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The wetting transition in binary Sullivan fluid mixtures

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Received 4 November 1991, in final form 10 April 1992

Abstract. The nature of the wetting transition in a binary Sullivan fluid mixture is studied by means of a dynamics approach. Analytical study of the two-phase coexistence system shows that the order of the wetting transition depends mainly on the strength of the fluid–fluid interaction and that the substrate does not play an essential role. The results on three-phase coexistence systems obtained by Hauge through Landau mean field theory are recovered by our treatment and some new results are obtained. A thin–thick transition might occur in such a short-range force system; a phase diagram of the wetting transition constructed from the two components of wall–fluid potential is obtained. The method employed in the present paper could be used to investigate the wetting behaviour in systems with more components.

1. Introduction

The wetting transition has received much attention in the last few decades [1]. The first question to be answered in this field is whether the transition is of first or second order. The wetting transition in a simple fluid system has already been thoroughly studied by many methods [1] including the dynamical approach. The dynamical approach has turned out to be very powerful in studying the order of the wetting transition in the Sullivan model [2] and its generalization [3–6]. This approach is based on a simulation of the wetting problem in simple fluids in which a classical particle moves in a one-dimensional space [3]. The wetting properties in binary mixture fluids have been studied by many authors using various methods [7–9]. It is natural to ask whether the dynamical approach could be used to discuss the wetting properties in fluid mixtures. Ding and Hauge have proved [10] that in a van der Waals framework [11], the wetting problem of the Sullivan model [2] for n -component mixtures can still be thought of as a dynamical problem where a classical particle moves in an n -dimensional hilly landscape. In this article, we discuss the Sullivan model [2] for a binary mixture system, i.e., both fluid–fluid and wall–fluid potentials have exponential form with the same force range. The density profile of a fluid with a free interface (i.e., no wall exists) is represented as a trajectory between two peaks of the dynamical potential, which is called a *reference trajectory* (RT). When a substrate is introduced, the fluid density profile will change and the motion orbit of the classical particle will deviate from the RT—this is called the *expansion trajectory* (ET). If the wall force is weak enough, the deviation of the ET from the RT (take h

to denote this deviation in the text) may be so small that we can regard it as a small quantity and the ET can effectively be expanded in h near the RT. As we have seen in the simple fluid case, however, h may not be a small quantity when the trajectory passes near a peak of potential. Fortunately, the potential itself can be expanded and a *local trajectory* (LT) of the particle in this region could be obtained. Joining ET and LT smoothly in a certain position (denoted by M_0 in figure 1) may yield a whole *physical trajectory* (PT) which represents a partial wetting state of the system. As for the complete wetting, the PT is constructed by connecting the RT and a piece of the LT passing through the peak of the wetting phase. This procedure is called the *trajectory expansion method*.

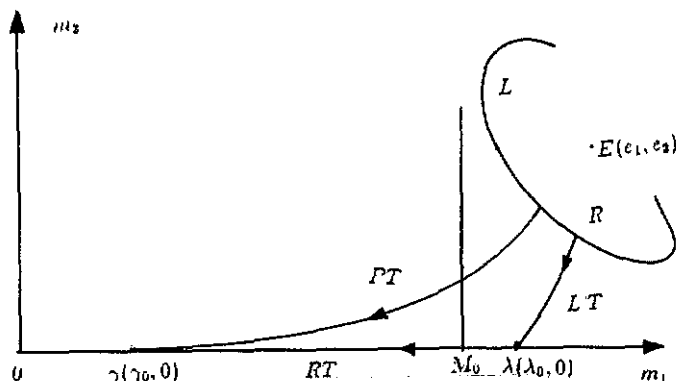


Figure 1. Distribution of two peaks of potential (8) in the case of two-phase coexistence.

In our discussion, we take h_0 (deviation h at M_0) as the order parameter for investigating the order of the wetting transition. In the complete wetting state, $h_0 = 0$, the particle must visit the peak of the wetting phase (denoted as λ in section 2) before it goes to the peak of the bulk phase (denoted as γ). In the partial wetting state, however, $h_0 \neq 0$, the particle goes to peak γ directly without passing through peak λ . Thus a continuous change of h_0 from zero to non-zero indicates a second-order wetting transition, and a jump in h_0 corresponds to a wetting transition of first order. As the wall-fluid force varies, the PT may change its shape (keeping its endpoint at peak γ , of course). The minimum principle of free energy will determine whether a partial or complete wetting state is more favourable. When both have an equal amount of free energy, a wetting transition may occur. In this way the separatrix of first-order and second-order transitions in the parameter space can be calculated, and the phase diagram of the wetting transition is also obtained.

In this paper we adopt the notation used before [10], where the attractive potential between molecules i and j is χ_{ij} (integrated over lateral dimensions), and that due to the wall and on the i th component of the fluid is Φ_i . The Sullivan model takes the form

$$\begin{aligned} \chi_{ij}(x) &= -\frac{1}{2}\alpha_{ij}e^{-|x|} \\ \Phi_i(x) &= -\varepsilon_i e^{-x} \end{aligned} \quad \alpha_{ij} \geq 0 \quad \alpha_{ij} = \alpha_{ji} \quad (1)$$

with constant α_{ij} and ε_i . In the following, the repeated indices imply a summation over indices 1 and 2, and a single subscript i always indicates number 1 or 2. The

surface free energy reads

$$\sigma\{\rho_i(x)\} = \int_0^\infty dx \{f_H[\{\rho_i(x)\}] - [\mu_i - \Phi_i(x)]\rho_i(x) + p\} + \frac{1}{2} \int_0^\infty \int_0^\infty dx dx' \rho_i(x) \chi_{ij}(x-x') \rho_j(x') \tag{2}$$

where $\rho_i(x)$ is the fluid density of the i th component and $\{\rho_i(x)\}$ denotes the totality of $\rho_i(x)$ ($i = 1, 2$), f_H is the Helmholtz free energy density for hard core systems, μ_i is the chemical potential of the i th component, and p is the equilibrium pressure. The equilibrium state should be determined by $\delta\sigma/\delta\rho_i = 0$, which leads to a set of second-order differential equations:

$$d^2\mu_{Hi}/dx^2 = \mu_{Hi}(x) - \mu_i - \alpha_{ij}\rho_j(x). \tag{3}$$

In the associated dynamical problem, x is regarded as time t . Introducing dimensionless quantities [10], we have

$$\begin{aligned} t = x & \quad \xi_i = \mu_{Hi}/k_B T & \quad A_{ij} = \alpha_{ij}/k_B T & \quad M_i = \mu_i/k_B T \\ r_H = p_H/k_B T & \quad r = p/k_B T & \quad E_i = \epsilon_i/k_B T. \end{aligned} \tag{4}$$

Equation (3) is then transformed into

$$d^2\xi_i/dt^2 = \xi_i - M_i - A_{ij}(\partial r_H/\partial \xi_j). \tag{5}$$

In the general symmetry case $A_{11} = A_{22} = A, A_{12} = A_{21} = B = kA, M_1 = M_2 = M$. The symmetry matrix with elements A_{ij} can be diagonalized using a real orthogonal matrix σ_{ij} : $\sigma_{ij} A_{jk} \sigma_{lk} = A_i \delta_{il}$ (no summation over i in this and the next expression!) Letting $\tau_{ij} = A_i^{-1/2} \delta_{ij}$ and $T_{ij} = \tau_{ik} \sigma_{kj}$, we get $T_{ij} A_{jk} T_{lk} = \delta_{il}$ where

$$(T_{ij}) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1/\sqrt{A+B} & 1/\sqrt{A+B} \\ -1/\sqrt{A-B} & 1/\sqrt{A-B} \end{pmatrix}. \tag{6}$$

