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On wetting and apparently asymmetric kinetics in free growth

J.C. Géminard, J. Bechhoefer [1] and P. Oswald

Ecole Normale Supérieure de Lyon, Laboratoire de Physique, 46 Allée d'Italie, F-69364 Lyon Cedex 07, France

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We have calculated analytically the shape and velocity of a moving front separating two phases of a pure substance. The material is confined between two parallel plates, which impose a contact angle and a meniscus at the interface between the two phases. Assuming the contact angle to be constant and the molecular attachment kinetics to be both linear and symmetric about the melting temperature T_c, we show that the meniscus shape and the front velocity are different above and below T_c if the wetting contact angle differs much from 90°. This effect can explain the apparently asymmetric growth kinetics observed in thin films of semiconductors, as well as certain anomalies observed in the moving nematic-isotropic interface of a liquid crystal.

1. Introduction

For several years, much attention has been focused on the dynamics of moving interfaces and the patterns they form. These interfaces may separate, for example, two immiscible fluids or two different thermodynamic phases of the same material. Because two-dimensional models are easier to study theoretically than three-dimensional ones, experimental studies of interface dynamics, in order to make contact with existing theories, have often adopted a pseudo-two-dimensional geometry, in which the material to be studied is confined between two parallel plates. The hope is that if the plate spacing is much smaller than the scale of the finest details in the pattern, the system will essentially be two-dimensional. Although the above scenario is true qualitatively, it is now clearly recognized to be false quantitatively. The main reason is that any contact angle between the interface and the supporting plates other than 90° will lead to a curved meniscus in the vertical direction of the experimental cell. This meniscus guarantees that the interface will have some structure whose scale is set by the plate spacing. Indeed, the shape of the meniscus depends not only on the wetting conditions of the plates, but also on the velocity at which the front propagates. Because the plate spacing in experiments is typically small, photographs or other records of the interface will show the vertical part of the meniscus without giving information about its structure. In short, the front motion will not be accurately described by a purely two-dimensional theory but must instead incorporate elements of a full three-dimensional theory.

Such effects have been studied in detail in the Saffman–Taylor hydrodynamic instability, in which the front separates air from oil [1]. They are equally important in free growth and directional solidification, where the interface usually separates a liquid phase from a more-ordered solid or liquid-crystalline phase. In the case of directional solidification, meniscus effects have been shown to decrease the velocity at which interfaces destabilize in thin samples [2]. Another consequence of a meniscus in directional solidification is an asymmetry between melting and freezing fronts. This effect is particularly clear in the case of the nematic–isotropic front of a liquid crystal, where experiments have shown that if the nematic wets the substrate, a large meniscus forms

[1] Permanent address: Department of Physics, Simon Fraser University Burnaby, BD, Canada V5A 1S6.

when the nematic "freezes", whereas, when it melts, no such deformation can be seen. Conversely, if (by changing the substrate) the liquid phase wets, the opposite is observed: a large meniscus forms upon melting, but nothing is observed when the sample freezes [3]. Another experimental example of such melting–freezing asymmetry is in the measurement of the kinetic coefficient of a thin silicon layer deposited on a sapphire substrate [4]. In this experiment, the front velocity near the coexistence temperature T_c increases linearly with $|T - T_c|$, but the proportionality constant (the kinetic coefficient) is different for melting and freezing. In this article, we show that such an asymmetry in the kinetic coefficient is not necessarily intrinsic to the material, as studies to date have assumed, but could rather be due to the presence of a meniscus.

2. Theoretical model

Consider a pure material confined between two parallel plates spaced a distance $2D$ apart from each other. Let the temperature T be different from T_c, so that a moving front separates the two phases. We assume that the contact angle θ_0 between the front and the plates is constant in time and independent of the front velocity. In other words, the angle θ_0 will be assumed equal to that fixed by thermodynamic equilibrium. (See fig. 1.) Let α_0 be the complement of θ_0. (Thus, $\alpha_0 = \pi/2 - \theta_0$.) We suppose, also, that the temperature is constant and homogeneous throughout the system. In particular, we neglect any latent heat released at the moving interface. As Sekerka and co-workers have discussed, this last assumption will be valid if the latent heat of the transition is small, if the plates have high thermal conductivity and if the sample thickness is small [5].

