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On Static and Dynamical Young's Condition at a Trijunction

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Abstract. — Using a consistent purely kinetic model we show that Young's condition at a trijunction results from a chemical and not a mechanical equilibrium, as is often believed in the literature. In an out-of equilibrium situation this condition is altered in a way such that the triple point acquires an effective mobility. The order of magnitude of the mobility is fixed by a velocity scale \tilde{V}_{att} associated with chemical attachment at the interface, and not by the sound speed. While for ordinary eutectics \tilde{V}_{att} is large (except in rapid solidification experiments) in comparison to the growth speed, implying a quasi-instantaneous mobility, finite mobility effects should show up for faceted eutectics as well as for eutectoid transformations.

1. Introduction

This note is concerned with a question which is in principle well understood [1], but in practice seems to give rise to systematic confusion — namely the physical origin of Young's equilibrium condition at a trijunction, *i.e.* a contact point between three phases of a binary mixture. This, typically, happens, for lamellar eutectics growing from the melt, at the triple point where the interfaces between the two solid phases α and β emerge on the growth front. The point which we want to illustrate here with the help of a simple model of isothermal kinetically-limited eutectics growth is the following: contrary to what is usually stated, Young's condition at the triple point does not express *mechanical* equilibrium, but chemical equilibrium. Consequently, any departure from thermodynamic equilibrium leads to a velocity-dependent correction to this condition, which can be interpreted in terms of an effective mobility of the triple point.

While this effect is in practice small enough to be neglected in the case of growth of a metallic eutectics from the liquid phase (except under conditions of rapid solidification), it is certainly important when dealing with the growth of faceted eutectics as well as for eutectoid

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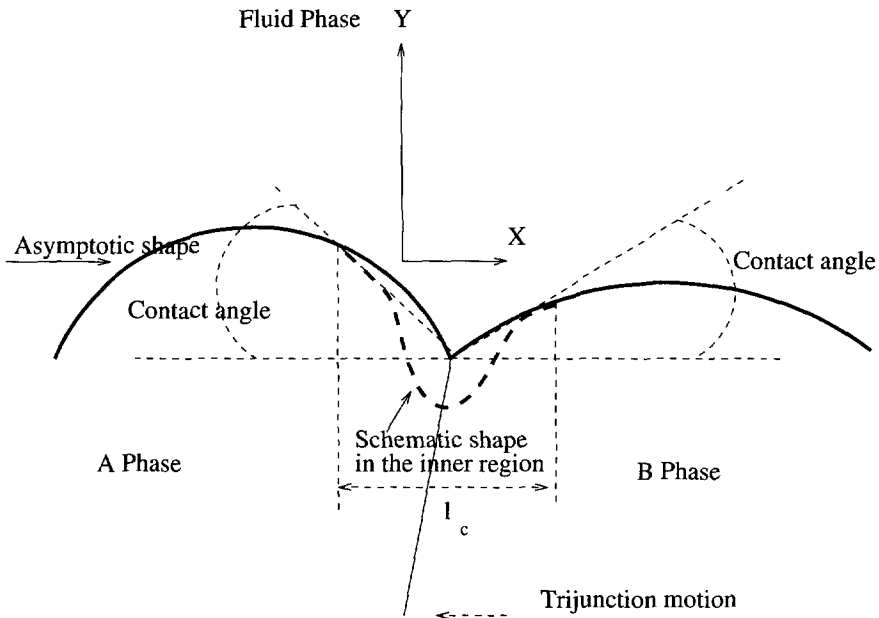


Fig. 1. — A schematic view of the tri-junction.

transformations (from a homogeneous mother solid phase into a two-phase daughter alloy), due to the slowness of diffusion in solids [2].

Indeed, in this latter situation, growth is commonly controlled by interface kinetics and/or diffusion, while diffusion lengths in the bulk may become comparable with interface thicknesses. Then, one expects on the one hand triple point mobility effects to become important. On the other hand, stress effects, which play an important role in solid/solid transformations, must be taken into account when imposing mechanical equilibrium of the interfaces, which gives rise to an *independent* condition.