With $m_i = T_{ij}(\xi_j - M_j)$, equation (5) can be transformed into Newtonian motion equations describing a classical particle with unit mass and coordinates (m_1, m_2) moving in a conservative potential U :

$$d^2m_i/dt^2 = -\partial U/\partial m_i \tag{7}$$

where $U = r_H - r - \frac{1}{2}m_1 m_2$. If an ideal lattice gas model is chosen for the hard core system, we have

$$U = \ln(1 + e^{\xi_1} + e^{\xi_2}) - r - \frac{1}{2}(m_1^2 + m_2^2) \tag{8}$$

where

$$\xi_1 = \sqrt{\frac{A+B}{2}} m_1 - \sqrt{\frac{A-B}{2}} m_2 + M \quad \xi_2 = \sqrt{\frac{A+B}{2}} m_1 + \sqrt{\frac{A-B}{2}} m_2 + M.$$

The initial conditions are

$$\dot{m}_i(0) = m_i(0) - e_i \quad (9)$$

where $e_i = 2T_{ij}E_j$ is the i th component of wall–fluid potential. The final conditions are

$$\dot{m}_i(\infty) = 0 \quad (10)$$

which means an auxiliary limitation: $m_i(\infty) =$ coordinates corresponding to the bulk phase far away from the wall.

The free energy (2) of the system can then be transformed into the form

$$\frac{\sigma}{k_B T} = -e_i e_i + \frac{1}{2} m_i(0) m_i(0) + \int_{-\infty}^{+\infty} \dot{m}_i \dot{m}_i dt. \quad (11)$$

The above preliminary formulation enables us to study the corresponding wetting properties systematically.

The rest of this present paper is organized as follows: section 2 investigates the wetting behaviour of a system in a two-phase coexistence state. Section 3 studies the three-phase coexistence system. The conclusions and some further discussions are included in the last section.

2. Two-phase coexistence system

If $(1-k)/2 < 1/A < (1+k)/8$ and $k < 1$ (area II in [10]), the dynamical potential has two peaks γ and λ . By choosing a certain value for M in equation (8), one may obtain a two-phase (γ and λ) coexistence state. The phase γ is the one with lower density and λ is the one with higher density as shown in figure 1, where $(\gamma_0, 0)$ and $(\lambda_0, 0)$ are their coordinates respectively. We define phase λ as the intruding phase and γ as the bulk phase, then the RT is along the m_1 axis directed to peak γ . We can expand the ET in $h(t)$ as follows:

$$\begin{aligned} m_1(t) &= a_0(t) + a_1(t)h(t) + a_2(t)h^2(t) + \dots \\ m_2(t) &= h(t) \\ \dot{h}(t) &= b_1(t)h(t) + b_2(t)h^2(t) + \dots \end{aligned} \quad (12)$$

where $a_0(t)$ and $b_0(t)$ are components of the RT. Substituting (12) into both dynamical equations (7) and the first integral

$$\frac{1}{2} \dot{m}_1^2 + \frac{1}{2} \dot{m}_2^2 + U(m_1, m_2) = 0 \quad (13)$$

gives the following set of equations:

$$\frac{1}{2} \dot{a}_0^2 + U_{00} = 0 \quad (14a)$$

$$\dot{a}_0(\dot{a}_1 + a_1 b_1) + a_1 U_{10} = 0 \quad (14b)$$

$$\frac{1}{2}(\dot{a}_1 + a_1 b_1)^2 + \dot{a}_0(\dot{a}_2 + a_1 b_2 + 2a_2 b_1) + \frac{1}{2} b_1^2 + a_2 U_{10} + \frac{1}{2} a_1^2 U_{20} + \frac{1}{2} U_{02} = 0 \quad (14c)$$

$$\dot{b}_1 + b_1^2 + U_{02} = 0 \quad (14d)$$

$$\dot{b}_2 + 3b_1 b_2 + a_1 U_{12} = 0 \quad (14e)$$

etc, where U_{00}, U_{10}, \dots are coefficients in the expansion of the dynamical potential U around the RT:

$$U_{00} = U(a_0, 0) \quad U_{ij} = \left. \frac{\partial^{i+j} U(m_1, m_2)}{\partial^i m_1 \partial^j m_2} \right|_{m_1=a_0, m_2=0}$$

Equations (14) define the ET for given initial conditions. Notice that equation (14a) is simply the equation for the RT.

Near peak λ , the LT takes the form

$$m_1 = \lambda_0 + C_1 e^{-at} + C_2 e^{at} \quad m_2 = C_3 e^{-bt} + C_4 e^{bt} \quad (15)$$

with the coefficients C_1, C_2, C_3 and C_4 to be determined, and a, b the curvatures of the dynamical potential along two principal axes at peak λ , determined by the expansion of U near the peak λ :

$$U(m_1, m_2) = -\frac{1}{2} a^2 (m_1 - \lambda_0)^2 - \frac{1}{2} b^2 m_2^2.$$

As long as the deviation of the ET from the RT is small enough, we may find some position $m_1 = M_0$ where both trajectory expansion (12) and the potential expansion near the peak λ are valid. Then we may connect them smoothly there and obtain the PT. Suppose that the particle passes this position at a moment t_0 ; the connecting conditions are

$$\dot{m}_i(t_0 - 0) = \dot{m}_i(t_0 + 0) \quad m_i(t_0 - 0) = m_i(t_0 + 0). \quad (16)$$

Appendix A supplies a discussion of equations (14) and coefficients in equation (15), and gives the following equations:

$$\begin{aligned} (1 + a)p^0 e^{at_0} h_0^2 - (\lambda_0 - e_1) - (1 - a)(a_0^0 - \lambda_0) e^{-at_0} &= 0 \\ (1 + b)(b - b_1^0) e^{bt_0} h_0 - 2be_2 + (1 - b)(b + b_1^0) e^{-bt_0} h_0 &= 0 \end{aligned} \quad (17)$$

where the superscript 0 indicates a quantity at moment t_0 , and p^0 is a positive constant. These expressions will be used to study the order of the wetting transition.

Letting $e_2 > 0$ be fixed (the case of $e_2 < 0$ can be treated in the same way), taking $h_0 \geq 0$ as a small quantity and using the second expression in equation (17), we get

$$e^{bt_0} \approx \frac{2be_2}{(1 + b)(b - b_1^0)h_0} + \frac{(-1 + b)(b_1^0 + b)}{2be_2} h_0 + O(h_0^2). \quad (18)$$

Substituting this into the first equation in (17) gives

$$e_1 - \lambda_0 = -K h_0^{2-a/b} + O(h_0^{a/b}, h_0^{4-a/b}) \quad (19)$$

where

$$K \equiv (1 + a) \left(\frac{2be_2}{(1 + b)(b - b_0)} \right)^{a/b} > 0$$

and the coefficients of $h_0^{a/b}, h_0^{4-a/b}$ terms are all negative.