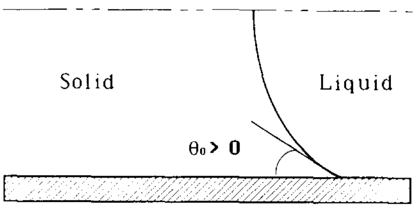

Fig. 1. Definition of the contact angle between the front and the plate.

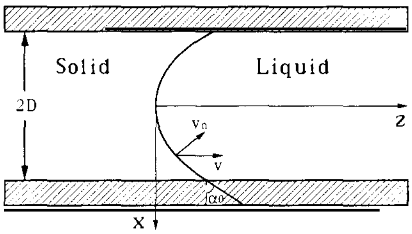

Fig. 2. Schematic representation of the meniscus separating the two phases.

Let V be the meniscus velocity and L the latent heat of transition per unit volume. (We neglect any density differences between the two phases.) We assume that attachment kinetics are linear and symmetric about T_c. The velocity of the interface normal is then given by

$$V_n = \zeta\, \delta T, \tag{1}$$

where $\delta T = T_e - T$ is the local kinetic undercooling, ζ the kinetic coefficient, and T_e the equilibrium temperature of the curved front given by the Gibbs–Thomson equation:

$$T_e = T_c(1 - d_0 \kappa). \tag{2}$$

Here, $d_0 = \Gamma / L$ is the capillary length, Γ the surface tension (assumed to be isotropic), and κ the local mean curvature of the interface.

To obtain the relation between the meniscus velocity V and the imposed undercooling $\Delta T = T_c - T$, we write the equations of motion for the meniscus in cartesian coordinates $Z = F(X)$. (See fig. 2.) We assume that in the transverse direction, the interface is flat; the problem is then one-dimensional. The normal velocity of the interface V_n is, from geometry,

$$V_n = V \cos(\alpha), \tag{3}$$

where α is the local angle that the tangent to the meniscus makes with the normal to the plates. In Cartesian coordinates, $\tan(\alpha) = \mathrm{d}F/\mathrm{d}X$, $\cos(\alpha) = 1/(1 + F'^2)^{1/2}$, and the curvature $\kappa = -F''/(1 + F'^2)^{3/2}$.

From eqs. (1)–(3), we can write

$$\frac{f''}{\sqrt{1+f'^2}} = v\sqrt{1+f'^2} - \Delta(1+f'^2), \tag{4}$$

where we have introduced the following dimensionless quantities:

$v = V/\zeta T_c, \quad \Delta = (T_c - T)/T_c, \quad f = F/d_0,$
$x = X/d_0.$

Defining $u(x) \equiv \sqrt{1+f'^2(x)}$, we can rewrite eq. (4):

$$\frac{u'}{u(1-\beta u)} = vf', \quad \text{with} \quad \beta \equiv \frac{\Delta}{v}. \tag{5}$$

Integrating this equation once, we obtain:

$$f(x) = \frac{\beta}{\Delta} \ln\left(\frac{1-\beta}{\cos(\alpha(x)) - \beta} \right). \tag{6}$$

The above equation (6) is a first-order differential equation in f, since α is a function of $f'(x)$. We can invert it so that f' is expressed in terms of f, which gives, with $\gamma \equiv \exp(-vf)$:

$$\beta \int_1^{\gamma(x)} \frac{\mathrm{d}\gamma}{\gamma\sqrt{1-[\beta+(1-\beta)\gamma]^2}} + (1-\beta) \times \int_1^{\gamma(x)} \frac{\mathrm{d}\gamma}{\sqrt{1-[\beta+(1-\beta)\gamma]^2}} = -\frac{\Delta x}{\beta}, \tag{7}$$

