Effects of nonequilibrium kinetics on velocity selection in dendritic growth

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The effects of nonequilibrium kinetic undercooling on the velocity selection in the two-dimensional nonlocal model of dendritic growth are studied with use of recently developed analytical and numerical methods. We study and compare the effect of anisotropy on the selected velocity in detail for both terms.

INTRODUCTION

It has recently been shown numerically and analytically that the addition of anisotropy to the surface tension is crucial to obtain velocity selection in the fully nonlocal model of dendritic growth. In this paper we study the effects of nonequilibrium kinetics on the velocity selection in the two-dimensional symmetric model of solidification of a pure substance.

In Sec. I we ignore surface tension and study the effects of the kinetic term alone. We find analytically that there is a continuous family of solutions in the limit of small kinetic undercooling. When the kinetic term is large enough our analytical analysis hints that this family should be completely destroyed; this is confirmed numerically.

In Sec. II we study the model when both the surface tension and the kinetic undercooling are present. In Sec. II A we predict analytically and observe numerically that when the model is completely isotropic there is no possible steady state. In Sec. II B we predict analytically that the addition of anisotropy to the kinetic term only is not enough to obtain a steady-state solution in the limit of small undercooling. However, we numerically find selection of a steady state for large enough undercoolings. In Sec. II C we study numerically the effect of kinetic anisotropy on the selected velocity when anisotropy is already included in the surface tension. In Sec. II D we study in detail the dependence of the selected velocity on the anisotropy in both the kinetic term and the surface tension.

I. EFFECT OF THE KINETIC TERM

IN THE ABSENCE OF SURFACE TENSION

The Gibbs-Thomson condition is an equilibrium condition which is not, strictly speaking, correct when the interface is moving. If \( \delta T = \frac{\partial g}{\partial \nu} \) in the linear-response limit we can write \( \delta T = \frac{\partial g}{\partial \nu} \bigg|_{\nu = 0} \). Clearly \( \delta T < 0 \) if the solid is to grow. We define \( \beta = -\frac{\partial g}{\partial \nu} \bigg|_{\nu = 0} c/L > 0 \), where \( c \) is the specific heat per unit volume and \( L \) the latent heat per unit volume.

Including the nonequilibrium correction the steady-state equation is

\[
\Delta - d_0^2 \frac{\partial \psi}{\partial \nu} = \frac{1}{2} \int_0^\infty \frac{d \tau}{\tau} \int_{-\infty}^{\infty} du \exp \left[ \frac{\left( (x - u)^2 + \left( \psi(x) - \psi(u) + \tau \right)^2 \right)}{2 \tau} \right].
\]

Here \( \Delta = (T_M - T_M^*) c / L \) is the dimensionless undercooling with \( T_M \) the solid’s melting temperature and \( T_M^* \) the temperature far away in the liquid. \( d_0^2 = T_M f c v / 2 DpL \) is the dimensionless capillary length, \( f \) the interface free energy per unit area, \( v \) the dendrite velocity and \( p \) the Peclet number defined by \( \Delta = (\nu p)^{1/2} \exp(p) e v / p^{1/2} \). \( \psi(x) \) is the position of the interface in the dendrite reference frame and lengths are measured in units of \( p \), the radius of curvature of the Ivantsov solution of the same velocity.

In this section we ignore the surface tension and we set \( d_0^2 = 0 \). Following Pelce and Pomeau, we linearize the equation around the Ivantsov solution by writing \( \psi(x) = \xi(x) + x^2/2 \) where \( \xi(x) \) is the correction to the Ivantsov parabola. We then take the small undercooling (small Peclet number \( p \)) limit. Expanding the kernel of the integral term around the singularity and keeping the leading contribution, we obtain

\[
e \frac{d \xi}{dx} - \left( 1 + x^2 \right)^{1/2} \xi_1 / x - \xi_1^{-1} \left( 1 + x^2 \right)^{1/2} \times P \int_{-\infty}^{\infty} du \xi_1(u)/(x - u) = -\epsilon(1 + x^2)/x,
\]

where we define \( \epsilon = \beta v / p \). \( P \) denotes the principal part.

