molecular orientation with the seed orientation in the bulk of the grown crystal is not substantially different for crystals grown in a temperature gradient (figure 8) and for crystals grown in a uniform temperature field. Within the limitations of this model, use of a temperature gradient to slow crystal growth does not improve the alignment of the molecular orientations within the bulk of the crystal
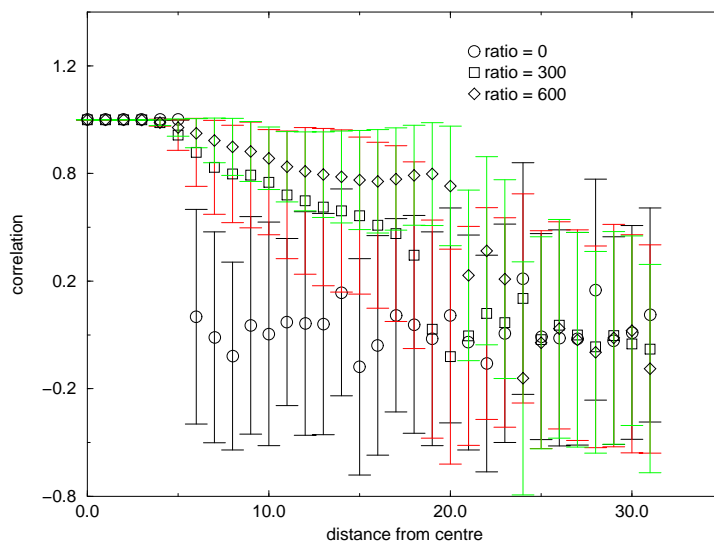
Figure 8. Average correlation of the molecular orientation with the seed orientation as a function of the distance from the seed centre for crystals grown in a temperature gradient.

4. Effects of the surface tension

The term with coefficient κ in the Landau free energy (equation (1)) represents a surface tension at the interface between the liquid and solid. To a large extent, it is the interaction between this term and the divergence and curl terms which determines the dynamics of crystal formation for this model.

The isotropic surface tension term $\kappa|\nabla\phi|^2$ represents an energy penalty for forming an interface. This term without the divergence and curl terms would result in an interface that moves with a velocity dependent on κ and the curvature of the interface, according to the Allen–Cahn equation [13]. For small κ then, the seed crystal will not grow quickly. If, in addition, Γ_θ is small enough, the divergence and curl terms will play a role, as molecular alignment will be slow. We wished to investigate whether the energy penalty associated with the divergence and curl terms would be large enough to limit the growth of the seed crystal in a uniform temperature field.

Therefore in addition to the studies described above at $\kappa = 0.5$, $k_1 = k_2 = 1$, we have repeated some of the growth studies in a uniform temperature field but with smaller values of κ. This revealed that there is a substantial structure to the early growth process, which is sensitive to the relaxation rate of the molecular orientation for small values of the surface tension.

To investigate growth for small values of κ, runs were done at a uniform temperature $U = -0.1$ and with $\kappa = 0.28$ and for different ratios $\Gamma_\theta/\Gamma_\phi$. It was seen that for a ratio of 0, the crystallite did not grow to fill the system. Rather, the crystal grows initially and then the total value of ϕ (interpreted as a crystal mass) levels off and remains steady. For just a

few runs, the growth levels off, jumps and then levels off again. We interpret this behaviour as the limitation of growth due to an energy penalty arising from random orientations within the system that do not change.

In effect the random orientations of the molecules results in random changes in the local effective critical temperature at points on the crystal interface. At higher values of κ where the interface is broad, these do not significantly perturb the growth process. However, at smaller values of kappa these local fluctuations are sufficient to inhibit or stop growth, if the local molecular orientation results in a large enough energy penalty through the divergence and curl terms in the free energy.

