Stability of a directional solidification front in subdiffusive media

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The efficiency of crystal growth in alloys is limited by the morphological instability, which is caused by a positive feedback between the interface deformation and the diffusive flux of solute at the front of the phase transition. Usually this phenomenon is described in the framework of the normal diffusion equation, which stems from the linear relation between time and the mean squared displacement of molecules $\langle x^2(t)\rangle \sim K_1 t$ (K_1 is the classical diffusion coefficient) that is characteristic of Brownian motion. However, in some media (e.g., in gels and porous media) the random walk of molecules is hindered by obstacles, which leads to another power law, $\langle x^2(t)\rangle \sim K_\alpha t^\alpha$, where $0 < \alpha \leqslant 1$. As a result, the diffusion is anomalous, and it is governed by an integro-differential equation including a fractional derivative in time variable, i.e., a memory. In the present work, we investigate the stability of a directional solidification front in the case of an anomalous diffusion. Linear stability of a moving planar directional solidification front is studied, and a generalization of the Mullins-Sekerka stability criterion is obtained. Also, an asymptotic nonlinear long-wave evolution equation of Sivashinsky's type, which governs the cellular structures at the interface, is derived.

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I. INTRODUCTION

The morphological instability of a solidification front [1,2], which is caused by a positive feedback between the solidification front distortion and the heat or solute flux disturbance at the front of the phase transformation, is a paradigmatic example of the pattern formation in nonequilibrium systems that has been studied for several decades (for a comprehensive review, see Ref. [3]). Among the basic achievements of the nonlinear theory of the morphological instability, let us mention the derivation of the long-wave evolution equation for front distortions known as the Sivashinsky equation [4]. It has been found that in contradistinction to another basic example of pattern formation, the Rayleigh-Bénard convection, where the instability leads to formation of steady patterns, in the case of morphological instability an unbounded growth of disturbances takes place [5], which leads to formation of deep cells, fingers, and dendrites. In the works mentioned above, the diffusion of the solute was governed by the standard diffusion equation, which describes the macroscopic limit of a Markovian random walk characterized by a linear relation between the mean squared displacement of molecules and time, $\langle x^2(t)\rangle \sim t$.

During the last decades, the solidification processes in gels and colloidal suspensions have become a subject of investigation. It has been found that those processes can lead to formation of dendrites [6–8] and other kinds of structures [9,10]. Usually the analysis is done under the assumption of normal diffusion of components. However, it has been found recently that diffusion in gels (as well as ceramic suspensions, porous media, and biological materials) may have some unusual features: because the random walk of molecules is significantly influenced by obstacles, another relation, $\langle x^2(t)\rangle \sim t^\alpha$, where $0 < \alpha < 1$, is observed [11–13]. This phenomenon is called subdiffusion [14]. In the case of subdiffusion, the diffusion equation is replaced by an integro-differential equation, which includes a memory effect expressed by a fractional derivative in time variable. The manifestation of subdiffusion in physical, chemical, and biological processes has been a subject of several books [15,16]. Specifically, the influence of the diffusion anomalies on the propagation of reaction-diffusion fronts has been studied extensively (for review, see Ref. [17]).

The implication of subdiffusion on the propagation of phase transition fronts are still hardly explored. Some exact solutions of the Stefan problem, which describes the propagation of plane melting front in the case of subdiffusion, have been found [18,19]. In Ref. [20], the particle growth due to the subdiffusion of a dissolved component has been studied, and exact self-similar solutions have been obtained. The stability of a plane front propagation has been investigated, and an instability similar to the well-known Mullins-Sekerka instability has been revealed.

In the present paper we revisit the classical problem of the propagation of a directional solidification front and its instability considering the case where the solute is subject to a subdiffusion process governed by the fractional diffusion equation. In contradistinction to the free front propagation considered in Ref. [20], in the case of the directional solidification the front velocity is prescribed by the motion of the solidifying body in a stationary temperature field. Section II contains the formulation of the problem. In Sec. III we analyze the linear stability of a plane solidification front. In Sec. IV an asymptotic nonlinear equation is derived in the limit of long waves. It turns out that it is identical to the Sivashinsky equation known in the case of the normal diffusion.

II. FORMULATION OF THE PROBLEM

Directional solidification is a process by which a liquid sample is pulled through a temperature gradient, with a part of the sample at a temperature below the freezing temperature.