To perform the integral we follow Ref. 8 and define

\[
\tilde{\xi}_1(k) = \left[ 1/(2\pi\epsilon) \right] \int_{-\infty}^{\infty} dx \xi_1(x) e^{ikx/\epsilon}.
\]

In \( k \) space, the homogeneous part of Eq. (2) becomes

\[
k \tilde{\xi}_1(k) + \left[ 1 - \epsilon^2(\partial^2_k)^{1/2}/(\epsilon (\partial_k) \tilde{\xi}_1(k) \right] = 0.
\]
This is a Wentzel-Kramers-Brillouin (WKB) problem when \( \epsilon \ll 1 \). We can write \( \xi_1(k) = \exp[S(k)/\epsilon + T(k) + \cdots] \) and to zeroth order in \( \epsilon \) Eq. (4) becomes

\[
k = F[\partial_k \bar{S}(k)] = -\left[1 - (\partial_k \bar{S}(k))^2\right]^{1/2} \times \left[1 + \text{sgn}(k)\partial_k \bar{S}(k)/\partial_k \bar{S}(k)\right]. \tag{5}
\]

Writing \( \zeta_1(x) = \exp[S(x)/\epsilon + T(x) + \cdots] \), and inverting Eq. (3) we have to lowest order

\[
\exp[S(x)/\epsilon] = \int_{-\infty}^{\infty} dk \exp[\{\bar{S}(k) - ikx\}/\epsilon]. \tag{6}
\]

Using the saddle-point approximation (for \( \epsilon \ll 1 \)) we find that \( S(x) = \bar{S}(k(x)) - ik(x)x \) if \( \partial_k \bar{S}(k) = ik \) and \( \bar{S}(k) = S(k) + ikx(k) \) if \( \partial_x S(x) = -ik \). Equation (5) becomes \( i\partial_k \bar{S}(x) = F[\text{ix}] \) and therefore

\[
dS_\pm(x)/dx = -iF[\text{ix}] = (1 + x^2)^{1/2}(1 \pm \text{ix})/x, \tag{7}
\]

where \( S_\pm(x) \) denotes the two results arising from the two branches associated with \( \text{sgn}(k) \). We would obtain the same expression by performing the integral of Eq. (2) by contour integration using the saddle-point approximation.\(^{3,4}\) Within this approximation, Eq. (7) can be solved exactly for \( S_\pm(x) \) and we obtain the general solutions \( \xi_\pm(x) = \exp[S_\pm(x)/\epsilon] \).

The physically acceptable solution must be real and is \( \xi_1(x) = \xi_\pm^*(x) + \xi_\pm(x)/2 \). We must set \( A = 0 \) and choose \( a = \infty \) when \( x > 0 \), \( a = -\infty \) when \( x < 0 \), to remove an obvious exponential divergence at large \( |x| \). The function is then well defined everywhere and even. We get

\[
\xi_1(x) = \exp[h(x)/\epsilon] \int_{-\infty}^{\infty} du [(1 + u^2)/u] \exp[-h(u)/\epsilon] \times \cos[(g(u) - g(x))/\epsilon],
\]

where

\[
\begin{align*}
h(x) &= (1 + x^2)^{1/2} \\
&\quad + \frac{1}{2} \ln\left[\left(1 + x^2\right)^{1/2} - 1\right]/\left(\left(1 + x^2\right)^{1/2} + 1\right) \tag{9}
\end{align*}
\]

\[
g(x) = \frac{1}{2} \left[|x| + (1 + x^2)^{1/2} + \ln|x + (1 + x^2)^{1/2}|\right].
\]

As \( x \to 0 \),

\[
\xi_1(x) = e + C \left| x \right|^{1/\epsilon}, \tag{10}
\]

where \( C \) is a constant. As \( x \to \infty \), \( \xi_1(x) \approx ex \) which agrees with the asymptotic behavior of the solution to the full nonlinear problem.\(^9\) From the above analysis we can see that the solution (9) is smooth at the tip for small \( \epsilon \). The correction at large \( x \) is of order \( \epsilon/x \) compared to the Ivantsov parabola. This implies the existence of a family of solutions provided that we do not require that \( d^n\zeta_1/dx^n \) or \( d^n\zeta_1/dx^n \) for all \( n \), since this condition will not be satisfied for \( n \gg 1 \). If we require that the solutions are differentiable an infinite number of times then Eq. (9) is obviously not an acceptable solution. If we look for solutions in the space of functions with continuous derivatives of all orders the nonequilibrium kinetic term is a singular perturbation that destroys the family of Ivantsov solutions.