When the ratio is increased to 5, an interesting behaviour emerges. Almost all of the runs show initial growth of the crystallite, followed by a period in which the growth is stopped or extremely slow before growth resumes (figure 9). We refer to the time during which the growth is halted after the initial growth as the waiting time. Although the initial growth appears to be smooth, growth after the waiting period is not and many of the runs exhibit further periods of stopped or very slow growth. The pattern of an initial growth stage followed by a waiting period followed by further growth is common to almost all of the simulation runs performed at significantly higher values of $\Gamma_\theta / \Gamma_\phi$. As the ratio $\Gamma_\theta / \Gamma_\phi$ is increased, the typical waiting times become smaller, though there is a considerable spread in the distribution of waiting times over different simulation runs at fixed $\Gamma_\theta / \Gamma_\phi$. The spread in the distribution is too broad to be fitted by a Poisson distribution, implying that the process required for growth to restart cannot be described by a simple classical nucleation theory. The mean waiting times for $\kappa = 0.28$ and various ratios are plotted in figure 10.
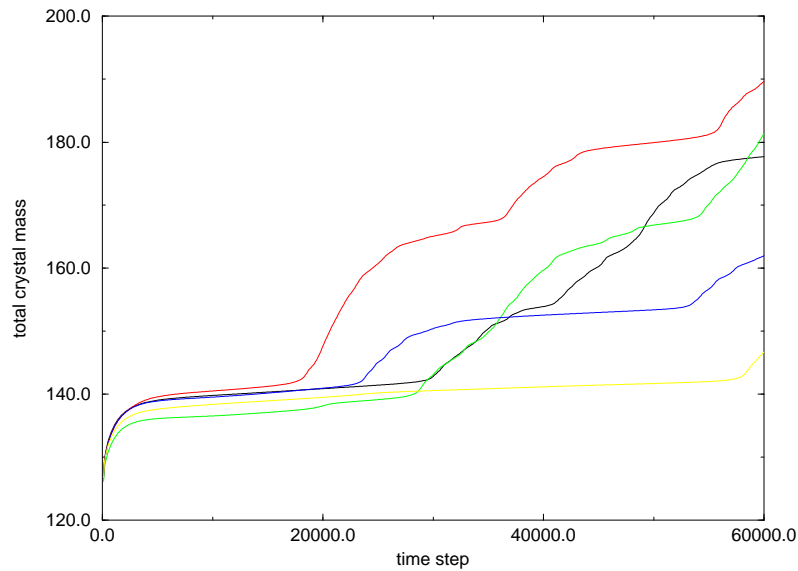
Figure 9. Typical simulation results for growth of a crystal in a uniform temperature field for $\kappa = 0.28$ and the ratio $\Gamma_\theta / \Gamma_\phi = 5$. Each curve represents a different simulation, i.e. a different initial configuration of orientations in the fluid. (The parameters for the simulations are described in section 4.)
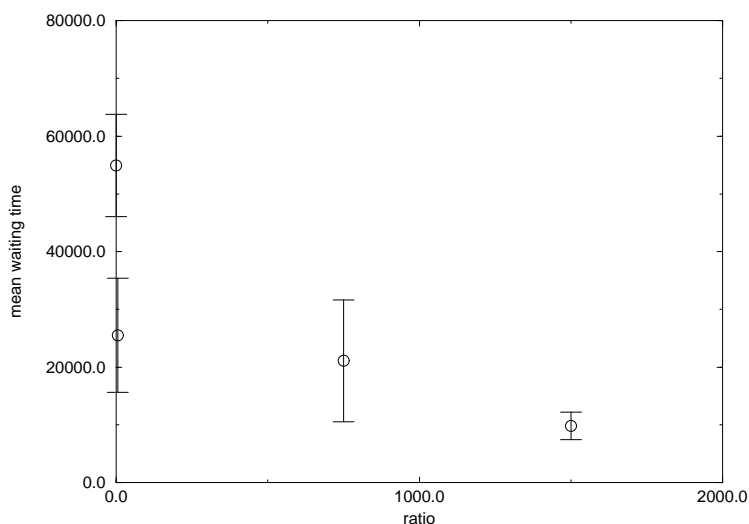
Figure 10. Mean waiting times for growth of a crystal in a uniform temperature field and with $\kappa = 0.28$ and different ratios $\Gamma_\theta / \Gamma_\phi$. Note that the point at $\Gamma_\theta / \Gamma_\phi = 0$ underestimates the waiting time, as many of the simulations exhibited waiting periods which did not terminate during the simulation.

5. Summary

We have introduced a free-energy functional for the modelling of the interaction between crystal growth conditions and the degree of molecular alignment in the resulting crystal. Simulations of this model indicate that if the time required for the molecules to rotate is long, compared with the time for the solid–liquid interface to move through a region of the system, the degree of alignment will be poor even though the crystal may be structurally good. Conversely, at higher values of the relaxation rate for the molecular orientation, the alignment saturates at its maximum value. At low values of the relaxation rate, the crystal may still have good molecular alignment near the seed (providing that the seed has good molecular alignment), but this decays rapidly with distance from the seed. If the relaxation rate is sufficiently low, this may also have a detrimental effect on the crystal growth rate.

In addition, this initial study has shown that for low values of the surface tension parameter κ, the coupling between the (initially) random molecular orientations at the crystal solution interface and the growth process leads to a multistage growth mechanism in which the initial and later periods of relatively rapid growth are separated by periods in which there is no (or very slow) growth. Broadly speaking this can be understood, as an initial period of rapid growth occurs in regions of the interface where the molecular alignments favour growth. Once these regions with favourable molecular alignments are used up, growth cannot proceed until molecules in the interface region become realigned in such a way as to again allow rapid growth. However, the precise manner in which the interplay between the molecular orientations, the surface tension and the initial conditions affect the dynamics requires further investigation. (For example, initial melting of the seed followed by growth has been observed for some values of the interface parameter and critical temperature parameter if growth is started from a seed/solution system with a sharp interface in a simplified model in which the coupling to the molecular orientations is removed. The relationship between such initial condition effects and effects due to coupling of the growth to the molecular orientation should be further clarified.)

Acknowledgments

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