Consider directional solidification of a binary gel with the solute subdiffusion (see Fig. 1). In the laboratory reference frame (X,y,z), a constant temperature gradient $G > 0$ is

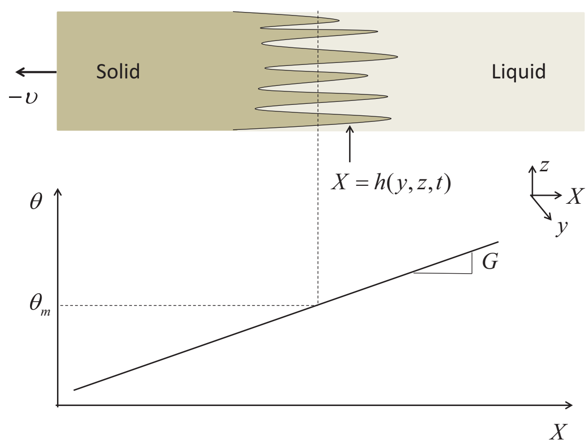

FIG. 1. (Color online) An illustration of directional solidification of a binary gel.

imposed, and the temperature distribution does not depend on time. The sample is pulled along the X axis with constant speed υ (i.e., in the direction of the cold region). The location of the solidification front is described by the function $X = h(y,z,t)$ (see Fig. 1).

In the reference frame connected with the pulled body, (x,y,z), $X = x - \upsilon t$, the location of the solidification front is determined by the relation

$$x = x^*(y,z,t),\, x^*(y,z,t) = \upsilon t + h(y,z,t). \tag{1}$$

The subdiffusion takes place in a semi-infinite domain $x > x^*(y,z,t)$, $-\infty < y,z < \infty$. The goal of the present paper is to investigate the dynamics of a solidification front.

A. The case of classical diffusion

First, let us recall the formulation of the problem in the case of the normal diffusion. In the reference frame connected with the pulled body, the diffusive flux of the component with the concentration c is determined by Fick 's law

$$\mathbf{j} = -\mathcal{D}\nabla c, \tag{2}$$

where $\mathcal{D}$ is the diffusion coefficient. Due to the continuity equation

$$\partial_t c = -\nabla \cdot \mathbf{j}$$

one obtains the normal diffusion equation,

$$\partial_t c = \mathcal{D}\nabla^2 c, \quad x > x^*(y,z,t). \tag{3}$$

The heat balance on the interface yields the Gibbs-Thomson condition [3]

$$m(c - c_0) = \frac{\theta_m \gamma}{L_\upsilon} 2\mathcal{H} + Gh, \qquad x = x^*(y,z,t), \tag{4}$$

where $m < 0$ is the liquidus slope, c_0 is the solute concentration on the liquid side of the equilibrium phase transition front, θ_m is the equilibrium melting temperature for concentration c_0, L_υ is the latent heat per unit volume, and $\mathcal{H}$ is the mean curvature of the interface,

$$2\mathcal{H} = -\frac{\nabla^2 h + h_{yy}h_z^2 - 2h_{yz}h_y h_z + h_{zz}h_y^2}{[1 + |\nabla h|^2]^{3/2}}.$$

The flux balance on the interface yields the Stefan condition

$$(k-1)c\frac{\partial_t x^*}{\sqrt{1 + (\nabla x^*)^2}} = \mathcal{D}\partial_n c, \tag{5}$$

where ∂_n is the directional derivative in the direction of the normal vector of the front surface pointing into the liquid phase.

The condition at infinity is

$$c = c_\infty = kc_0, \quad x \to \infty, \tag{6}$$

where $c_\infty = kc_0$ is the concentration on the solid side of the front (k is the segregation coefficient). For more details, see Refs. [3,21].

B. The case of subdiffusion

Let us discuss now the modification of the problem (3)–(6) in the case of subdiffusion. In the reference frame connected with the pulled body, the subdiffusive flux is determined by the expression [14]

$$\mathbf{j}(x,y,z,t) = -\mathcal{D}\nabla\, {}_{t_0}\mathbb{D}_t^{1-\alpha} c(x,y,z,t),\, 0 < \alpha < 1, \tag{7}$$

where

$${}_{t_0}\mathbb{D}_t^{1-\alpha} c(x,y,z,t) = \frac{1}{\Gamma(\alpha)}\frac{d}{dt}\int_{t_0}^{t} (t-\tau)^{\alpha-1} c(x,y,z,\tau)\, d\tau \tag{8}$$

is the Riemann-Liouville fractional derivative. Here t_0 is the time instant when the subdiffusion process starts. Because we are interested in the behavior of the system at large t, later we take $t_0 = -\infty$. Then diffusion equation (3) is replaced by the subdiffusion equation

$$\partial_t c(x,y,z,t) = \frac{\mathcal{D}}{\Gamma(\alpha)}\nabla^2 \partial_t \int_{-\infty}^{t} (t-\tau)^{\alpha-1} c(x,y,z,\tau)\, d\tau, \quad x > x^*(y,z,t), \tag{9}$$

or alternatively

$$\partial_t c = \mathcal{D}\nabla^2\, {}_{-\infty}\mathbb{D}_t^{1-\alpha} c,\, x > x^*(y,z,t). \tag{10}$$