\( \zeta_1(x) \) is not the shape correction that one would obtain from an expansion of \( \zeta_1(x) \) in powers of \( \epsilon \); it is truly the lowest-order part of the WKB solution of Eq. (2). One should therefore not be surprised to find an \( \left| x \right|^{1/\epsilon} \) behavior for \( x \) small, even though one would certainly ignore that term in an expansion of \( \zeta_1(x) \) in \( \epsilon \). Note that if the above analysis is still valid for \( \epsilon \approx 1 \) then Eq. (10) hints that there will be a finite cusp at the tip and the family of solutions will be destroyed.

The existence of a family of solutions is consistent with an alternative formulation of the solvability condition requiring the zero mode of the adjoint equation to be orthogonal to the homogeneous term of Eq. (2).\(^{10}\) Let \( \phi(x) \) be the zero mode. Then the homogeneous adjoint equation to Eq. (2) is

\[
ed\phi/dx + (1 + x^2)^{1/2}\phi/x + \pi^{-1}(1 + x^2)^{1/2} \times P \int_{-\infty}^{\infty} du \phi(u)/(u - x) = 0. \tag{11}
\]

We find the solution to this equation in exactly the same way we found the solution to Eq. (2),

\[
\phi^\pm(x) = A^\pm \exp\left[-\epsilon^{-1} \int_{-\infty}^{\infty} ds (1 + s^2)^{1/2}(1 \pm is)/s\right]. \tag{12}
\]

Both \( \phi^+(x) \) and \( \phi^-(x) \) diverge as \( \left| x \right|^{1/\epsilon} \) as \( x \to 0 \). Imposing antisymmetricity on \( \phi(x) \) yields a linear combination of \( \phi^+(x) \) and \( \phi^-(x) \) that diverges as \( \left| x \right|^{1/\epsilon - 1} \). The fact that Eq. (11) does not have a well-behaved zero mode is consistent with the fact that Eq. (2) has a family of solutions.

Numerically, we study the steady state Eq. (1) using a method first proposed by Vander Broeck\(^{11}\) and then applied to the dendritic growth problem by Meiron\(^{1}\) and Kessler and Levine.\(^2\) The idea is to allow a possible cusp in the solution at the tip by mapping the problem from \( xe^{-\infty} \) to \( xe^{0 \infty} \). We expect a physically acceptable shape to be smooth so that the cusp at the tip vanishes. From this "solvability condition," we are able to determine the physical solution by examining the right slope at the tip: When the slope vanishes we find a solution with at least a continuous second derivative at \( x = 0 \).

We discretize the domain of integration and approximate the function by parabolic elements. The integrodifferential equation then reduces to a system of nonlinear
equations solved by Newton's method. The algorithm converges more slowly when the kinetic term is included. A typical data for \( N = 20 \) takes about 20 sec on a Cyber 205 at the JVNCC. We changed the discretization to check that our results converged to the continuum limit.

The numerical results for the kinetic term alone are plotted in Fig. 1, where we define \( h \equiv \beta v = \epsilon p \). No solutions are found (apart from the Ivantsov solution at \( h = 0 \)). Since \( p = 0.1 \) then \( \epsilon = 1 \) when \( h = 0.1 \) and as we already noted for \( \epsilon \approx 1 \) we expect that the family of solutions will be destroyed. It was not possible to study the regime \( \epsilon \ll 1 \) because of our limited numerical resolution.

II. EFFECT OF THE KINETIC TERM

IN THE PRESENCE OF SURFACE TENSION

In this section we study the combined effect of the surface tension and the kinetic undercooling. Both \( \beta v \) and \( d'_{0} \) are proportional to the velocity \( v \) and their ratio is fixed for a given substance and a given undercooling. Defining \( \sigma \equiv d'_{0} / p \) and \( r \equiv \epsilon / \sigma \) (so \( r = 2 \beta D p L^{2} / T_{M} c f \)), the linearized equation at small undercooling is

\[
\sigma d_{\xi_{1}}^{2} / dx^{2} - \sigma f(x) d_{\xi_{1}} / dx + (1 + x^{2})^{1/2} \xi_{1} / A(x)
+ [x(1 + x^{2})^{1/2}] / [\pi A(x)]
\times \mathcal{P} \int_{-\infty}^{\infty} du \xi_{1}(u)/(x - u) = \sigma t(x),
\]

where

\[
t(x) = [1 + r B(x)(1 + x^{2}) / A(x)],
\]

\[
f(x) = 3x / (1 + x^{2})
+ r(x B(x) - 16b(1 - x^{2}) / (1 + x^{2})^{2}) / A(x).
\]