2. The Model

Figure 1 displays the geometry of the tri-junction. We use here the model of reference [3], in which:

- The solid-liquid interface is considered to be sharp, with isotropic surface tension γ .
- The growing solid eutectics is treated in the Cahn-Hilliard representation. Namely, the *Helmholtz* free energy of a volume V of the solid is given by

$$F = \int_V dV [f(T, c, \rho) + \frac{1}{2} \tilde{\alpha} (\nabla c)^2], \quad (1)$$

N_A and N_B will denote the numbers of A and B atoms in the binary mixture. For a homogeneous solid the solute concentration c and the number density ρ of the mixture are

$$c = \frac{N_B}{N_A + N_B}; \quad \rho = \frac{N_A + N_B}{V} \quad (2)$$

Since we only consider here isothermal solidification, temperature is a passive parameter, which we will omit from now on.

- The two solid phases are assumed, for the sake of simplicity, to have identical physical properties [$f(c) = f(1-c)$] and the partial volumes of the two species are taken equal [4]: $v_A(c) = v_B(c)$.
- The liquid concentration is assumed to be constant and equal to 1/2. These assumptions are consistent both with the situation of global equilibrium of the three phases, and with kinetically controlled growth. We shall consider a linear kinetic law

$$J_A = W(\mu_{FA} - \mu_{SA}); \quad J_B = W(\mu_{FB} - \mu_{SB}) \quad (3)$$

where $J_{A,B}$ are the mass currents of the two substances across the solid-liquid interfaces, W is a phenomenological kinetic coefficient, and μ_{FA}, μ_{FB} are the (constant) fluid chemical potentials. The mass currents are related to the normal growth velocity \tilde{V}_n by

$$J_A = (1-c)\tilde{V}_n; \quad J_B = c\tilde{V}_n. \quad (4)$$

The chemical potentials are related to the Helmholtz free energy by

$$\mu_{SA} = -\frac{c}{\rho} \left(\frac{\partial f}{\partial c} \right)_{T,\rho} + \left(\frac{\partial f}{\partial \rho} \right)_{T,c} \quad (5)$$

$$\mu_{SB} = \frac{1-c}{\rho} \left(\frac{\partial f}{\partial c} \right)_{T,\rho} + \left(\frac{\partial f}{\partial \rho} \right)_{T,c} \quad (6)$$

Because we consider a symmetric model with the liquid concentration equal to 1/2, we must have $\mu_{FA} = \mu_{FB} \equiv \mu_F$. Equations (1-4) describe completely the growth dynamics of a diffusionless eutectic, if $\mu_{S(A,B)}(c)$ are known as a function of the 'order-like' parameter c . Therefore, we must relate explicitly the chemical potentials with the solid composition field. For an inhomogeneous solid phase, and taking into account the Laplace capillary pressure, we obtain from (6) (where derivatives are now interpreted in the functional sense)

$$\mu_{SA} = -\frac{c}{\rho} \left[\left(\frac{\partial f}{\partial c} \right)_{\rho} - \tilde{\alpha} \nabla^2 c \right] + \left(\frac{\partial f}{\partial \rho} \right)_c + \frac{(\nabla c)^2}{2} \left(\frac{\partial \tilde{\alpha}}{\partial \rho} \right)_c + v_{SA} \gamma \kappa \quad (7)$$

$$\mu_{SB} = \frac{1-c}{\rho} \left[\left(\frac{\partial f}{\partial c} \right)_{\rho} - \tilde{\alpha} \nabla^2 c \right] + \left(\frac{\partial f}{\partial \rho} \right)_c + \frac{(\nabla c)^2}{2} \left(\frac{\partial \tilde{\alpha}}{\partial \rho} \right)_c + v_{SB} \gamma \kappa, \quad (8)$$

where κ is the interface curvature, and v_{SA}, v_{SB} are the specific volumes of the two substances in the solid phase. Note at this point that expressions (7, 8) differ from the corresponding equations (3, 4) of reference [3]. Indeed, in that work, a confusion was made between Helmholtz and Gibbs energies, leading to erroneous expressions of the chemical potentials. While the qualitative conclusions of that work about the existence of steady and modulated solutions remain valid, the quantitative results about interface shapes, are incorrect.

The basic source of the above mentioned confusion lies in the fact that expression (1) implies that variations such as those needed to define chemical potentials are made at constant volume and not constant pressure. One could of course recover the correct result in terms of the Gibbs free enthalpy density (as used in Ref. [2]) provided one would enforce the condition of a constant volume by means of a Lagrange multiplier, namely the pressure.

