Segregation Instabilities of Moving Interfaces

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The segregation of solute particles on a moving interface leads to the appearance of two types of instabilities near competing velocity thresholds. This behavior is shown to occur in a variety of exactly solvable models where the interface motion is coupled to a diffusion process of the solute particles. These models directly apply to the propagation of internal domain walls, but can also be generalized to surfaces of growing crystals in the kinetics-limited regime.

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The externally controlled motion of domain walls, as well as the propagation of metastable fronts are of basic interest for a variety of phenomena, including reversible switching effects and the growth of a stable new phase. As outlined in [1] for many practical applications, the interface dynamics can be significantly influenced by the segregation of mobile impurities or, in case of an alloy, of solute particles.

A conspicuous example of this is the solute-drag effect in grain-boundary motion, discussed in a seminal paper by Cahn [2]. In this work a one-dimensional model for the uniform motion of a planar grain boundary through a dilute atmosphere of diffusing impurity atoms has been considered. In spite of the simplicity of this model, a hysteresis effect was found in the force-velocity diagram which, according to Cahn, gives rise to a jerky motion of the grain boundary.

In a later contribution, Roy and Bauer [3] proposed a two-dimensional model which allows deformations of the grain boundary and lateral diffusion of the impurity atoms. Within this model a new inherent instability of the boundary shape was discovered and traced back to transverse convective flow of segregated impurity atoms.

More recently, an improper assumption on the drag force in the Roy-Bauer model has been pointed out [4] which deletes the instability in the predicted form, and especially its appearance in the low-velocity regime. The arguments, presented in [4], do not rule out, however, the very existence of a convection-induced instability above some finite velocity threshold.

We now will demonstrate that both of the discussed instabilities generically occur in a whole class of model systems, describing the interaction of a moving interface with an atmosphere of diffusing solute particles. The instabilities become visible in the response function of the defect geometry to a change of the external driving force. Starting from a phase-field description, a general form of this response function is calculated exactly, up to the evaluation of a single integral which discriminates between individual members of the model ensemble.

For each system the effective Hamiltonian H depends on the phase field $\phi(\mathbf{r}, t)$ and the particle-diffusion field $C(\mathbf{r}, t)$ in the general form

$$H = \int d^3r\left\{\frac{\delta^2}{2}(\nabla\phi)^2 + \mathcal{W}(\phi) + \frac{1}{2}[C - \mathcal{U}(\phi)]^2\right\}, \quad (1)$$

where δ is a microscopic length of order 10^{-7} cm.

In order to establish appropriate expressions for the potentials $\mathcal{W}(\phi)$ and $\mathcal{U}(\phi)$, we consider the equilibrium conditions $\delta H/\delta\phi = \delta H/\delta C = 0$. The standard choice $\mathcal{W} = (\phi^2 - \phi_0^2)^2$, combined with boundary conditions $\phi_k(z = \pm\infty) = \pm\phi_0$, allows a solution $\phi_k(z)$ with a pronounced kink, describing a static planar interface of thickness δ. Furthermore, $C_k(z) = \mathcal{U}(\phi_k(z)) \equiv U(z)$ is the segregation profile in thermal equilibrium which has constant, in general, different values in the two bulk phases. Close to the interface it will develop a peak, the height of which can be tuned by temperature T which enters via the representation $C_k(z) \propto \exp[-E(z)/kT]$, where $E(z)$ is the attractive or repulsive particle-interface interaction.

Since we are mainly interested in universal properties, which are independent of the details of the potentials, we in the following assume that $\mathcal{W}(\phi)$ is a double-well potential with minima at $\phi = \pm\phi_0$, and that $\mathcal{U}(\phi)$ is a single-well potential, carrying a parametric dependence on temperature.

For the dynamics we adopt the model-C equations [5]

$$\partial_t\phi = -\Lambda\delta H/\delta\phi, \qquad \partial_t C = D\nabla^2\delta H/\delta C, \quad (2)$$

where Langevin forces have been neglected. In (2) Λ is a relaxation rate and D a diffusion constant which both have

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an Arrhenius dependence on temperature and on the material. Near the melting point of metals these quantities are of order $\Lambda \approx 10^{10}$ s, and $D \approx 10^{-9}$ cm^2/s whereas in the liquid phase $D \approx 10^{-5}$ cm^2/s.