On the interface $x = x^*(y,z,t)$, the mass conservation leads to the following boundary condition:

$$(k-1)c(x^*(y,z,t),y,z,t)\upsilon_n = -j_n, \tag{11}$$

where υ_n is the normal velocity of the solidification front, and j_n is the normal component of the mass flux. Taking into account the expressions (7) and (8) for the subdiffusive flux and the relation

$$\upsilon_n = \frac{\partial_t x^*(y,z,t)}{\sqrt{1 + (\nabla x^*)^2}}, \tag{12}$$

we obtain the following flux balance condition on the interface:

$$(k-1)c(x^*(y,z,t),y,z,t)\frac{\partial_t x^*(y,z,t)}{\sqrt{1 + (\nabla x^*)^2}} = \frac{\mathcal{D}}{\Gamma(\alpha)}\partial_n \partial_t \left[\int_{-\infty}^{t} (t-\tau)^{\alpha-1} c(x,y,z,\tau) d\tau\right]\Bigg|_{x=x^*(y,z,t)}. \tag{13}$$

Equations (4) and (6) remain unchanged.

C. Laboratory reference frame

It is convenient to consider the process in the laboratory reference frame, v, i.e., applying the coordinate transformation $X = x - vt$ and $T = t$. Here x is the coordinate in the reference frame connected with the pulled body, whereas X is the relative position with respect to the laboratory reference frame. The temperature distribution along the sample does not depends on time, and it is described by the relation

$$\theta = \theta_m + GX. \tag{14}$$

Define

$$c(x,y,z,t) = \bar{C}(x - vt,y,z,t) = \bar{C}(X,y,z,T), \tag{15}$$

then

$$c(x,y,z,\tau) = \bar{C}(x - v\tau,y,z,\tau) = \bar{C}(X + v(T - \tau),y,z,\tau)$$

The subdiffusion equation takes the form

$$\begin{aligned}(\partial_T - v\partial_X)\bar{C}(X,y,z,T) &= \frac{\mathcal{D}}{\Gamma(\alpha)}\left(\partial_X^2 + \partial_y^2 + \partial_z^2\right)(\partial_T - v\partial_X) \\ &\quad\times \int_{-\infty}^{T} (T - \tau)^{\alpha-1}\bar{C}(X + v(T - \tau),y,z,\tau)\, d\tau. \end{aligned}\tag{16}$$

It is convenient to define $\xi = v(T - \tau)$, then Eq. (16) becomes

$$\begin{aligned}(\partial_T - v\partial_X)\bar{C} &= \frac{\mathcal{D}}{\Gamma(\alpha)}\left(\partial_X^2 + \partial_y^2 + \partial_z^2\right)(\partial_T - v\partial_X) \\ &\quad\times \frac{1}{v^\alpha}\int_0^\infty \xi^{\alpha-1}\bar{C}\left(X + \xi,y,z,T - \frac{\xi}{v}\right) d\xi. \end{aligned}\tag{17}$$

Similarly, the flux balance condition (13) on the front $X = h(y,z,T)$ becomes

$$\begin{aligned}&\bar{C}(h(y,z,T),y,z,T)(k - 1)\frac{v + \partial_T h}{\sqrt{1 + (\nabla h)^2}} \\ &\quad= \frac{\mathcal{D}}{\Gamma(\alpha)}\partial_n(\partial_T - v\partial_X)\frac{1}{v^\alpha} \\ &\quad\quad\times \int_0^\infty \xi^{\alpha-1}\bar{C}\left(X + \xi,y,z,T - \frac{\xi}{v}\right) d\xi, \end{aligned}\tag{18}$$

where $\partial_n = (\partial_X,\partial_y,\partial_z) \cdot \hat{n}$.

Note that the structure of problem (17) and (18) is rather nontrivial. In addition to memory terms, which are calculated along the trajectories of material points, it includes convective terms caused by the imposed motion of the body with respect to the fixed temperature distribution. While the fractional diffusion is time subordinated to the normal diffusion process, the imposed motion of the solidification front does not obey the corresponding time scale change. Therefore, in a contradistinction to the case of fractional diffusion without solidification, the problem under consideration has no self-similar solutions.