We now specify for f the usual generic form:

$$f = f_0 - \tilde{a}\tilde{\eta}^2 + \tilde{b}\tilde{\eta}^4; \quad \tilde{\eta} = c - \frac{1}{2}. \quad (9)$$

The three coefficients \tilde{a} , \tilde{b} , $\tilde{\alpha}$ are functions of the density ρ (and of the passive parameter T , which we omit).

Our assumption of a completely symmetric model entails, in particular, that the partial volumes v_i are equal. It is shown in the appendix that this is true provided that \tilde{a} , \tilde{b} , $\tilde{\alpha}$ are proportional to the density ρ , so that, for example: $\partial\tilde{\alpha}/\partial\rho = \tilde{\alpha}/\rho$. So finally, we get for the chemical potentials on the solid side of the curved L/S interface

$$\mu_{SA} = \frac{(\frac{1}{2} + \tilde{\eta})}{\rho} [2\tilde{a}\tilde{\eta} - 4\tilde{b}\tilde{\eta}^3 + \tilde{\alpha}\nabla^2\tilde{\eta}] + \frac{\partial f_0}{\partial\rho} + \rho^{-1}[-\tilde{a}\tilde{\eta}^2 + \tilde{b}\tilde{\eta}^4 + \frac{\tilde{\alpha}}{2}(\nabla\eta)^2] + \gamma\rho^{-1}\kappa \quad (10)$$

$$\mu_{SB} = \frac{(\frac{1}{2} - \tilde{\eta})}{\rho} [2\tilde{a}\tilde{\eta} - 4\tilde{b}\tilde{\eta}^3 + \tilde{\alpha}\nabla^2\tilde{\eta}] + \frac{\partial f_0}{\partial\rho} + \rho^{-1}[-\tilde{a}\tilde{\eta}^2 + \tilde{b}\tilde{\eta}^4 + \frac{\tilde{\alpha}}{2}(\nabla\eta)^2] + \gamma\rho^{-1}\kappa. \quad (11)$$

Note that $\partial f_0/\partial\rho = \mu_s(c = 1/2)$.

We find it convenient to use, rather than equations (3) separately, the two linear combinations $[(1-c)3(a) + c3(b)]$ and $[3(a) - 3(b)]$, which yield, upon use of equations (10, 11),

$$\eta'' + 2\eta - 2\eta^3 = \eta \frac{V}{\sqrt{1+y'^2}} \quad (12)$$

$$\eta'^2 - 2\eta^2 + \eta^4 - d_0 \frac{y''}{(1+y'^2)^{3/2}} + \Delta = -\frac{V}{\sqrt{1+y'^2}}(1/a + 2\eta^2), \quad (13)$$

where

$$\eta \equiv \frac{\tilde{\eta}}{(\tilde{a}/2\tilde{b})^{1/2}}, \quad d_0 \equiv \frac{4\tilde{b}\gamma}{\tilde{a}^2 l_c}, \quad l_c \equiv \sqrt{\frac{\tilde{\alpha}}{\tilde{a}}}, \quad V \equiv \frac{2\tilde{V}\rho}{\tilde{a}W} \quad (14)$$

and the dimensionless undercooling Δ is given by

$$\Delta = \frac{4\rho\tilde{b}}{\tilde{a}^2} [\mu_S(1/2) - \mu_L(1/2)]. \quad (15)$$

Note that we specialize our calculation to the case where a one-dimensional front $[\tilde{y}(\tilde{x})]$ is growing steadily along \tilde{y} at the physical velocity \tilde{V} . In equations (12, 13) the a-dimensional quantities are measured in units of l_c .

3. Equilibrium *versus* Moving Trijunction

We first consider the case where the system is in thermodynamical equilibrium. Equations (12, 13) then reduce to

$$\eta'' + 2\eta - 2\eta^3 = 0 \quad (16)$$

$$\eta'^2 - 2\eta^2 + \eta^4 - d_0 \frac{y''}{(1+y'^2)^{3/2}} + \Delta = 0. \quad (17)$$