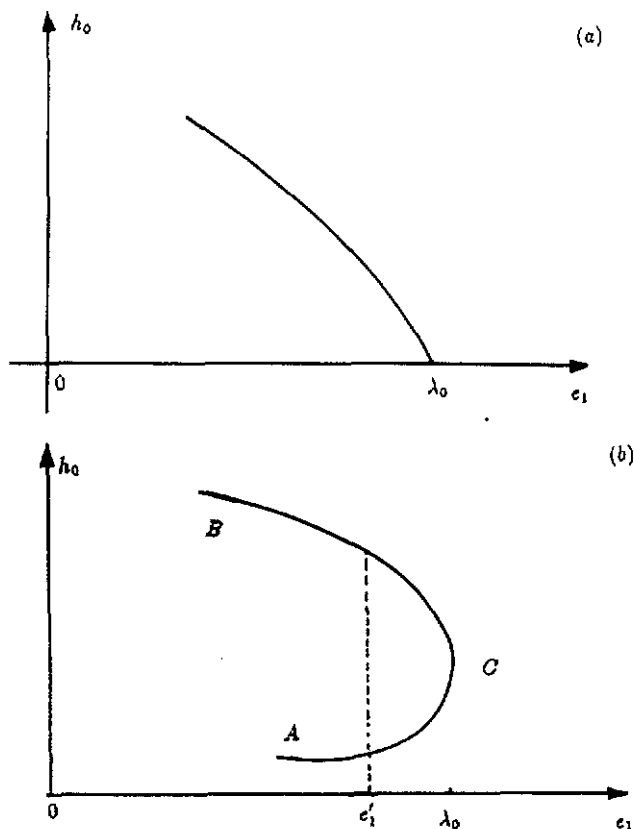


Figure 2. (a) A second-order transition takes place at $e_1 = \lambda_0$ for the case of $a \leq 2b$. (b) A first-order transition takes place at e'_1 for the case of $a > 2b$.

(i) If $2b \geq a$ (including $b > a$; thus the dominant term of $e_1 - \lambda_0$ is of order $h_0^{a/b}$), $e_1 - \lambda_0 \rightarrow 0$ when $h_0 \rightarrow 0$, as shown in figure 2(a). Since h_0 varies continuously as e_1 decreases, the transition is of second order.

(ii) If $a > 2b$, the first term in the right-hand side of (19) diverges when $h_0 \rightarrow 0$. The correcting term describes the behaviour when h_0 is larger as shown by the branch BC in figure 2(b): h_0 may have a sudden jump at e'_1 when e_1 decreases, so the transition is of first order. Numerical calculation shows that the transition of the wetting state from complete (along axis e_1) to partial (along branch BC) wetting is permitted only once when e_1 moves leftward; no intermediate state (on branch AC) has minimum free energy, thus no thin-thick transitions occur in this case. Obviously, the transition of second order happens at $e_1 = \lambda_0$ and that of first order takes place at $e'_1 < \lambda_0$ but its exact position should be determined by minimizing the free energy.

In appendix B the free energy is calculated for the partial wetting state as $\sigma_1/k_B T$ and for the complete wetting as $\sigma_2/k_B T$. Equating them may give a relation between t_0 and h_0 , which determines the existence condition for the first-order wetting transition. We denote the values of e_1 and e_2 at which the first-order wetting transition takes place by adding a prime. When h_0 is very small we have

$$e'_2 \simeq (\lambda_0 - e'_1)^{1-b/a}. \quad (20)$$

Because of the symmetry, the locus of the first-order wetting transition for $h_0 < 0$ can

also be obtained by the same procedure. The separatrix for the first-order transition is shown in figure 3(a), where the right half-plane to the separatrix is the area of complete wetting, while the left half is of partial wetting. The separatrix is symmetric with respect to permutation of the two constituents of the fluid because the potential (8) itself is symmetric about axis m_1 . Figure 3(b) is a sketch of the phase diagram, where a first-order transition occupies the half-space $a/b > 2$, and a continuous transition occurs when $a/b \leq 2$. It is worth pointing out that the system will return to Sullivan's case itself if $e_2 = 0$ remains unchanged (the two components of the fluid have equal densities); the transition will thus always be continuous [2]. This indicates that the Sullivan model has a marginal version, and a very small deviation might lead to a first-order transition, just like that shown in figure 3(b).

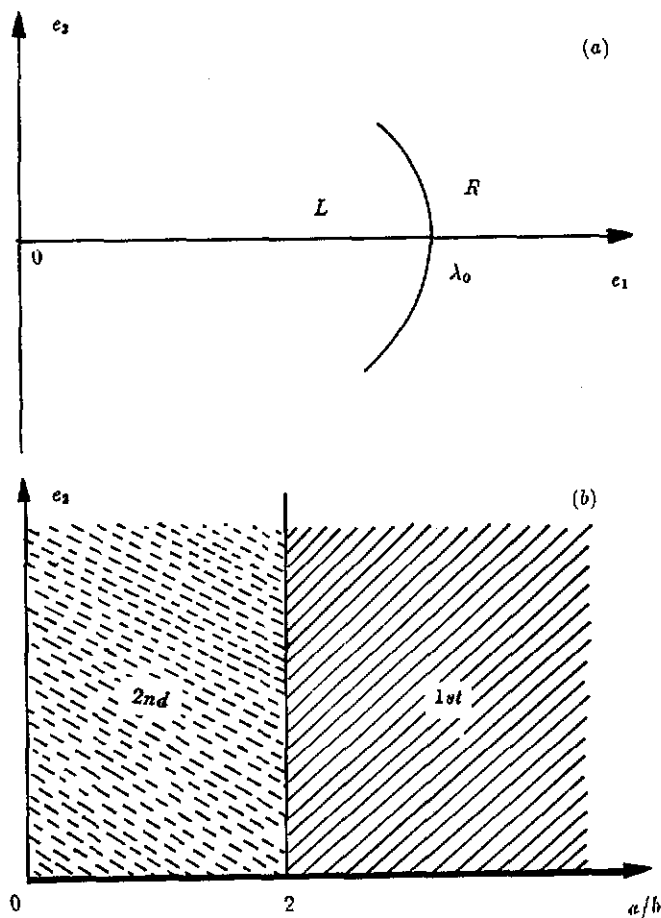


Figure 3. (a) Separatrix of partial wetting (area L) and complete wetting (area R) in a two-phase coexistence state when $a > 2b$. (b) Phase diagram of a two-phase coexistence state. The first-order transition occurs when $a/b > 2$ and $e_2 \neq 0$, while the second-order transition takes place when $a/b \leq 2$, or $e_2 = 0$.

From the discussion above, we know that the order of the wetting transition at the two-phase coexistence boundary of a binary Sullivan fluid mixture depends mainly on the relative magnitude of the curvatures along the two principal axes at peak λ . Since both a and b are functions of A and B (parameters describing the fluid–fluid

potential defined in section 1), the order of transition is controlled mainly by the interaction between fluid molecules, and the substrate does not play an essential role. It plays, however, a major role in determining whether the system is in a partial or complete wetting state. The substrate will play an important role in a more general system discussed in the next section where the RT is no longer along the symmetry axis for the dynamical potential.