D. Dimensional analysis

Let L, T, and c_0 be the length, time, and concentration scales, respectively. Taking into account that the natural scale of the subdiffusion coefficient $\mathcal{D}$ is L^2/T^α, and that of the velocity is L/T, we choose the length and time scales as

$$L = \frac{\mathcal{D}^{1/(2-\alpha)}}{v^{\alpha/(2-\alpha)}}, \qquad T = \frac{\mathcal{D}^{1/(2-\alpha)}}{v^{2/(2-\alpha)}}. \tag{19}$$

We define

$$\begin{aligned}\bar{C}(X^*,y^*,z^*,T^*) &= \bar{C}\left(LX,Ly,Lz,\frac{L}{v}T\right) \\ &= c_0 C(X,y,z,T), \\ \bar{C}\left(X^* + \xi^*,y^*,z^*,T^* - \frac{\xi^*}{v}\right) &= c_0 C(X + \xi,y,z,T - \xi),\end{aligned}$$

and obtain the following problem in the nondimensional form:

$$\begin{aligned}&(\partial_T - \partial_X)C(X,y,z,T) \\ &\quad= \frac{1}{\Gamma(\alpha)}\left(\partial_X^2 + \partial_y^2 + \partial_z^2\right)(\partial_T - \partial_X) \\ &\quad\quad\times \int_0^\infty \xi^{\alpha-1}C(X + \xi,y,z,T - \xi)\, d\xi, \quad X > h, \end{aligned}\tag{20}$$

$$C = 1 - \beta(1 - k)2\mathcal{H} - w(1 - k)h, \quad X = h, \tag{21}$$

$$\begin{aligned}&(k - 1)\frac{(1 + \partial_T h)C}{\sqrt{1 + (\nabla h)^2}} = \frac{1}{\Gamma(\alpha)}\partial_n(\partial_T - \partial_X) \\ &\quad\times \int_0^\infty \xi^{\alpha-1}C(X + \xi,y,z,T - \xi)\, d\xi, \quad X = h, \end{aligned}\tag{22}$$

$$C = k, \quad X \to \infty. \tag{23}$$

The obtained problem contains two nondimensional parameters,

$$\beta = \frac{\theta_m \gamma v^{\alpha/(2-\alpha)}}{L_v m c_0 \mathcal{D}^{1/(2-\alpha)}(k - 1)},$$

$$w = \frac{G\mathcal{D}^{1/(2-\alpha)}}{m c_0 v^{\alpha/(2-\alpha)}(k - 1)},$$

which are the surface energy number and the morphological number, respectively.

III. LINEAR STABILITY THEORY

A. General dispersion relation

The boundary value problem (20)–(23) has the base solution

$$C_b(X,y,z,T) = k + (1 - k)e^{-X}, \quad h_b = 0, \tag{24}$$

which corresponds to a plane solidification front. Let the base solution be perturbed,

$$C = C_b + \hat{C}, \quad h = \hat{h}. \tag{25}$$

In the present section we consider the stability of solution (24) with respect to disturbances (25) in the framework of a linearized problem. By linearization of boundary conditions, we use relations

$$C(h,y,z,T) \sim C_b(0) + C_b'(0)\hat{h} + \hat{C}(0,y,z,T), \quad (26)$$

$$2\mathcal{H} \sim -\frac{(\partial_y^2 + \partial_z^2)\hat{h}}{[1+(\nabla\hat{h})^2]^{3/2}} = -\nabla^2\hat{h} + O(\hat{h}^3). \quad (27)$$

Substituting (25)–(27) into the system (20)–(23) and neglecting nonlinear terms, we obtain the following linearized problem for disturbances:

$$(\partial_T - \partial_X)\hat{C}(X,y,z,T) = \frac{1}{\Gamma(\alpha)}(\partial_X^2 + \partial_y^2 + \partial_z^2)(\partial_T - \partial_X) \times \int_0^\infty \xi^{\alpha-1}\hat{C}(X+\xi,y,z,T-\xi)\,d\xi \;\; X > 0, \quad (28)$$

$$\hat{C} = (1-k)(1-w)\hat{h} + \beta(1-k)\nabla^2\hat{h}, \quad X = 0, \quad (29)$$

$$(k-1)[\partial_T\hat{h} + (k-1)\hat{h} + \hat{C}] = (1-k)\hat{h} + \frac{1}{\Gamma(\alpha)}\partial_X(\partial_T - \partial_X) \times \int_0^\infty \xi^{\alpha-1}\hat{C}(X+\xi,y,z,T-\xi)\,d\xi, \quad X = 0, \quad (30)$$

$$\hat{C}(X,y,z,T) = 0, \quad X \to \infty. \quad (31)$$

Since the coefficients of this linear system are independent of x,y,z, and T, we can introduce the normal modes