When each solid phase is in equilibrium with the liquid one with a planar interface equations (16, 17) possess the following solutions $\eta = \pm 1$ and $\Delta = 1$. When the three phases coexist, a planar front is no longer a solution (because of the tri-junction). Equation (16) admits the following solution

$$\eta(x) = \tanh(x). \quad (18)$$

Plugging this solution into equation (17), integrating from 0 to ∞ (this is taken to mean from 0 to distances much larger than l_c ; recall that lengths are reduced by l_c), and taking advantage of the symmetry of $y(x)$ we readily obtain

$$d_0 \sin(\theta) = \frac{4}{3}; \quad \sin(\theta) \equiv \frac{y'}{\sqrt{1+y'^2}} \Big|_{x=\infty} \tag{19}$$

where θ designates the usual contact angle. Note that this relation relates the contact angle to the liquid-solid surface tension (the surface tension γ enters in the definition of d_0). What remains to be shown is that the contact angle is related to the solid/solid wall energy as well, and this leads precisely to Young's condition. For that purpose we calculate the 'wall' (or surface) energy starting from the Gibbs definition, and it will appear clearly that the capillary condition is intimately related to the fact that l_c is finite. Let f_w denote that energy. The Gibbs definition reads (in physical units)

$$f_w = \lim_{(L \rightarrow \infty)} \int_{-L}^L d\tilde{x} [f_{s0} - \tilde{a}\tilde{\eta}^2 + \tilde{b}\tilde{\eta}^4 + \frac{\tilde{\alpha}}{2}\tilde{\eta}'^2] - L[f(\tilde{\eta}_{eq}) + f(-\tilde{\eta}_{eq})] \tag{20}$$

where the last term represents the energy in the case where each solid phase would be alone (remember that $\tilde{\eta}_{eq} = \sqrt{\tilde{a}/2\tilde{b}}$). Upon substitution of expression (18) into (20) a simple calculation provides us with

$$f_w = \frac{4l_c\tilde{a}^2}{3\tilde{b}} = 2\gamma \sin(\theta) \tag{21}$$

where use has been made of the definition of d_0 together with relation (19). This is precisely the Young condition for a symmetric model. Had we taken a non-symmetric model we would then have obtained the general form of Young's condition: $\gamma_1 \sin(\theta_1) + \gamma_2 \sin(\theta_2) = f_w$, and $\gamma_1 \cos(\theta_1) = \gamma_2 \cos(\theta_2)$, where γ_1 and γ_2 are the surface tension between the liquid phase and the two solid ones, θ_1 and θ_2 are the two contact angles. For a tilted pattern the extension should be feasible along the same lines.

We now consider the case of a growing solid and derive the *dynamical* Young condition. The nonlinear terms due to y in equations (12, 13) preclude an exact analytical solution. If $y'^2 \ll 1$, however, an exact solution is obtained for η (see also Ref. [3])

$$\eta = \sqrt{1 - \frac{V}{2}} \tanh \left[x \sqrt{1 - \frac{V}{2}} \right] \tag{22}$$

with the condition $V < 2$. Far away from the triple point a planar front solution exists with composition $\eta_0 = \pm(1 - V/2)$, and $\Delta = 1 - V^2/4 + 2V[1 - 2(\tilde{a}/\tilde{b})(1 - V/2)]$. Equation (13) can be rewritten as

$$d_0 y'' = \eta'^2 - 2(\eta^2 - \eta_0^2) + (\eta^4 - \eta_0^4). \tag{23}$$

Integrating from 0 to ∞ and using equation (22), we obtain the dynamical Young condition

$$2\gamma \sin(\theta) = f_w \sqrt{1 - \frac{V}{2}} \left(1 + \frac{V}{4} \right) \tag{24}$$

where f_w is the *equilibrium* wall energy (which enters Eq. (21)). For small V we can write $2\gamma \sin(\theta) - f_w \simeq -f_w V^2/16$. This is a simple dynamical equation for the motion of the trijunction. Remember that the physical velocity is reduced by $W\tilde{a}/\rho$, and from a dimensional analysis this is a velocity related to the molecular attachment, and not to the sound speed which involves the *compressibility* constant.