Dietrich and Schick [8] have studied the two-phase coexistence system near a wall via a sharp-kink approximation within the framework of mean field theory for long-range force fluid. They showed that both first- and second-order transitions are possible and the prewetting line attaches to the first-order line tangentially in a phase space expanded by temperature, pressure and chemical potential. The results for the short-range force system presented here are qualitatively the same.

3. Three-phase coexistence system

This section is dedicated to the discussion of the three-phase coexistence system. In the parameter space $(k, 1/A)$ the area for this case roughly corresponds to

$$0 < \frac{1}{A} < \frac{(3+k)(1-k)}{2(5-k)}$$

with some exceptions which are denoted as area V in [10]. (For the exact boundary, see [10].) The three peaks of potential (8) indicate three phases γ , δ and β in a coexistence state. Their locations are shown in figure 4. If the value of M is suitably adjusted, the three peaks may have the same height. The phase γ has lower density with equal content of two constituents and its representative peak is situated on axis m_1 with coordinates $(\gamma_0, 0)$. The phases δ and β have higher density and their peaks are symmetrically situated at (δ_1, δ_2) and (β_1, β_2) with $\beta_1 = \delta_1$ and $\beta_2 = -\delta_2$. The phase β is richer in one constituent and δ richer in the other. In this section we shall study the wetting behaviour of phases δ and γ . We suppose that the wall favours the δ phase and that the bulk is filled with γ , so the RT deviates from axis m_1 , the symmetry axis of potential (8).

The ET now takes the form

$$\begin{aligned} m_1(t) &= a_0(t) + a_1(t)h(t) + a_2(t)h^2(t) + \dots \\ m_2(t) &= b_0(t) + h(t) \\ \dot{h}(t) &= b_1(t)h(t) + b_2(t)h^2(t) + \dots \end{aligned} \quad (21)$$

where $(a_0(t), b_0(t))$ represents the RT. As in section 2, the expansion method can yield a set of differential equations to determine the ET. In the vicinity of the peak δ it is more convenient to introduce a principal-axes coordinate system via the following transformation:

$$\begin{aligned} g_1 &= \sqrt{1-\eta}(m_1 - \delta_1) - s\sqrt{\eta}(m_2 - \delta_2) \\ g_2 &= s\sqrt{\eta}(m_1 - \delta_1) + \sqrt{1-\eta}(m_2 - \delta_2). \end{aligned} \quad (22)$$

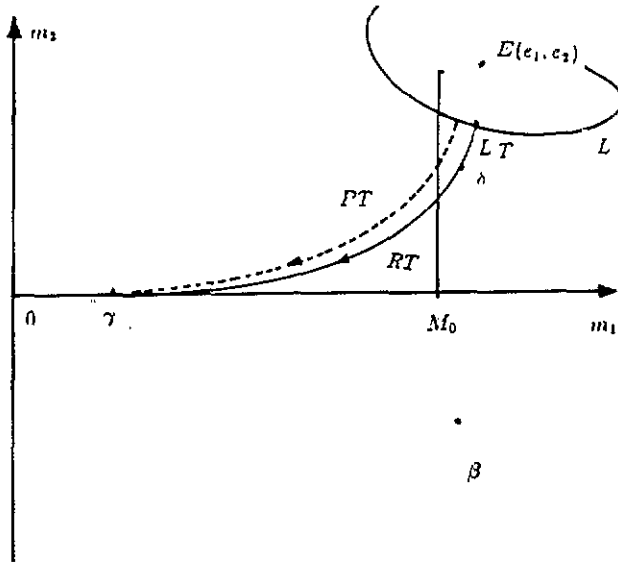


Figure 4. Location of three peaks of potential (8) in the case of three-phase coexistence.

(g_1, g_2) plays the same role as (m_1, m_2) in section 2, η is a constant and $s = 1$. (In the case where one considers the peak β we put $s = -1$.) The analogues of equation (15) takes the form

$$\begin{aligned} g_1(t) &= \Gamma_1 e^{\alpha(t-t_0)} + \Gamma_2 e^{-\alpha(t-t_0)} \\ g_2(t) &= \Gamma_3 e^{\beta(t-t_0)} + \Gamma_4 e^{-\beta(t-t_0)} \end{aligned} \tag{23}$$

where $\Gamma_1, \Gamma_2, \Gamma_3$ and Γ_4 are constants, α and β are principal curvatures of the potential at peak δ , and t_0 is the moment at which the particle passes through M_0 in figure 4. The two expansions (21) and (23) must be connected by joining the conditions at M_0 . The Γ coefficient can be expanded as

$$\Gamma_i = \Gamma_{i0} + \Gamma_{i1} h_0 + \Gamma_{i2} h_0^2 + \dots \quad (i = 1, 2, 3, 4).$$

Initial conditions (9) become

$$\dot{g}_1(0) = g_1(0) - H_1 \quad \dot{g}_2(0) = g_2(0) - H_2$$

where

$$\begin{aligned} H_1 &= \Gamma_1(1 - \alpha)e^{-\alpha t_0} + \Gamma_2(1 + \alpha)e^{\alpha t_0} \\ H_2 &= \Gamma_3(1 - \beta)e^{-\beta t_0} + \Gamma_4(1 + \beta)e^{\beta t_0} \end{aligned} \tag{24}$$

which correspond to (17). From (9) and (23), we have also

$$\begin{aligned} H_1 &= \sqrt{1 - \eta}(e_1 - \delta_1) - s\sqrt{\eta}(e_2 - \delta_2) \\ H_2 &= s\sqrt{\eta}(e_1 - \delta_1) + \sqrt{1 - \eta}(e_2 - \delta_2) \end{aligned} \tag{25}$$

which are similar in form to equation (22).

Appendix C gives the locus for the first-order wetting transition in the parameter space (H_1, H_2)

$$H_2' \sim (H_1')^{-(\alpha-2\beta)/\beta}. \tag{26}$$

It is easy to see that the phase diagrams have different forms for $\alpha > 2\beta$ and $\alpha < 2\beta$. We must discuss them separately. It is proved in appendix C that $\Gamma_1\Gamma_2$ and $\Gamma_3\Gamma_4$ have opposite signs. Their values can be obtained analytically when the details of peak δ and the RT are known. Here we assume that $\Gamma_{10} > 0, \Gamma_{21} < 0, \Gamma_{30} < 0, \Gamma_{41} < 0$, which is one of the possible sets of coefficients required by (C2). Other choices will lead to a similar conclusion and will not be discussed here.

Keeping H_1 unchanged we have from the first expression of equation (24)

$$e^{\alpha t_0} \simeq \frac{H_1 \pm \sqrt{H_1^2 - 4\Gamma_{10}\Gamma_{21}(1-\alpha^2)h_0}}{2\Gamma_{21}(1+\alpha)h_0}. \tag{27}$$

We now discuss the order of the wetting transition for the two cases $h_0 > 0$ and $h_0 < 0$ respectively.