$$(\hat{C},\hat{h}) = (C_0(X),h_0)e^{iay+ibz+\sigma T}, \quad q^2 = a^2 + b^2, \quad (32)$$

where s is the growth rate and $\mathbf{q} = (a,b)$ is the wave vector of the disturbance. Substituting expressions (32) into the linearized system (28)–(31), we obtain

$$(\sigma - \partial_X)C_0(X) = \frac{1}{\Gamma(\alpha)}(\partial_X^2 - q^2)\int_0^\infty \xi^{\alpha-1}[\sigma C_0(X+\xi) - \partial_X C_0(X+\xi)]e^{-\sigma\xi}\,d\xi, \quad X > 0, \quad (33)$$

$$C_0 = (1-k)(1-w-\beta q^2)h_0, \quad X = 0, \quad (34)$$

$$(k-1)[(\sigma+k-1)h_0 + C_0(0)] = (1-k)h_0 + \frac{1}{\Gamma(\alpha)}\partial_X\int_0^\infty \xi^{\alpha-1}(\sigma - \partial_X) \times C_0(X+\xi)e^{-\sigma\xi}\,d\xi, \quad X = 0, \quad (35)$$

$$C_0 \to 0, \quad X \to \infty. \quad (36)$$

Now we substitute the ansatz $C_0(X) = Ae^{-pX}$ in (34) to obtain the following equation:

$$1 = \frac{p^2 - q^2}{\Gamma(\alpha)}\int_0^\infty \xi^{1-\alpha}e^{-(\sigma+p)\xi}\,d\xi. \quad (37)$$

In order to guarantee convergence of the integral in (37), we have to impose the constraint $Re(\sigma + p) > 0$, and then after calculating the integral we obtain the following transcendental equation for p:

$$(\sigma + p)^\alpha = p^2 - q^2. \quad (38)$$

Due to condition (36), we are interested in solutions with $Re(p) > 0$. After we utilize the boundary conditions (34) and (36), we obtain the characteristic equation,

$$(1 - w - \beta q^2)[1 - k - p(\sigma + p)^{1-\alpha}] + k + \sigma = 0, \quad (39)$$

which determines the dependence of the growth rate σ on the wave number q and other parameters of the problem. In the case $\alpha = 1$, indeed Eqs. (38) and (39) reproduce the result of Ref. [3] for the classical diffusion case. Note that in the case of the subdiffusion, only solutions with $Re(\sigma) > 0$ are meaningful (otherwise the integrals over ξ diverge).

Define $s = (\sigma + p)^\alpha = p^2 - q^2$. Then the dispersion relation can be written as

$$(1 - w - \beta q^2)[1 - k - s(s+q^2)^{1/2}] + k + s^{1/\alpha} - (s+q^2)^{1/2}] = 0. \quad (40)$$

B. Instability region

In order to determine the stability region in the (q,w) plane for given values of α,β, and k, we consider the neutral stability curve ($\sigma \to 0$). In that limit the dependence $p(q,\alpha)$ is determined by the relation

$$p^\alpha = p^2 - q^2. \quad (41)$$

The value of $p(q,\alpha)$ decreases monotonically with the decrease of α from $p(q,1) = [1 + \sqrt{1+4q^2}]/2$ (the limit of the normal diffusion) to $p(q,0) = \sqrt{1+q^2}$. In the small wave number limit $q \ll 1$, one can find the asymptotic expansion for the solution of equation (38)

$$p = 1 + \frac{q^2}{2-\alpha} + o(q^2). \quad (42)$$

The neutral stability curve can be written as

$$w(q) = q^2\left[\frac{1}{kp(q,\alpha)^\alpha + q^2} - \beta\right] \quad (43)$$

or

$$w(q) = q^2\left[\frac{1}{kp(q,\alpha)^2 + (1-k)q^2} - \beta\right]. \quad (44)$$

For small q, the following asymptotic expansion for the neutral curve is obtained:

$$w(q) = \frac{q^2}{k}\left[1 - \beta k - \left(\frac{\alpha}{2-\alpha} + \frac{1}{k}\right)q^2 + o(q^2)\right]. \quad (45)$$

The instability is possible as $1 - \beta k > 0$, and this criterion does not depend on α. In the opposite limit of large q, $p \sim q$, and $w(q) \sim 1 - \beta q^2 < 0$ for any $\beta > 0$, which is incompatible with the physical condition $w > 0$. Thus, the instability is possible only in a finite interval of q, $0 < q < q_m$. Because $kp^\alpha + q^2$ never tends to zero, function $w(q)$ is