4. Discussion

We have shown that

- The two solid phases at thermodynamic equilibrium with the liquid at the eutectic composition have front profiles which satisfy asymptotically Young's condition, and that this simply follows from imposing the condition of chemical equilibrium only. By asymptotic we mean for distances larger than l_c .
- Although it is clear in some papers [1] that Young's condition follows from chemical equilibrium, confusions are still present in the literature. It must be emphasized that expressing chemical equilibrium does not imply at all, that mechanical equilibrium is satisfied. To make this point stronger let us consider the following case. For example, in the presence of a mechanical stress, surface energy does not affect mechanical equilibrium (its contribution is negligible except for very large stress values which are of the order of the Young modulus, that is close to the fracture threshold). Thus at a trijunction, the mechanical condition in the presence of stress would simply involve the stress tensor and not surface energy!! The surface energy would in turn be essential in the *chemical equilibrium* (chemical and mechanical forces or stresses have different nature!). A typical example is the Asaro-Tiller-Grinfeld problem. For further considerations, see reference [1].

At finite growth velocities, the Young condition is altered by kinetic effects; the trijunction acquires a finite mobility. Moreover, when diffusion in the liquid phase is the limiting factor, we expect Young's condition to be modified by a contribution which is of the order of the Peclet number. This reinforces the fact that Young's condition is affected by any departure from global chemical equilibrium. The non-equilibrium modification of Young's condition is not only an interesting fact in itself on the conceptual level, but also is expected to play a practical role at least in the three following situations: (i) at large enough growth velocities where kinetics together with finite Peclet effects are decisive, (ii) at small growth rates in faceted eutectics, (iii) in eutectoid transformations.

- A point worth of mention, in view of the recent development of phase field models [5,7,8] is that we derived Young's condition without resorting to the sharp interface limit, in the spirit of what may be termed the physicists' point of view [6,7]. In this approach, one keeps in mind the fact that interfaces associated with a first order phase transition have finite, though, usually, atomically small thickness. This underlies the very Gibbs definition of surface (extensive) thermodynamic quantities such as the surface energy. In this perspective, the so-called sharp interface equations, one of which is precisely Young's condition, only make physical sense on "outer" length scales much larger than the physical length l_c , and do not depend structurally on the details of the interface shape on the inner l_c scale. The mathematical question, formulated in the frame of phase field models, of formally recovering the sharp interface description *via* an asymptotic (multi-scale) expansion in the $l_c \rightarrow 0$ limit is, from this point of view, irrelevant.

Appendix

In this appendix we derive the condition under which the specific volumes in both solid phases are equal. The specific volume is related to the chemical potential by $v_i = \partial\mu_i/\partial p|_{T,c}$ ($i = A, B$). Because $\mu_i = \mu_i(T, \rho, c)$ we can write that $v_i = \partial\mu_i/\partial\rho|_{T,c} \partial\rho/\partial p|_{T,c}$. Using

the definition of the pressure $P = -f + \rho \partial f / \partial \rho$, we can rewrite the specific volume as

$$v_i = \frac{\partial \mu_i}{\partial \rho} \Big|_{T,c} \frac{1}{\rho \partial^2 f / \partial \rho^2}. \quad (25)$$

The relation between the chemical potential and f is given in equations (7, 8), so that the expression for the two specific volumes take the form

$$v_A = \left[\frac{c}{\rho^2} \frac{\partial f}{\partial c} - \frac{c}{\rho} \frac{\partial^2 f}{\partial c \partial \rho} \right] \frac{1}{\rho \partial^2 f / \partial \rho^2} + \frac{1}{\rho} \quad (26)$$

$$v_B = \left[\frac{c-1}{\rho^2} \frac{\partial f}{\partial c} + \frac{1-c}{\rho} \frac{\partial^2 f}{\partial c \partial \rho} \right] \frac{1}{\rho \partial^2 f / \partial \rho^2} + \frac{1}{\rho} \quad (27)$$

Imposing that $v_A = v_B$, then implies

$$\frac{1}{\rho} \frac{\partial f}{\partial c} = H(c, T), \quad (28)$$

where H is a function which depends on c and T only. Using the definition of f (Eq. (9), we immediately get that \tilde{a} , \tilde{b} , $\tilde{\alpha} \sim \rho$. In order that v be independent on c we must then have $\rho = \rho(T, P)$. Using the above definition of the pressure and the fact that the phenomenological constants that enter f are proportional to ρ , we obtain $P = -f_{s0} + \rho \partial f_{s0} / \partial \rho$, which is a function of ρ and T only. Since P does not depend on c , and that the system is isothermal, we conclude that ρ does not depend on c . This completes our proof.

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