(i) When $h_0 > 0$, equation (27) has only one choice: $e^{\alpha t_0} \simeq H_1/[\Gamma_{21}(1+\alpha)h_0]$ which requires $H_1 < 0$. With this solution, the second expression of (24) gives

$$H_2 \simeq \Gamma_{30}(1-\beta) \left(\frac{H_1}{\Gamma_{21}(1+\alpha)}\right)^{-\beta/\alpha} + \Gamma_{41}(1+\beta) \left(\frac{H_1}{\Gamma_{21}(1+\alpha)}\right)^{\beta/\alpha} h_0^{1-\beta/\alpha} < 0$$

for $0 < \beta/\alpha < 1, 0 < 1 - \beta/\alpha < 1$; the coefficients of the two terms of the above expression are all negative. The system should be in a complete wetting state when $h_0 \rightarrow 0$. As H_2 decreases from positive to negative, a second-order transition may occur at $H_2 = 0$.

(ii) When $h_0 < 0$, equation (27) takes one of two forms:

$$e^{\alpha t_0} \simeq \frac{H_1}{\Gamma_{21}(1+\alpha)h_0} \quad \text{or} \quad e^{\alpha t_0} \simeq \frac{\Gamma_{10}(1-\alpha)}{H_1}$$

so only $H_1 > 0$ is possible. With these two roots we get from (24) that

$$H_2^{(1)} \simeq \Gamma_{30}(1-\beta) \left(\frac{H_1}{-\Gamma_{21}(1+\alpha)}\right)^{-\beta/\alpha} (-h_0)^{\beta/\alpha} - \Gamma_{41}(1+\beta) \left(\frac{H_1}{-\Gamma_{21}(1+\alpha)}\right)^{\beta/\alpha} (-h_0)^{1-\beta/\alpha} \tag{28}$$

and

$$H_2^{(2)} \simeq \Gamma_{30}(1-\beta) \left(\frac{\Gamma_{10}(1-\alpha)}{H_1}\right)^{-\beta/\alpha} - \Gamma_{41}(1+\beta) \left(\frac{\Gamma_{10}(1-\alpha)}{H_1}\right)^{\beta/\alpha} (-h_0). \tag{29}$$

In the following we consider the wetting behaviour for $\alpha > 2\beta$ and $\alpha < 2\beta$ separately.

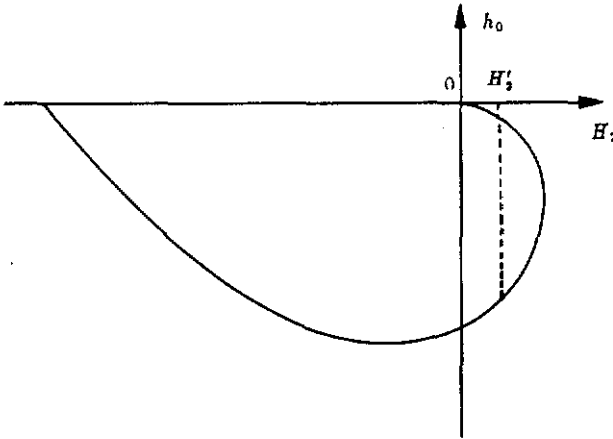


Figure 5. A first-order transition occurs at $H_2 = H_2'$ when $\alpha < 2\beta$.

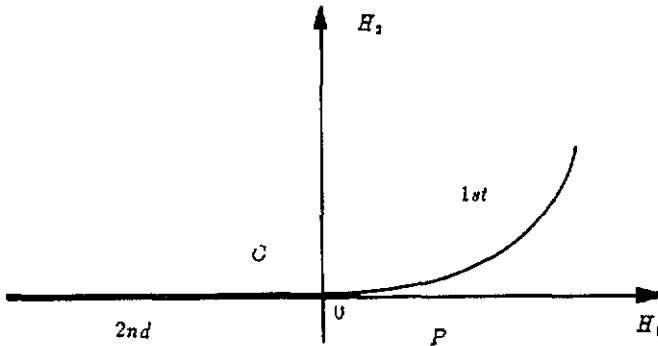


Figure 6. Phase diagram of a three-phase coexistence system when $\alpha < 2\beta$, where area C indicates the complete-wetting region and P indicates the partial-wetting region, '1st' (thin line) represents a first-order transition and '2nd' (wide line) represents a second-order transition.

(i) When $\alpha < 2\beta$, we have $\beta/\alpha > 1 - \beta/\alpha$, so $H_2^{(1)} \sim -\Gamma_{41}(-h_0)^{1-\beta/\alpha}$. However, $H_2^{(2)}$ is linear in $(-h_0)$; hence, as shown in figure 5 there is a first-order transition when H_2 decreases through a value of H_2' . Combining the results for $H_1 < 0$ above and the separatrix equation (26), we then obtain the phase diagram in a dynamical picture as shown in figure 6.

(ii) When $\alpha > 2\beta$, we have $\beta/\alpha < 1 - \beta/\alpha$. If H_1 is very large, H_2 varies with h_0 as shown in figure 7, and there is a first-order transition. If, on the other hand, H_1 is very small, the dependence of H_2 on h_0 might be different, as shown in figure 8, and a second-order transition may occur. For intermediate values of H_1 , numerical calculations show that there may be the behaviour shown in figure 9: besides a second-order transition at the origin, there may also be a 'thin-thick transition' [4], which reveals a finite jump in thickness of the wetting film from $h_0^{(1)}$ to $h_0^{(2)}$. Their corresponding free energies are equal; the minimum of free energy is changed from branch AO to branch BC when H_2 decreases as shown in figure 9. Summarizing all cases for H_1 above we can give a dynamical description for the phase diagram when $\alpha > 2\beta$ as shown in figure 10, where only a segment of large H_1 can be determined

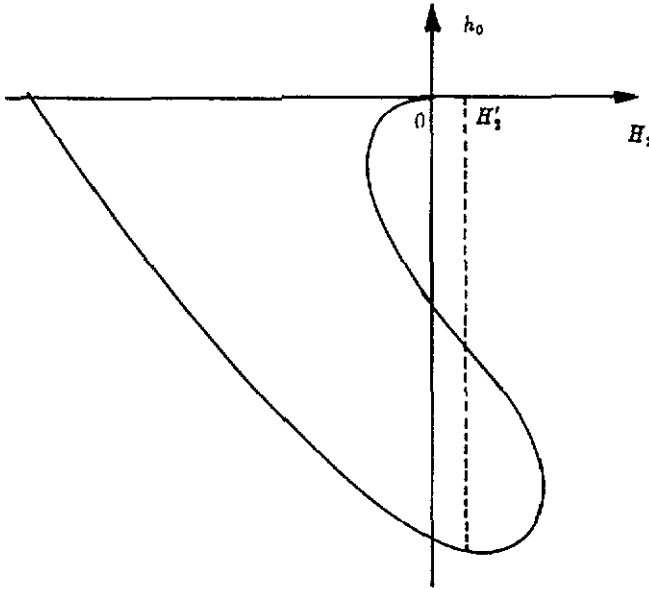


Figure 7. A first-order transition occurs at $H_2 = H_2^1$ when $\alpha > 2\beta$ and H_1 is very large.