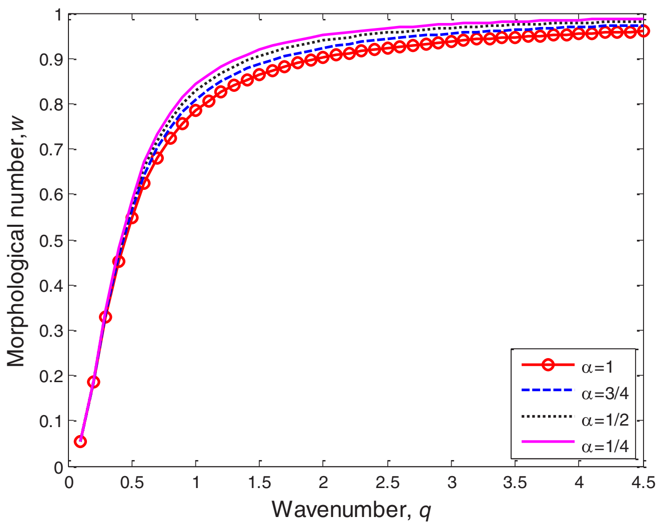

FIG. 2. (Color online) Neutral curves for several values of α in the case of zero surface energy ($\beta = 0$).

bounded in the interval $0 < q < q_m$. With the decrease of α from 1 to 0, $w(q,\alpha)$ grows monotonically from

$$w(q,1) = q^2\left[\frac{1}{k(1+\sqrt{1+4q^2})/2+q^2} - \beta\right]$$

(the limit of the normal diffusion) to

$$w(q,0) = q^2\left(\frac{1}{k+q^2} - \beta\right).$$

Thus, with the decrease of α a certain destabilization of the front takes place, but the qualitative behavior of the neutral curve does not change. Typical neutral curves found numerically are shown in Figs. 2 and 3.

Let us present also the dispersion relation (39) in the limit of small k. Using the scaling [4]

$$\begin{aligned} &w = 1-\epsilon^2, \quad k = \kappa\epsilon^4, \quad \sigma = \Sigma\epsilon^4, \\ &q = Q\epsilon, \quad p = 1 + P\epsilon^2, \quad 0 < \epsilon \ll 1, \end{aligned} \tag{46}$$

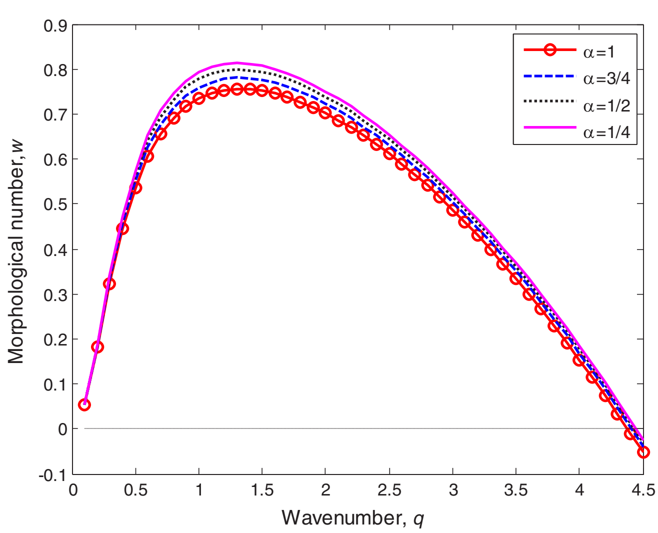

FIG. 3. (Color online) Neutral curves for several values of α in the case of nonzero surface energy ($\beta = 5.88 \times 10^{-2}$).

we obtain at the leading order:

$$P = \frac{Q^2}{2-\alpha}, \quad \Sigma = -\kappa + Q^2 - \beta Q^4. \tag{47}$$

It is remarkable that the expression for the rescaled growth rate Σ at the leading order does not include α at all.

IV. LONG-WAVE NONLINEAR THEORY

Let us derive now the asymptotic equation governing finite amplitude disturbances slowly changing in space and time. First, following Ref. [4] we introduce the curvilinear coordinates $\tilde{x} = X - h(y,z,T)$, $\tilde{y} = y$, $\tilde{z} = z$, $\tilde{t} = T$, and define $\tilde{h} = h(\tilde{x},\tilde{y},\tilde{t})$:

$$C(X,y,z,T) = C(\tilde{x}+\tilde{h},\tilde{y},\tilde{z},\tilde{t}) = \tilde{C}(\tilde{x},\tilde{y},\tilde{z},\tilde{t}).$$