Here the first term in the right hand side is anisotropic and the second anisotropic by multiplying \( \sigma d'_{0} \) by \( A(d\xi / dx) \) and by multiplying \( \beta \) by \( B(d\xi / dx) \), where \( A(x) = 1 + 8ax^{2} / (1 + x^{2})^{2} \) and \( B(x) = 1 + 8bx^{2} / (1 + x^{2})^{2} \).

To compare Eq. (13) with the work of Barbieri, Hong, and Langer we state the equation for the zero mode \( \phi \) of the adjoint operator

\[
\sigma d^{2} \phi / dx^{2} + \sigma f \phi / dx + \sigma \phi / dx + (1 + x^{2})^{1/2} \phi / A(x)
+ [x(1 + x^{2})^{1/2}] / [\pi A(x)]
\times \mathcal{P} \int_{-\infty}^{\infty} du \phi(u)/(x - u) = 0.
\]

Let \( \phi(x) = \exp[-1/2 S(x)] + T(x) + \cdots \) Using the WKB method we recover the expression of \( S(x) \) given in Ref. 3. Kinetic undercooling corrections appear only in \( T(x) \) and in the inhomogeneous part of Eq. (13). We can include them by multiplying the integral appearing in the solvability condition of Ref. 3 by the prefactor

\[
p(x) = [1 + r B(x)(1 + x^{2}) / A(x)] \times \exp \left[ -r \left( \int_{0}^{x} du [u B(u) - 16b(1 - u^{2}) / (1 + u^{2})^{2}] / A(u) \right)^{1/2} \right].
\]

The solvability condition is then given by

\[
\Lambda = \Re \int_{-\infty}^{\infty} dx \ p(x) m(x) \exp \left[ i \sigma^{-1/2} \left( \int_{0}^{\infty} du (1 + u^{2})^{1/2} (1 + iu)^{1/2} / A(u)^{1/2} \right) \right] = 0,
\]

where

\[
m(x) = A(x)^{1/4}(1 - ix)^{1/4} / (1 + x^{2})^{9/8}.
\]

We now present a systematic summary of the analytical and numerical results.

A. Isotropic case

Let us first turn off the anisotropy and set \( a = b = 0 \). Following Barbieri et al.\(^3\) it is easily seen by doing the integral using the method of steepest descent around \( x = i \), that it is not possible to satisfy Eq. (18) and therefore that there are no solutions. This result agrees with our numerical calculations. In Fig. 2 we plot the slope at the tip versus the rescaled velocity \( d_{0} = cT_{M} v / 2D L^{2} \) when \( p = 0.1 \). \( (d_{0} = p d'_{0}) \). In Fig. 2(a) \( h = 0 \) and we reproduce the results obtained by Meiron.\(^1\) In Fig. 2(b) and 2(c) the ratio \( h / d_{0} \) is fixed with \( h = d_{0} \) in 2(b) and \( h = 5d_{0} \) in 2(c). The kinetic term sharpens the cusp at the tip, and no solutions are found. This was also verified with \( p = 1 \).
In Fig. 3(a) and 3(b) we plot the slope as a function of $d_0$ for $h=d_0$ and $h=5d_0$ with $b=0.3$ and $p=1$. For small $d_0$ the curve crosses zero a few times. It then increases and finally crosses zero again at $d_0=0.014$ in both cases. It is this largest value of $d_0$ that will be dynamically selected. We therefore get a steady-state solution.

The numerical calculations were done with $p=1$ because reliable calculations with $p=0.1$ would take a prohibitive amount of time. Although they apparently contradict our analytical prediction, one must note that the WKB method we used is not expected to be valid for $p \approx 1$. If both the analytical and the numerical calculations are right then this indicates that the kinetic anisotropy may play a different physical role at small undercooling. When $p$ is vanishingly small then so is the growth velocity; this is why the kinetic term becomes irrelevant compared to the surface tension.