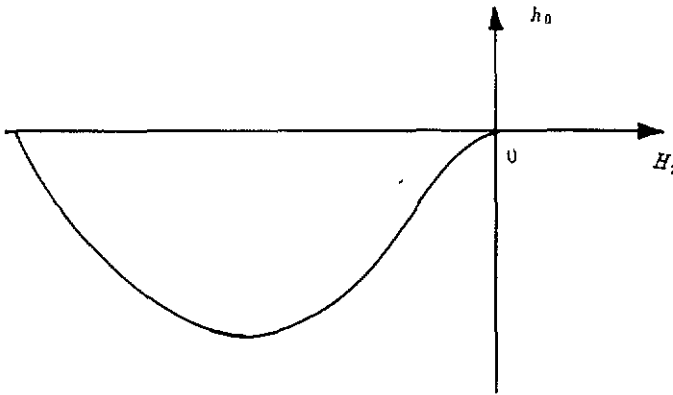


Figure 8. A second-order transition occurs at $H_2 = 0$ when $\alpha > 2\beta$ and H_1 is very small.

analytically; for other parts numerical work is necessary.

All the studies above were performed with constant H_1 and varying H_2 . The alternative situation will also lead to the same results; we omit the repeated discussion here.

The study reveals that the wetting properties depend not only on the interaction between fluid molecules (which is reflected by the dependence on α and β) but also on the interaction between molecules of the fluid and the substrate (which is reflected by the dependence on H_1 and H_2); this is different from that of the two-phase coexistence system.

Hauge once studied the wetting behaviour of a binary system with a three-phase coexistence state using Landau theory [9]. The dynamical potential he discussed is

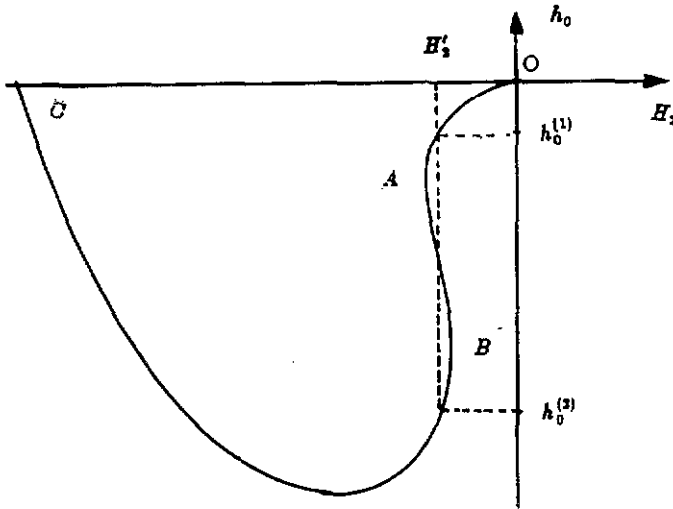


Figure 9. A 'thin-thick' transition takes place at $H_2 = H_2'$ when $\alpha > 2\beta$ and H_1 has an intermediate value. In the decreasing of H_2 from positive to negative, a second-order transition occurs at origin O and follows a sudden jump of layer thickness at H_2' from $h_0^{(1)}$ to $h_0^{(2)}$.

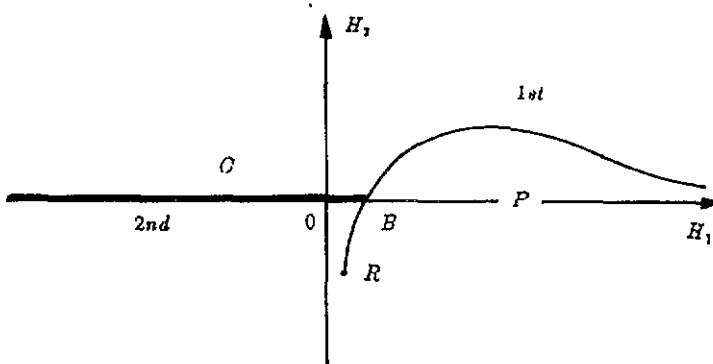


Figure 10. Phase diagram of a three-phase coexistence system when $\alpha > 2\beta$, where BR is the 'thin-thick' transition line. The symbols C , P , '1st' and '2nd' have the same meaning as in figure 6.

similar to the one that we studied here as in figure 4. His conclusion is in agreement with the present paper. However, the thin-thick transition revealed in the present study was not found in his Landau mean field theory discussion.

4. Discussion

Our technique is valid only when expansion parameter h is small enough, so our results are valid only in a small area in the phase diagram of figures 3 and 10, which requires that the wall force should not be too large, and the initial condition curve L determined by equations (9) and (13) for a given point $E(e_1, e_2)$ should be located near the peak λ (see figure 1). If the point $E(e_1, e_2)$ moves away from peak λ , and

the value of h_0 is no longer small, the ET may deviate substantially from the RT and the trajectory expansion method is not then valid; some numerical work is required.

For the sake of concreteness, we suppose in section 2 that phase λ is adsorbed on a flat wall and phase γ is in the bulk, so the particle will move from peak λ to γ ; the opposite case is also true if the RT is directed from peak γ to peak λ —the treatment is quite similar to that in section 2. In section 3 we can also investigate other cases, such as that in which the phase δ is filled in the bulk and the wall favours phase γ , so long as we reverse the direction of the RT. The wetting transition for the coexistence state of phases δ and β can be treated by our approach too; we need only exchange m_1 and m_2 in equation (21). The study procedure is almost the same.

The fact that the thin-thick transition occurs in a ‘fairly short-range’ force system and that it precedes a critical wetting transition has been revealed in some other systems (see [12] and references therein). Our phase diagram in figure 10 is quite similar to some parts of the phase diagram of the simple fluid [12].

Acknowledgment

This work is supported by the National Natural Science Foundation of China.

Appendix A

The dominating term of \dot{m}_2 is $b_1(t)h(t)$; here $b_1(t)$ is determined by (14d) and

$$U_{02} = \frac{A - B}{2} \frac{1}{1 + \frac{1}{2} \exp(-\sqrt{(A + B)/2} a_0 - M)} - 1.$$

Since $(1 - k)/2 < 1/A$ in area II [10], $U_{02} < 0$, and, as a_0 reduces monotonically with t , so does U_{02} , but its absolute value increases; we rewrite (14d) as

$$\dot{b}_1 = |U_{02}(a_0)| - b_1^2.$$

When $t \rightarrow +\infty$, $\dot{b}_1 \rightarrow 0$, so $b_1^2(\infty) = |U_{02}(\gamma_0)|$. Now the PT cannot arrive at peak γ unless $m_2(t)$ has opposite sign to $\dot{m}_2(t)$. So $b_1(t) < 0$ and $\dot{b}_1(\infty) = -\sqrt{|U_{02}(\gamma_0)|}$, which shows that the solution we wanted is the non-stable one, and initial values are confined in the range

$$-\sqrt{|U_{02}(\gamma_0)|} < b_1(t_0) < -\sqrt{|U_{02}(a_0(t_0))|}.$$

Hence $b(t)$ decreases monotonically after t_0 . From (14b) we get

$$\dot{a}_1 + \left(b_1 + \frac{U_{10}}{-\sqrt{-2U_0}} \right) a_1 = 0.$$

It can be proved in the present model that

$$b_1 + \frac{U_{10}}{-\sqrt{-2U_0}} < 0$$

and only $a_1(t \rightarrow +\infty) = 0$ can give $\dot{a}_1(t \rightarrow +\infty) = 0$, so $a_1 \equiv 0$.