with

$$\gamma(x) = \frac{\cos[\alpha(x)] - \beta}{1-\beta}.$$

Evaluating these integrals [6], we obtain

$$\Phi(\alpha(x), \beta) = \Delta x, \tag{8}$$

with

$$\Phi(\alpha, \beta) = \beta\left[\alpha - \sqrt{\frac{\beta^2}{\beta^2 - 1}} \times \arccos\left(\frac{1-\beta\cos(\alpha)}{\cos(\alpha)-\beta} \right)\right],$$

$$\text{for } |\beta| > 1, \tag{9a}$$

$$\Phi(\alpha, \beta) = \beta\left[\alpha - \frac{\beta}{\sqrt{1-\beta^2}} \times \ln\left(\frac{\cos(\alpha) - \beta}{\sqrt{1-\beta^2}\sin(a) + 1 - \beta\cos(\alpha)} \right)\right]$$

$$\text{for } |\beta| < 1. \tag{9b}$$

On the plates, $\alpha = \alpha_0$ and $x = d = D/d_0$. This boundary condition, along with eqs. (8) and (9), fixes the front velocity as a function of undercooling:

$$v = \Delta/\beta, \tag{10}$$

where β is now a function of Δd and of α_0 defined by $\Phi(\alpha_0, \beta) = \Delta d$.

For this value of β, eq. (8) unambiguously determines $\alpha(x)$. The meniscus profile satisfies the following equation:

$$f(x) = \frac{\beta}{\Delta} \ln\left(\frac{1-\beta}{\cos(\alpha(x)) - \beta} \right). \tag{11}$$

The depth of the meniscus $p = f(d)$ (measured relative to $f(0) = 0$) is obtained by setting $\alpha = \alpha_0$ in the preceding equation:

$$p = \frac{\beta}{\Delta} \ln\left(\frac{1-\beta}{\cos(\alpha_0) - \beta} \right). \tag{12}$$

We note, finally, that β becomes infinite when $V = 0$ and $\Delta d = -\sin(\alpha_0)$. This limit corresponds to a round, stationary meniscus whose radius $r = d/\sin(\alpha_0)$ and depth $p = d[1 - \cos(\alpha_0)]/\sin(\alpha_0)$.

3. Discussion

Fig. 3 illustrates the above results for a contact angle $\alpha_0 = 1$ radian. There are five points to be noted:

First, although the meniscus shape is triangular while freezing, it is flat while melting. This conclusion is reversed if we invert the sign of the contact angle α_0. This asymmetry is reminiscent of that observed for the nematic–isotropic interface in directional solidification [3].