C. Kinetic and surface tension anisotropy

We now include anisotropy in both the surface tension ($a \neq 0$) and the kinetic ($b \neq 0$) terms. In Eq. (18) there is a new branch cut appearing because of the presence of the term $A(u)^{1/2}$ in the denominator of the exponential. As

B. Kinetic anisotropy

If we introduce anisotropy in the kinetic term, and therefore if we let $b \neq 0$ but keep $a=0$, there are no new branch cuts appearing in Eq. (18). Again, it means that the solvability condition cannot be satisfied. Our WKB analysis therefore predicts that there should be no solutions.

FIG. 2. Slope at $x=0$ vs $d_0$ for $p=0.1$ with (a) $h=0$, (b) $h=d_0$, and (c) $h=5d_0$.

FIG. 3. Slope at $x=0$ vs $d_0$ for $p=0.1$ with $b=0.3$ and (a) $h=d_0$, (b) $h=5d_0$. 
is explained in Ref. 3 we have to deform the contour of integration to evaluate $\Lambda$ by steepest descent and as a result it is now possible to satisfy the solvability condition. As is well known this remains true if we set $b$, the kinetic term anisotropy, to zero. This is confirmed by our numerical calculations. In Fig. 4(a) we see that for $a = 0.3$ and $b = 0$, with $h = d_0$ and $p = 1$, there is a solution at $d_0 = 0.014$. In Fig. 4(b) we include anisotropy in the kinetic term $(b = 0.3)$ and the solution is shifted to $d_0 = 0.021$.

**D. Study of the selected velocity as a function of $a$ and $b$**

In view of the importance of the anisotropy for the obtainability of steady-state solutions we include in Fig. 5 a plot of the selected value of $d_0$ as a function of $a$. The kinetic term is set to zero, $p = 0.5$ for the crosses, and $p = 1$ for the dots. The selected value of $d_0$ increases monotonically and saturates after $a = 0.5$. The selected value also increases with increasing $p$. Similarly in Fig. 6 we plot the selected value of $d_0$ as a function of $b$. Here $h = 5d_0$, $a = 0$, and $p = 0.5$ for the crosses and $p = 1$ for the dots. The same kind of behavior is observed, except that the selected value of $d_0$ decreases for large $b$.

**CONCLUSION**

In Sec. I we showed analytically that for small undercooling, in the absence of surface tension, there is a family of solutions. For larger undercoolings ($\beta \theta \approx p$) there is no steady state. In Sec. II we added the surface tension. Section II A: When the model is isotropic we predicted analytically and checked numerically that there should be no steady-state solution. Section II B: When anisotropy is included only in the kinetic term we showed analytically (for small undercooling) that there should be no steady-state solutions. This is not surprising since $u \to 0$ as $\Delta \to 0$ so the kinetic term becomes irrelevant compared to the surface tension. For large undercooling ($p = 1$) a steady-state solution is found numerically. Section II C: When anisotropy is included in the surface tension it is well known,1-5 that a velocity is selected. The addition of anisotropy to the kinetic term shifts the value of the selected velocity. Section II D: We found that there is saturation of the value of the selected velocity as a function of $a$ and $b$ for large $a$ and $b$. 

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**FIG. 4.** Slope at $x = 0$ vs $d_0$ for $p = 1$ with $h = d_0$, $a = 0.3$, and (a) $b = 0.0$, (b) $b = 0.3$.

**FIG. 5.** Selected $d_0$ vs $a$ in the absence of the kinetic term. $p = 0.5$ for the crosses and $p = 1$ for the dots.

**FIG. 6.** Selected $d_0$ vs $b$ with $h = 5d_0$ and $a = 0$. $p = 0.5$ for the crosses and $p = 1$ for the dots.
Our work confirms that anisotropy is a key ingredient that must be included either in the surface tension or in the kinetic term in order to obtain steady-state solutions. It also shows that the WKB method is a powerful tool but one should be careful extrapolating the conclusions drawn with this method outside the domain where the method is valid. The method fails quantitatively in predicting the saturation of the selected velocity for large anisotropy. It does not give any hint that steady states exist for large enough values of an anisotropic kinetic term.

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