Hence (14e) becomes $\dot{b}_2 + 3b_1 b_2 = 0$, and similar arguments show that $b_2 \equiv 0$. Thus (14c) becomes

$$\dot{a}_2 + (2b_1 + U_{10}/\dot{a}_0)a_2 = -(b_1^2 + U_{02})/2\dot{a}_0$$

or, using (14d),

$$\dot{a}_2 + (2b_1 + U_{10}/\dot{a}_0)a_2 = \dot{b}_1/2\dot{a}_0. \tag{A1}$$

Since

$$2b_1 + U_{10}/\dot{a}_0 < 0 \quad \dot{b}_1/2\dot{a}_0 = \frac{1}{2}db_1/da_0 > 0$$

then

$$F(t) \equiv \frac{(\dot{b}_1/2\dot{a}_0)}{(2b_1 + U_{10}/\dot{a}_0)} < 0.$$

Thus (A1) becomes

$$\dot{a}_2 = -(2b_1 + U_{10}/\dot{a}_0)[a_2 - F(t)].$$

To ensure $\dot{a}_2(t \rightarrow +\infty) = 0$ there must be $a_2(t \rightarrow +\infty) = F(\infty)$. When $a_2 > F$, $\dot{a}_2 > 0$; but when $a_2 < F$, $\dot{a}_2 < 0$, $a_2(t_0)$ must be carefully chosen in order to avoid divergence. It is clear that

$$F(t_0) \leq a_2(t_0) < 0$$

is appropriate. From the discussion above, we can get the behaviour of the ET at $t > t_0$.

From (15) combined with conditions (16), the coefficients can be determined as

$$C_1 = \frac{1}{2}e^{at_0} \left[\left(a_0^0 - \lambda_0 - \frac{\dot{a}_0^0}{a} \right) + \left(a_2^0 - \frac{\dot{a}_2^0 + 2a_2^0 b_1^0}{a} \right) h_0^2 \right]$$

$$C_2 = \frac{1}{2}e^{-at_0} \left[\left(a_0^0 - \lambda_0 + \frac{\dot{a}_0^0}{a} \right) + \left(a_2^0 + \frac{\dot{a}_2^0 + 2a_2^0 b_1^0}{a} \right) h_0^2 \right]$$

$$C_3 = (1/2b)(b - b_1^0)h_0 e^{bt_0}$$

$$C_4 = (1/2b)(b + b_1^0)h_0 e^{-bt_0}$$

where $h_0 = h(t_0)$; the superscript 0 indicates the quantity at $t = t_0$.

Near peak λ ,

$$U_0 = -\frac{1}{2}a^2(a_0 - \lambda_0)^2 \quad U_{02} = -b^2.$$

Thus

$$a_0^0 - \lambda_0 - \dot{a}_0^0/a = 0 \quad a_0^0 - \lambda_0 + \dot{a}_0^0/a = 2(a_0^0 - \lambda_0)$$

and

$$b_1 \leq -\sqrt{-2U_{01}} = -b$$

i.e. $(b_1^0)^2 \geq b^2$. From (14c),

$$\dot{a}_2 = -\frac{b_1^2 + U_{02}}{2\dot{a}_2} - \left(2b_1 + \frac{U_{02}}{\dot{a}_0}\right) a_2 = \frac{b^2 - b_1^2}{2a(a_0 - \lambda_0)} - (2b_1 - a)a_2.$$

Hence

$$\frac{\dot{a}_2 + 2a_2b_1}{a} = \frac{b^2 - b_1^2}{2a^2(a_0 - \lambda_0)} + a_2.$$

When $t = t_0$, the expression above $= 2p^0 + a_2 \geq a_2$ where

$$p^0 = \frac{b^2 - (b_1^0)^2}{4a^2(a_0^0 - \lambda_0)} \geq 0.$$

Thus the complete solution of equation (15) is obtained.

Appendix B

The free energy (11) can be rewritten as

$$\frac{\sigma}{k_B T} = -(e_1^2 + e_2^2) + \frac{1}{2}[\dot{m}_1^2(0) + \dot{m}_2^2(0)] + \int_0^{t_0} (\dot{m}_1^2 + \dot{m}_2^2) dt + \int_{t_0}^{\infty} (\dot{m}_1^2 + \dot{m}_2^2) dt. \quad (\text{B1})$$

Using (15) (neglecting the higher orders of h_0), we can get $\dot{m}_1^2 + \dot{m}_2^2$; the last term of (B1) is:

$$\int_{t_0}^{\infty} \dot{a}_0^2 dt + \int_{t_0}^{\infty} [2\dot{a}_0(\dot{a}_2 + 2a_2b_1) + b_1^2] h^2 dt + \dots$$

The first term can be written as

$$\int_{-\infty}^{+\infty} \dot{a}_0^2 dt - \int_{-\infty}^{t_0} \dot{a}_0^2 dt = S_0 - \frac{1}{2}a(a_0^0 - \lambda_0)^2$$

where S_0 is the contribution of the RT. Thus we get the free energy of partial wetting in the form

$$\begin{aligned} \sigma_1/k_B T = & S_0 - (e_1^2 + e_2^2) + \frac{1}{2}a(1+a)e^{2at_0}ph_0^4 - \frac{1}{2}a(1-a)(a_0^0 - \lambda_0)^2e^{-2at_0} \\ & + (1/8b)(1+b)(b-b_1^0)^2e^{2bt_0}h_0^2 - (1/8b)(1-b)(b+b_1^0)^2e^{-2bt_0} \\ & + (G - \frac{1}{2}ap^2 + \frac{1}{2}b_1^0)h_0^2 + O(h_0^2) \end{aligned}$$

where

$$G \equiv \frac{1}{h_0^2} \int_{h_0}^{\infty} [2\dot{a}_0(\dot{a}_2 + 2a_2b_1) + b_1^2] h^2 dt$$

is the PT's major contribution to the free energy.

The free energy of complete wetting comprises two parts: one is from a trajectory that starts at point R near peak λ and ends at λ as shown in figure 1, which can be denoted as $\sigma_2''/k_B T$; the other part is S_0 , the contribution of the RT. The first part can be calculated using

$$m_1 = \lambda_0 + C_1 e^{-at} \quad m_2 = C_2 e^{-bt}$$

where

$$C_1 = \frac{e_1 - \lambda_0}{1 + a} \quad C_2 = \frac{e_2}{1 + b}.$$

Inserting these into expressions (11) yields

$$\frac{\sigma_2''}{k_B T} = -(e_1^2 + e_2^2) + \frac{a(e_1 - \lambda_0)}{2(1 + a)} + \frac{be_2}{2(1 + b)}$$

so

$$\sigma_2/k_B T = \sigma_2''/k_B T + S_0.$$

Equating the free energies for the two wetting states immediately gives (20).