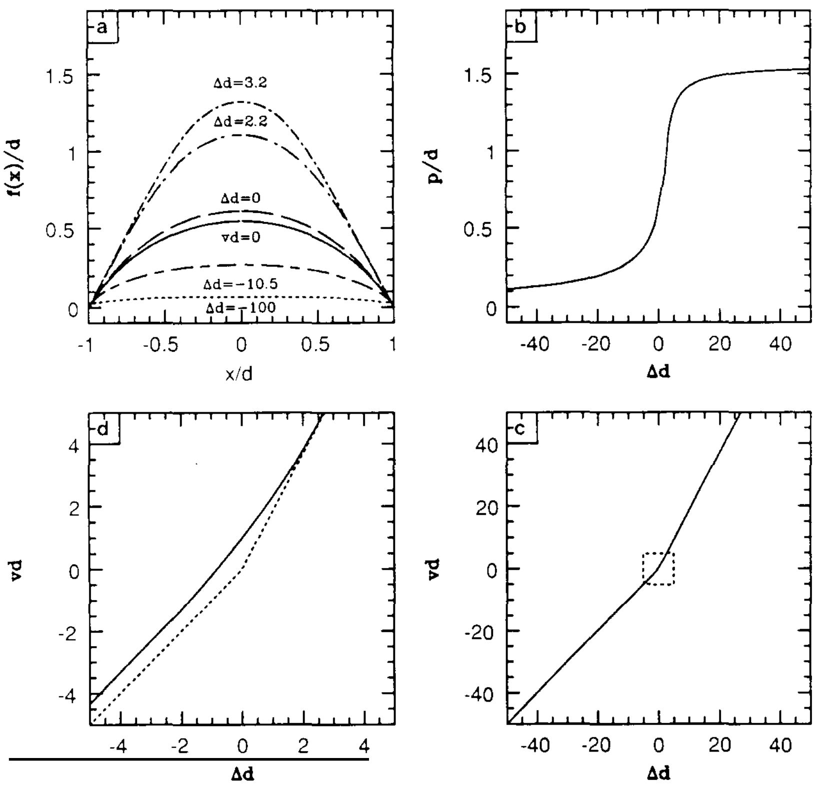

Fig. 3. (a) Shape of the meniscus in free growth for various values of Δd; the solid line corresponds to the static meniscus. (b) Depth of the meniscus versus Δd. (c) Velocity v of the meniscus versus undercooling Δ. (d) Enlargement of the preceding curve near $\Delta d = 0$. All of these curves have been calculated for $\alpha_0 = 1$ rad.

Second, the slope $\zeta \partial v / \partial \Delta$ gives the apparent kinetic coefficient ζ_{app}, which is what is measured experimentally. Although ζ_{app} depends on the wetting angle, the thickness and the undercooling, its value saturates for small Δd at one of two different limits: for freezing, $\zeta_{app} = \zeta$, while for melting, $\zeta_{app} = \zeta / \cos(\alpha_0)$. These limiting values depend only on the wetting angle α_0. Wetting effects thus lead to an apparent kinetics asymmetry about T_c, in the thin-plate geometry, even though the bulk kinetics are perfectly symmetrical. Our model should be relevant to the analysis of the observed asymmetry in the kinetics of thin layer of silicon [4].

Another set of experiments on the nematic–smectic A front in liquid crystals would a priori be a second situation in which one would expect to see these effects; however, recent experiments show no evidence of any asymmetry [7]. The same result was observed for several materials. If we take the experiments at face value – and one must remember that the measurements are difficult – we can conclude that the contact angle in these extremely weak first-order transitions must generically be $90°$ ($\alpha_0 = 0$). The conclusion is significant because just the opposite occurs in binary mixtures near a critical point and in Ising-like systems [8]. The argument, which is fairly general, compares the rate at which the surface tension ($\Gamma_{\alpha\beta}$) between two phases (α and β) vanishes with the rate that the difference between the substrate (x) surface tensions vanishes ($\Gamma_{\alpha x} - \Gamma_{\beta x}$). For Ising model, $\Gamma_{\alpha\beta} \propto \Delta^{1.3}$ and $\Gamma_{\alpha x} - \Gamma_{\beta x} \propto \Delta^{0.3}$. Near a critical point, $\cos(\theta_0)$ diverges as $\Delta^{-1.0}$. Thus, $\theta_0 = 0°$ at some temperature below T_c, and one or the other phases totally wets. Apparently, the results for nematic–smectic A systems suggest that the reverse is true ($\cos(\theta_0)$

$\to 0$ or $\theta_0 \to 90°$), implying that the exponent for $\Gamma_{\alpha\beta}$ is smaller than that governing $(\Gamma_{\alpha x} - \Gamma_{\beta x})$. Of course, we have also assumed that the system remains at local equilibrium and that the contact angles are well defined and independent of velocity. But typically, if the contact angle changes as a front's velocity increases, the effect is to drive the system towards a complete wetting by the phase that partially wets at equilibrium. So it is not clear whether the variation of contact angle with velocity is of any help in explaining the observations in the experiments of Cladis et al. [7]. All of these hypotheses would have to be re-examined in systems near a critical point. Finally, we might expect this result on contact angles to be sensitive to the orientation of molecules in the nematic–smectic A sample. Since the experiments of Cladis et al. were done for a planar molecular alignment, it would be worthwhile repeating them for a homeotropic alignment.