Insertion of (1) into (2) leads to the explicit equations

$$\begin{aligned} \partial_t \phi &= \Lambda\{\delta^2 \nabla^2 \phi - \mathcal{W}'(\phi) + [C - \mathcal{U}(\phi)]\mathcal{U}'(\phi)\}, \\ \partial_t C &= D\nabla^2[C - \mathcal{U}(\phi)]. \end{aligned} \tag{3}$$

We are interested in solutions $\phi_s(z - Vt)$, $C_s(z - Vt)$ of (3) with the same boundary conditions for ϕ as before, but with $C_s(+\infty) = C_s(-\infty) \equiv C_0$. They describe, in a comoving frame, the motion of a planar interface with constant velocity $V > 0$ in the z direction where the interface is joined by a stationary solute-density profile.

If, for this case, the first Eq. (3) is multiplied by ϕ_s' and integrated over z, one is led to the equations

$$V = \Gamma[G + F], \qquad -V[C_s - C_0] = D[C_s' - U']. \tag{4}$$

Here, $\Gamma \equiv \Lambda\delta^2/\sigma$ is the interface mobility, involving the surface tension $\sigma \equiv \delta^2(\phi_s', \phi_s')$ where the scalar product means integration over z. Typical orders of magnitude for surface tensions vary from $\sigma \approx 10^2$ erg/cm^2 in solids down to $\sigma \approx 10^{-2}$ erg/cm^2 in liquid crystals.

In (4) $F \equiv \mathcal{W}(+\phi_0) - \mathcal{W}(-\phi_0) + (1/2)[C_0 - \mathcal{U}(+\phi_0)]^2 - (1/2)[C_0 - \mathcal{U}(-\phi_0)]^2 > 0$ acts as an external driving force, and

$$\begin{aligned} G &\equiv -\int d\zeta U'(\zeta)[C_s(\zeta) - C_0] \\ &= -\frac{V}{D}\int d\zeta[C_s(\zeta) - C_0]^2 \end{aligned} \tag{5}$$

appears as a solute-drag force.

The second Eq. (4) represents the first integral of the resulting second-order differential equation for $C_s(\zeta)$. Its full solution reads

$$C_s(\zeta; V) - C_0 = \int_{-\infty}^{\zeta} d\eta U'(\eta)\exp\left[-\frac{V}{D}(\zeta - \eta)\right], \tag{6}$$

which, inserted into (5), determines the drag force for any given function $U(\zeta)$.

In order to test the stability of the above solution, we go back to the Eqs. (3), now written for a solution $\phi(\mathbf{r}, t) = \phi_s[z - Vt - h(\mathbf{x}, t)]$, which is generated by an external force $F + f(\mathbf{x}, t)$. Following the steps, outlined below Eqs. (3), and in more detail in [6], one arrives, to lowest order of a gradient expansion, at the result

$$\begin{aligned} \partial_t h &= \Gamma[\sigma\partial^2 h + g + f] \\ \partial_t c &= V\partial_\zeta c - D(\partial^2 + \partial_\zeta^2)c \\ &\quad + U'\partial_t h - (V/D)(C_s - C_0)(\partial_t - D\partial^2)h, \end{aligned} \tag{7}$$

where $c(\mathbf{x}, \zeta, t) \equiv C(\mathbf{x}, z, t) - C_s(\zeta) + C_s'(\zeta)h(\mathbf{x}, t)$, and $\partial^2 \equiv \nabla^2 - \partial_z^2$.

In (7) we have introduced a local-drag force

$$g(\mathbf{x}, t) \equiv -\int d\zeta U'(\zeta)c(\mathbf{x}, \zeta, t), \tag{8}$$

which, together with $h(\mathbf{x}, t)$, forms a pair of collective field variables. The quantity (8) is very different from the excess concentration of the solute at the interface, chosen as a second field by Roy and Bauer [3]. This is, to our belief, the basic reason for the failure of their approach. Independently of this discrepancy, the transverse flow of the solute, appearing according to Roy and Bauer in case of a tilted defect, shows also up in our treatment in form of the last term $\propto \partial^2 h$ of Eqs. (7).