The governed equations (20)–(23) are transformed to the following form:

$$\begin{aligned} &[\partial_{\tilde{t}} - (1+\tilde{h}_{\tilde{t}})\partial_{\tilde{x}}]\tilde{C} \\ &\quad = \frac{1}{\Gamma(\alpha)}[\partial_{\tilde{t}} - (1+\tilde{h}_{\tilde{t}})\partial_{\tilde{x}}] \\ &\qquad \times \left[\partial_{\tilde{x}}^2 + \partial_{\tilde{y}}^2 + \partial_{\tilde{z}}^2 - \nabla^2\tilde{h}\partial_{\tilde{x}} - 2\nabla\tilde{h}\cdot\nabla\partial_{\tilde{x}} + |\nabla\tilde{h}|^2\partial_{\tilde{x}}^2\right] \\ &\qquad \times \int_0^\infty \xi^{\alpha-1}\tilde{C}(\tilde{x}+\xi,\tilde{y},\tilde{z},\tilde{t}-\xi)\,d\xi, \quad \tilde{x} > 0, \end{aligned} \tag{48}$$

$$\tilde{C} = 1 - \beta(1-k)2\mathcal{H} - w(1-k)\tilde{h}, \quad \tilde{x} = 0, \tag{49}$$

$$\begin{aligned} &(k-1)(1+\tilde{h}_{\tilde{t}})\tilde{C} \\ &\quad = \frac{1}{\Gamma(\alpha)}[\partial_{\tilde{x}} - \nabla\tilde{h}\cdot\nabla + |\nabla\tilde{h}|^2\partial_{\tilde{x}}][\partial_{\tilde{t}} - (1+\tilde{h}_{\tilde{t}})\partial_{\tilde{x}}] \\ &\qquad \times \int_0^\infty \xi^{\alpha-1}\tilde{C}(\tilde{x}+\xi,\tilde{y},\tilde{z},\tilde{t}-\xi)\,d\xi, \quad \tilde{x} = 0, \end{aligned} \tag{50}$$

$$\tilde{C} = k, \quad \tilde{x} \to \infty. \tag{51}$$

The linear stability theory provides the appropriate scaling for the variables and parameters. When the deviation of w from its critical value w_0 is $O(\varepsilon^2)$, $\varepsilon^2 \ll 1$, the anticipated scaling is as follows: $\tilde{x} = \chi$, $\tilde{y} = \varepsilon\eta$, $\tilde{z} = \varepsilon\zeta$, $\tilde{t} = \varepsilon^4\tau$, $k = \varepsilon^4\kappa$, and $w = w_0(1-\varepsilon^2)$. We substitute the asymptotic expansions

$$\begin{aligned} \tilde{C} &= N^0(\chi,\eta,\zeta,\tau) + \varepsilon^2 N^2 + \varepsilon^4 N^4 + \varepsilon^6 N^6 + \cdots, \\ \tilde{h} &= \varepsilon^2(H^0(\chi,\eta,\zeta,\tau) + \varepsilon^2 H^2 + \varepsilon^4 H^4 + \cdots) \end{aligned}$$

into (48)–(51) and collect the terms of the same order.

At the leading order, we obtain a homogeneous integro-differential equation with three boundary conditions:

$$\partial_\chi N^0 - \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^3 N^0(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi = 0$$

$$\chi > 0,$$

$$N^0(0,\eta,\zeta,\tau) = 1,$$

$$N^0 = \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^2 N^0(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi, \quad \chi = 0,$$

$$N^0 = 0, \quad \chi \to \infty.$$

The solution of the obtained problem exists: $N^0 = e^{-\chi}$. Note that this solution does not depend on time and the transverse spatial coordinates.

At order $O(\varepsilon^2)$, we obtain a homogeneous integro-differential equation with three boundary conditions:

$$\partial_\chi N^2 - \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^3 N^2(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi = 0,$$
$$\chi > 0,$$
$$N^2(0,\eta,\zeta,\tau) = -w_0 H^0,$$
$$N^2 = \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^2 N^2(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi, \quad \chi = 0,$$
$$N^2 = 0, \quad \chi \to \infty.$$

The solution is $N^2 = -w_0 H^0 e^{-\chi}$, like in the case of a normal diffusion.