Third, the origin of the apparent asymmetry may be traced back to the Gibbs–Thomson equation, which relates the interface curvature to a change in equilibrium temperature. The curvature is a signed quantity and will thus be sensitive to whether the interface bows out or in. Fundamentally, the effect is a geometrical one brought about by the geometry of two parallel plates separated by a small gap. One could observe similar effects in a round or square capillary, as well.

Fourth, like ζ_{app}, the meniscus depth p is a function of Δd; however, its limit $p_{lim} = d \tan(\alpha_0)$ is attained for values of Δd long after which ζ_{app} has saturated at $\zeta/\cos(\alpha_0)$: the meniscus velocity saturates when part of the meniscus is flat or, roughly, when the radius of curvature is less than half the plate spacing D. By contrast, the meniscus depth saturates only when the radius of curvature of the tip is small with respect to D, which implies a much higher front velocity.

Fifth, the triangular meniscus that appears during solidification (or melting, for appropriate contact angles) is unstable with respect to fluctuations in the contact angle on one of the plates. One can easily redo the above calculations for wetting angles that differ on each plate. The result is that the tip of the meniscus moves away from the plate the solid "wets" the most (See fig. 4.) This meniscus instability does not qualitatively change the kinetics: if the solid wets the plates with two different contact angles θ_1 and θ_2 such that $\theta_1 > \theta_2$, the apparent kinetic coefficient will have a limiting value $\zeta/\cos(\alpha_2)$, with $\alpha_2 = \pi/2 - \theta_2$ when the solid grows. We see that the velocity of a meniscus will fluctuate if it encounters inhomogeneous wetting conditions on one or the other plates. In directional solidification experiments on the nematic–isotropic interface, such fluctuations of the meniscus depth are in fact commonly observed.

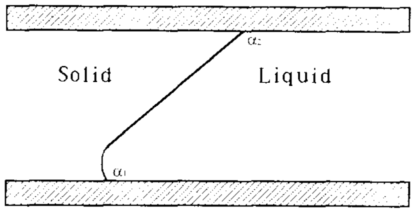

Fig. 4. Shape of the meniscus when the two contact angles are different.

4. Generalization to directional solidification

Let us now consider the same sample in a temperature gradient parallel to the z axis. We assume that the low temperature phase partially wets the substrate and that the temperature gradient is positive. In this case, the curvature of the meniscus is positive. (See fig. 5.) The undercool-

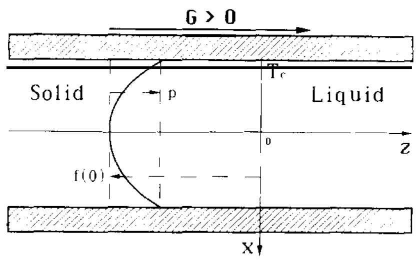

Fig. 5. Schematic representation of the meniscus in directional solidification.

ing now varies with position, and we can write $T(z) = T_c + Gz$. Eq. (4) takes the form

$$\frac{f''}{\sqrt{1+f'^2}} = v\sqrt{1+f'^2} - \Delta\frac{f}{f(0)}\left(1+f'^2\right), \qquad (13)$$

where we have introduced the following dimensionless quantities:

$$v = V/\zeta T_c, \quad \Delta = -GF(0)/T_c, \quad f = F/d_0,$$
$$x = X/d_0.$$

The parameter Δ is now the undercooling at the tip of the meniscus; $f(0)$ is the dimensionless distance that the front recedes because of kinetic effects.