A remarkable advantage of our class of models is that, for arbitrary $U(\zeta)$, the local-drag force $g(\mathbf{x}, t)$ can be extracted from the second Eq. (7) in a form which only contains features of the uniform background motion (4). In order to see this, we use in (7) the substitution $c = n - (V/D)(C_s - C_0)h$ which leads to the equation

$$\partial_t n - V\partial_\zeta n - D(\partial^2 + \partial_\zeta^2)n = (U'\partial_t - U''V)h. \tag{9}$$

In terms of Fourier-Laplace transforms $\hat{n}_\zeta(\mathbf{q}, s)$ and $\hat{h}(\mathbf{q}, s)$, permitting the replacements $\partial \rightarrow i\mathbf{q}$, $\partial_t \rightarrow s$ Eq. (9) has the solution

$$\begin{aligned} \hat{n} = {} & \frac{(Ds - V\alpha)\hat{h}}{D(\alpha - \beta)}\int_{\zeta}^{\infty} d\eta U'(\eta)\exp\left[\frac{\alpha}{D}(\zeta - \eta)\right] \\ & + \frac{(Ds - V\beta)\hat{h}}{D(\alpha - \beta)}\int_{-\infty}^{\zeta} d\eta U'(\eta)\exp\left[\frac{\beta}{D}(\zeta - \eta)\right], \end{aligned} \tag{10}$$

where $\alpha \equiv -(V/2) + \sqrt{(V/2)^2 + D(s + Dq^2)} \equiv -\beta - V$. This solution only applies to the regime $\mathrm{Re}(s) + Dq^2 > 0$ where an instability might occur.

The crucial observation now is that the second integral in (10) is similar to that appearing in (6) and therefore can be expressed in terms of $C_s(\zeta; -\beta)$. In a similar way, the first integral in (10) is related to the trapping profile $\bar{C}_s(\zeta; -\alpha)$ for negative velocities, giving rise to a drag force $\bar{G}(-\alpha)$. This finally implies that the Fourier-Laplace transform $\hat{g}(\mathbf{q}, s)$ of the local-drag force (8) is fully determined by the global drag forces G and $\bar{G}$.

The quantity $\Sigma(\mathbf{q}, s) \equiv -\Gamma\hat{g}(\mathbf{q}, s)/\hat{h}(\mathbf{q}, s)$ appears as a kind of self-energy in the Fourier-Laplace transform

$$\hat{R}(\mathbf{q}, s) = \frac{1}{s + \Gamma\sigma q^2 + \Sigma(\mathbf{q}, s)} \tag{11}$$

of the response function $R(\mathbf{x}, t) \equiv \delta h(\mathbf{x}, t)/\delta f(0, 0)$, and has the explicit form

$$\begin{aligned} \Sigma(\mathbf{q}, s) = {} & \frac{\alpha^2 - D^2q^2}{D(\alpha - \beta)}\Gamma\bar{G}(-\alpha) - \frac{\beta^2 - D^2q^2}{D(\alpha - \beta)}\Gamma G(-\beta) \\ & + \frac{V}{D}\Gamma G(V). \end{aligned} \tag{12}$$

Equations (11) and (12) represent a central result of the present Letter. For each specific potential $U(\zeta)$ the density profiles $C_s(\zeta)$, $\bar{C}_s(\zeta)$ and, consequently, the drag forces G,

$\bar{G}$ can be calculated by simple integrations. The results then determine the response function $R(\mathbf{x}, t)$ which is the quantity of principal interest, since it signals the existence of any instability.

Instabilities are most conveniently characterized by the behavior of the eigenmode frequencies of the system. Within the regime $\mathrm{Re}\,(s) + Dq^2 \geq 0$ these are determined by the condition $1/\hat{R}(\mathbf{q}, s) = 0$. Expressed in terms of $\bar{F}(-\alpha) = -\alpha/\Gamma - \bar{G}(-\alpha)$, $F(-\beta) = -\beta/\Gamma - G(-\beta)$ this condition is found to be of the general form

$$[F(V+\alpha) - \tilde{F}(-\alpha)]\frac{D^2q^2 - \alpha^2}{V + 2\alpha} = [F(V+\alpha) - F(V)]V + D\sigma q^2 \tag{13}$$

which is another main result of our investigation.

At $q = 0$, Eq. (13) generally has a solution $\alpha = 0$, belonging to a branch of eigenmodes $s_1(q)$ which passes through the origin $q = s = 0$. By expanding (13) in powers of q and s, one furthermore finds that, at the origin, this branch has a horizontal slope and a curvature

$$s_1''(0) = \frac{2D[F(V)/V - F'(V) - \sigma/D]}{F'(V)}. \tag{14}$$

The numerator in (14) assumes the value -2σ for $V \longrightarrow 0$ as well as for $V \longrightarrow \infty$, since, according to (5) and (6), $F(V)$ approaches a linear function in V in both limits.