At order $O(\varepsilon^4)$, we obtain an inhomogeneous equation with three boundary conditions

$$\partial_\chi N^4 - \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^3 N^4(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi$$
$$= -(1-w_0)\nabla^2 H^0 e^{-\chi}, \quad \chi > 0,$$
$$N^4(0,\eta,\zeta,\tau) = -w_0 H^2 + w_0 H^0 + \beta\nabla^2 H^0,$$
$$N^4 - \kappa = \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^2 N^4(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi,$$
$$\chi = 0,$$
$$N^4 = \kappa, \quad \chi \to \infty.$$

The solvability condition of that problem gives

$$(w_0 - 1)\nabla^2 H^0 = 0.$$

In an infinite region, or in the case of periodic boundary condition, a bounded solution H^0 cannot be a harmonic function, hence $w_0 = 1$ and $N^4 = m + (-H^2 + H^0 + \beta\nabla^2 H^0 - m)e^{-\chi}$. Note that the obtained expression for N^4 is identical for that in the case of normal diffusion.

Finally, collecting the terms of order $O(\varepsilon^6)$ in (48), we obtain the following equation:

$$\partial_\chi N^6 - \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^3 N^6(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi$$
$$= \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\big[-H_\tau^0 \xi e^{-\chi-\xi}$$
$$+ \nabla^2\partial_\chi N^4(\chi+\xi,\eta,\zeta,\tau-\xi)$$
$$+ (H^0\nabla^2 H^0 + |\nabla H^0|^2 + \nabla^2 H^2)e^{-\chi-\xi}\big]d\xi, \quad \chi > 0.$$

Substituting the expression for N^4 into (52) and calculating integrals, we find for $\chi > 0$:

$$\partial_\chi N^6 - \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^3 N^6(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi = Re^{-\chi}, \tag{52}$$

where

$$R = -\big[\alpha H_\tau^0 + \nabla^2 H^0 + \beta\nabla^4 H^0 - \nabla\cdot(H^0\nabla H^0)\big]. \tag{53}$$

Equation (53) has to be solved with boundary conditions

$$N^6(0,\eta,\zeta,\tau) = -H^4 + H^2 + \kappa H^0 + \beta\nabla^2 H^2, \tag{54}$$

$$N^6 - \frac{1}{\Gamma(\alpha)}\int_0^\infty \xi^{\alpha-1}\partial_\chi^2 N^6(\chi+\xi,\eta,\zeta,\tau-\xi)\,d\xi$$
$$= -\kappa H^0 - (1-\alpha)H_\tau^0, \quad \chi = 0, \tag{55}$$

$$N^6 = 0,\ \chi \to \infty. \tag{56}$$

Solving Eq. (53) with boundary condition (54) and (56), we find

$$N^6 = (-H^4 + H^2 + \kappa H^0 + \beta\nabla^2 H^2)e^{-\chi}$$
$$+ \frac{1}{\alpha-2}\big[-\alpha H_\tau^0 - \nabla^2 H^0 - \beta\nabla^4 H^0$$
$$+ \nabla\cdot(H^0\nabla H^0)\big]\chi e^{-\chi}.$$

Substituting the obtained solution into the flux continuity condition (55), we obtain an amplitude equation *identical* to the Sivashinsky equation [4] derived in the case of the normal diffusion,

$$H_\tau^0 + \kappa H^0 + \nabla^2 H^0 + \beta\nabla^4 H^0 - \nabla\cdot(H^0\nabla H^0) = 0. \tag{57}$$

The absence of the subdiffusion parameter α in the linear terms of Eq. (57) is the consequence of formula (47) for the linear growth rate of long-wave disturbances in the limit of a small segregation coefficient. The nonlinear term in (57) has a geometric origin, and therefore it is not influenced by the subdiffusion parameter either.

V. CONCLUSIONS

We have investigated the development of the Mullins-Sekerka instability of a directional solidification front in a subdiffusive medium. Though the analysis is more technically involved than in the case of the normal diffusion, it turns out that in the limit of a small segregation coefficient the results are surprisingly similar. The temporal and spatial scaling of long-wave disturbances is the same in both cases. The long-wave limit for the growth rate and even the weakly nonlinear equation governing the evolution of long-wave disturbances do not include the subdiffusion parameter α.

The development of the Mullins-Sekerka instability in the case of a directional solidification can be contrasted to the case of a solid nucleus growth studied in Ref. [20]. The main physical difference is as follows. The front velocity of a free nuclear growth is determined by the subdiffusion process itself. The motion of the directional solidification front is induced by the externally imposed motion of the body. In the former case, the dispersion relation that determines the development instability contains only the power of the growth rate, σ^α, rather than σ itself, which is the consequence of the time subordination of subdiffusion to the normal diffusion process. In the case of the directional solidification, the structure of the dispersion relation (40) is more complex. Though the expression in the left-hand side of (40) has some singular points, the long-wave expansion (47) turns out to be perfectly analytical, like in the case of the normal diffusion. This is the origin of the similarity of the development of the long-wave instability in the subdiffusion case and the normal diffusion case.

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