Fig. 6 illustrates the results obtained numerically for a contact angle $\alpha_0 = 1$ rad. We note that there is no qualitative difference between the case of directional solidification and that of free growth. The differences become significant quantitatively only when the meniscus depth approaches $f(0)$. (i.e., when the undercooling is small)

Finally, we discuss briefly the role of impurities in directional solidification. If the velocity is small enough so that the diffusion length is much

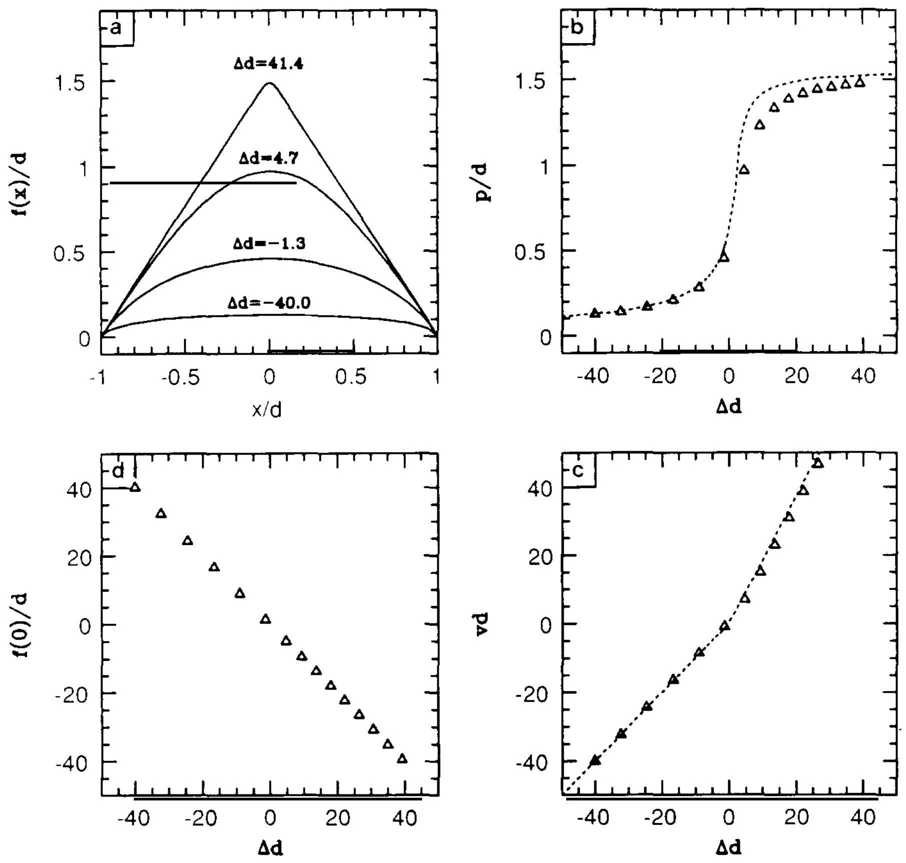

Fig. 6. (a) Shape of the meniscus in directional solidification for various values of Δd. (b) Depth of the meniscus versus Δd. (c) Velocity v of the meniscus versus undercooling Δ. (d) Kinetic receding versus Δd. All of these curves have been calculated for $\alpha_0 = 1$ rad. Triangles have been computed numerically for directional solidification; dashed lines correspond to the previous analytical results for free growth.

larger than the meniscus depth, then the impurity gradient is constant over that length scale with a value that is approximately that found for a planar front. The main effect of impurities then is to renormalize the temperature gradient to an effective value.

$$G_{\mathrm{eff}} = G - |m| \ \Delta c / L_{\mathrm{d}}, \tag{14}$$

where m is the slope of the liquidus, Δc the gap of impurity at the interface and $L_{\mathrm{d}} = D/V$ the diffusion length. Note that in the limit we are considering, $(G_{\mathrm{eff}} - G)/G$ is necessarily much less than one: the correction to the gradient must be small.

5. Conclusions

We have thus shown that apparent asymmetries in the kinetic coefficient can be observed in restricted geometries even when kinetic effects are intrinsically symmetric about T_{c}. The asymmetries result from the presence of a meniscus, which qualitatively modifies the interface dynamics. If one can extend the theoretical analysis given here to incorporate explicitly the contribution of impurities at large velocity, the results might be compared with those obtained from directional solidification experiments [3].

Acknowledgments

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