A positive value of the numerator will, however, arise within an interval $V_A(T) < V < V_B(T)$, defined by $F(V_{A,B}, T)/V_{A,B} - \partial_V F(V_{A,B}, T) = \sigma(T)/D(T)$. Here, the dependence on temperature T is relevant, since the excess density of the solute particles at the interface will progressively evaporate with increasing temperature which causes the interval $V_B(T) - V_A(T)$ to shrink to zero. This, in fact, happens at some finite temperature T_C, fixed by the conditions $\partial_V^2 F(V_C, T_C) = -2\sigma(T_C)/V_C$, and $V_C \equiv V_A(T_C)$.

From these considerations we conclude that, provided $\partial_V F(V, T) > 0$, the planar form of the interface becomes unstable in the regime $V_A(T) < V < V_B(T)$, $T < T_C$. This type of instability is caused by the convective flow of solute particles, contributing to the local-drag force $g(\mathbf{x}, t)$. The latter constraint is worth mentioning, since, even in presence of a particle flow, $\hat{g}(0, 0)$ turns out to be zero, in agreement with our results in [4].

If the anomalous behavior $\partial_V F(V, T) \leq 0$ happens to occur in some range $V_a(T) \leq V \leq V_b(T)$, then (13) allows another branch $s_2(q)$ which again has zero slope at the origin. However, close to the boundary values $V_a(T)$ and $V_b(T)$, given by $\partial_V F(V_a, T) = \partial_V F(V_b, T) = 0$, one finds

$$s_2(0) = -\frac{4V_{a,b}\partial_V F}{D(F/V_{a,b}^2 + 2\partial_V^2 F)}, \tag{15}$$

which is positive for $V \gtrsim V_a(T)$, and for $V \lesssim V_b(T)$, respectively, indicating an instability of a different origin.

Inside this new regime an increase in velocity leads to a decrease of the solute drag, initiating a self-amplifying destabilizing process. Since this may already happen at $q = 0$, this case corresponds to an instability where the whole interface may keep its planar geometry, supporting Cahn's picture of a jerky dynamical behavior. The nondiffusive character of this process derives from the fact that, contrary to the density $c(\mathbf{r}, t)$, the quantity $g(\mathbf{x}, t)$ is nonconserved.

This type of instability can only occur at temperatures T below some critical point, defined by the conditions $\partial_V^2 F(V_c, T_c) = 0$, and $V_a(T_c) = V_c$. Another constraint is $V_A(T) > V_a(T)$, since, otherwise, the planar form of the interface is already unstable, before the threshold $V_a(T)$ is reached. Even then, one has to take care of the additional source of an instability due to the change of sign of the denominator of (14).

In order to corroborate all these conclusions, we now will consider a specific model, defined by $U(\zeta) = U(-\zeta)$

$$U(\zeta) = C_0 + U_0(1 - \zeta/\delta) \tag{16}$$

for $0 \leq \zeta \leq \delta$, and $U(\zeta) = C_0$ for $\zeta \geq \delta$. The properties of this model will be described in terms of the scaled variables $X \equiv V\delta/D$, $Y \equiv D/(\Gamma\delta U_0^2)$, $Z \equiv F\Gamma\delta/D$, where Y is a measure of temperature.

Within the model (16) the uniform motion of a planar interface, carrying a layer of solute particles, is described by the equation

$$Z = X + [2X - (e^{-X} - 1)(e^{-X} - 3)]/(YX^2). \tag{17}$$

This result is illustrated in Fig. 1 by a set of isotherms which shows all expected features. The shaded region is a kind of spinodal regime, with the critical point located at $X_c = 3.611$, $Y_c = 0.0387$.

An estimate for the threshold X_A of the first instability can be obtained in the regime $X \ll X_c$ by an expansion of

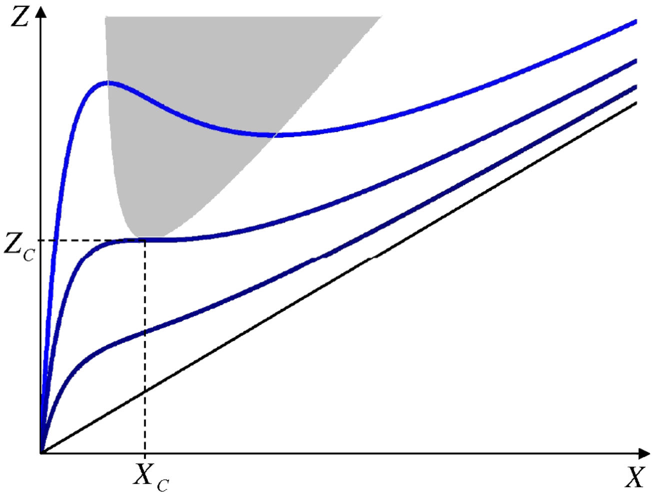

FIG. 1 (color online). Isotherms according to Eq. (17) for $Y > Y_c$, $Y = Y_c$, $Y < Y_c$ (from above to below). Spinodal-like instabilities occur in the shaded region.

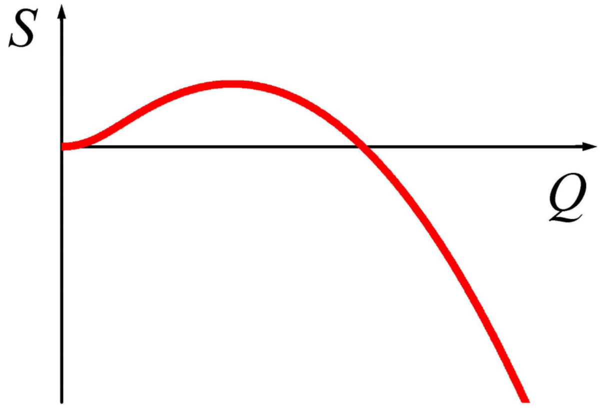

FIG. 2 (color online). Eigenspectrum $S(Q)$ in the case $X_A(Y) < X_\alpha(Y)$.

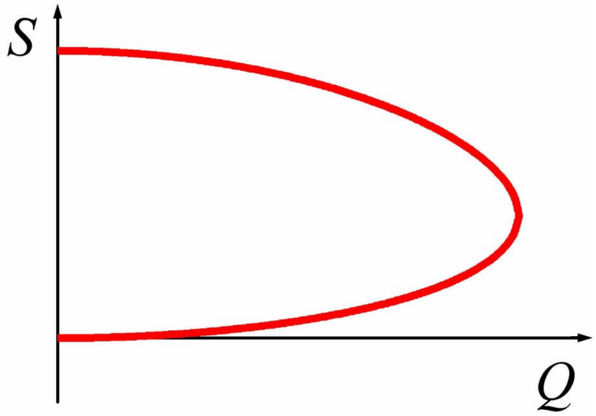

FIG. 3 (color online). Eigenspectrum $S(Q)$ in the case $X_\alpha(Y) < X_A(Y)$.

$Z(X, Y)$ in X up to second order, and insertion into the condition $s_1''(0) = 0$. This leads to the approximate result $X_A = 2Y\Gamma\sigma/D$ which, in terms of the original variables, means $V_A = 2D\sigma/(\delta U_0)^2$. Accordingly, the threshold V_A is shifted to lower values with increasing size δU_0 of the particle cloud at the interface.

The spectrum of real eigenmode frequencies, written in terms of the scaled variables $Q \equiv q\delta$ and $S \equiv s\delta^2/D$, is shown in Fig. 2 for $X_A(Y) < X_a(Y)$, and in Fig. 3 for the opposite case $X_a(Y) < X_A(Y)$. Figure 3 also reveals that the two branches $S_1(Q)$ and $S_2(Q)$, in fact, form a single connected curve.

Coming back to the general discussion, we have to say that all treatments which, like the recent ones in [7], and in [8], are basically one dimensional, not only miss the convection-induced instability, but also the hybridization of the two instabilities which inevitably emerges in the case $V_a(T) < V_A(T)$, $T < T_c, T_C$.

We believe that both segregation instabilities have a chance to be seen in many real systems, since the class of models, chosen in the present Letter, contains all the essentials of interface motion in presence of mobile solute particles. Modifications, like anisotropic surface tensions or space-dependent and anisotropic kinetic coefficients, are not expected to remove these attributes.

Concerning a variable diffusivity, a generalization of the Cahn theory has already been proposed in [9], also with regard to phase interfaces in alloys. However, like in most other approaches, the procedure is limited to the one-dimensional case which only allows to treat the bare hysteresis effect.

If, within our class of models, the diffusion coefficient is assumed to be different in the two bulk phases, the resulting model should also allow to discuss segregation processes at the interface of a growing crystal. On the basis of a phase-field representation, as described in [10], and in [11], such an approach has been presented in [12]; however, again evaluated for the one-dimensional case only. In higher dimensions we expect the appearance of a convective segregation instability in the kinetics-limited regime as a kind of counterpart of the Mullins-Sekerka instability [13] in the diffusion-controlled regime.

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