Appendix C

Equations (22) transform the potential expansion

$$U(m_1, m_2) = -\frac{1}{2}a^2(m_1 - \delta_1)^2 + sc^2(m_1 - \delta_1)(m_2 - \delta_2) - \frac{1}{2}b^2(m_2 - \delta_2)^2$$

into

$$\tilde{U}(g_1, g_2) = -\frac{1}{2}\alpha^2 g_1^2 - \frac{1}{2}\beta^2 g_2^2$$

where

$$a^2 = |U_{20}|_s = \left| \frac{\partial^2 U}{\partial m_1^2} \right|_s \quad b^2 = |U_{02}|_s = \left| \frac{\partial^2 U}{\partial m_2^2} \right|_s \quad c^2 = |U_{11}|_s = \left| \frac{\partial^2 U}{\partial m_1 \partial m_2} \right|_s$$

$$\alpha^2 = \frac{1}{2} \left[a^2 + b^2 + \sqrt{(a^2 - b^2)^2 + 4c^4} \right] \quad \beta^2 = \frac{1}{2} \left[a^2 + b^2 - \sqrt{(a^2 - b^2)^2 + 4c^4} \right]$$

and

$$\eta \equiv (\alpha^2 - a^2)/(\alpha^2 - \beta^2).$$

It can easily be proved that $\beta < \alpha < 1$. So the LT takes the form

$$g_1(t) = C_1 e^{\alpha t} + C_2 e^{-\alpha t} \quad g_2(t) = C_3 e^{\beta t} + C_4 e^{-\beta t}.$$

The joining conditions give the coefficients as

$$C_1 = \Gamma_1 e^{-\alpha t_0} \quad C_2 = \Gamma_2 e^{\alpha t_0} \quad C_3 = \Gamma_3 e^{-\beta t_0} \quad C_4 = \Gamma_4 e^{\beta t_0}$$

where

$$\Gamma_1 \equiv \frac{1}{2}(g_1^0 + \dot{g}_1^0/\alpha) = \frac{1}{2} \left[\sqrt{1 - \eta(m_1^0 - \delta_1 + \dot{m}_1^0/\alpha)} - s\sqrt{\eta(m_2^0 - \delta_2 + \dot{m}_2^0/\alpha)} \right]$$

$$\Gamma_2 \equiv \frac{1}{2}(g_1^0 - \dot{g}_1^0/\alpha) = \frac{1}{2} \left[\sqrt{1 - \eta(m_1^0 - \delta_1 - \dot{m}_1^0/\alpha)} - s\sqrt{\eta(m_2^0 - \delta_2 - \dot{m}_2^0/\alpha)} \right]$$

$$\Gamma_3 \equiv \frac{1}{2}(g_1^0 + \dot{g}_1^0/\beta) = \frac{1}{2} \left[s\sqrt{\eta(m_1^0 - \delta_1 + \dot{m}_1^0/\beta)} + \sqrt{1 - \eta(m_2^0 - \delta_2 + \dot{m}_2^0/\beta)} \right]$$

$$\Gamma_4 \equiv \frac{1}{2}(g_1^0 - \dot{g}_1^0/\beta) = \frac{1}{2} \left[s\sqrt{\eta(m_1^0 - \delta_1 - \dot{m}_1^0/\beta)} + \sqrt{1 - \eta(m_2^0 - \delta_2 - \dot{m}_2^0/\beta)} \right].$$

Here the superscript 0 still indicates values at the moment t_0 . Using (21), we get the expansion coefficients of Γ , such as

$$\Gamma_{10} = \frac{1}{2} \left[\sqrt{1 - \eta(a_0^0 - \delta_1 + \dot{a}_0^0/\alpha)} - s\sqrt{\eta(b_0^0 - \delta_2 + \dot{b}_0^0/\alpha)} \right]$$

$$\Gamma_{20} = \frac{1}{2} \left[\sqrt{1 - \eta(a_0^0 - \delta_1 - \dot{a}_0^0/\alpha)} - s\sqrt{\eta(b_0^0 - \delta_2 - \dot{b}_0^0/\alpha)} \right]$$

$$\Gamma_{11} = \frac{1}{2} \left\{ \sqrt{1 - \eta[a_0^0 + (\dot{a}_0^0 + a_1^0 b_1^0)/\alpha]} - s\sqrt{\eta(1 + b_0^0/\alpha)} \right\}$$

$$\Gamma_{21} = \frac{1}{2} \left\{ \sqrt{1 - \eta[a_0^0 - (\dot{a}_0^0 + a_1^0 b_1^0)/\alpha]} - s\sqrt{\eta(1 - b_0^0/\alpha)} \right\}.$$

The ET should coincide with the RT when $h_0 \rightarrow 0$, which requires

$$\Gamma_{20} = 0 \quad \Gamma_{40} = 0.$$

Putting $h_0 = 0$, we get the behaviour of the LT at $t < t_0$:

$$g_{10}(t) = \Gamma_{10} e^{\alpha(t-t_0)} \quad g_{20}(t) = \Gamma_{30} e^{\beta(t-t_0)}. \quad (\text{C1})$$

In the principal-axes coordinates (g_1, g_2) , the first integral (13) at $t = t_0$ gives

$$\alpha^2 \Gamma_1 \Gamma_2 + \beta^2 \Gamma_3 \Gamma_4 = 0 \quad (\text{C2})$$

which requires that $\Gamma_1 \Gamma_2$ has the opposite sign to $\Gamma_3 \Gamma_4$.

The free energy for partial wetting can be rewritten as

$$\frac{\sigma_1}{k_B T} = -(e_1^2 + e_2^2) + \frac{1}{2} [\dot{g}_1^2(0) + \dot{g}_2^2(0)] + \int_0^{t_0} (\dot{g}_1^2 + \dot{g}_2^2) dt + \int_{t_0}^{\infty} (\dot{m}_1^2 + \dot{m}_2^2) dt.$$

The last term can be written as

$$S_0 - S_1 + Jh_0 + O(h_0^2)$$

where

$$S_0 \equiv \int_{-\infty}^{+\infty} (\dot{a}_0^2 + \dot{b}_0^2) dt$$

is the contribution from the RT;

$$S_1 \equiv \int_{-\infty}^{t_0} (\dot{a}_0^2 + \dot{b}_0^2) dt = \int_{-\infty}^{t_0} (\dot{g}_{10}^2 + \dot{g}_{20}^2) dt$$

is the contribution of the LT; and

$$Jh_0 \equiv 2 \int_{t_0}^{\infty} [\dot{a}_0(\dot{a}_1 + a_1 b_1) + \dot{b}_0 b_1] h dt$$

is the major part of the ET's contribution to the free energy.

Using (C1) in S_1 , we have

$$\begin{aligned} \sigma_1/k_B T = S_0 - (e_1^2 + e_2^2) - \frac{1}{2}\alpha(1 - \alpha)\Gamma_1^2 e^{-2\alpha t_0} + \frac{1}{2}\alpha(1 + \alpha)\Gamma_2^2 e^{2\alpha t_0} \\ - \frac{1}{2}\beta(1 - \beta)\Gamma_3^2 e^{-2\beta t_0} + \frac{1}{2}\beta(1 + \beta)\Gamma_4^2 e^{2\beta t_0} \\ + \alpha\Gamma_{10}\Gamma_{11} + \beta\Gamma_{30}\Gamma_{31} + Jh_0 + O(h_0^2). \end{aligned}$$

The free energy for complete wetting can similarly be calculated, as in section 3:

$$\frac{\sigma_2}{k_B T} = S_0 - (e_1^2 + e_2^2) + \frac{\alpha H_1^2}{2(1 + \alpha)} + \frac{\beta H_2^2}{2(1 + \beta)}.$$

Equating σ_1 and σ_2 , we get the condition at the transition point

$$h'_0 = \frac{\alpha(1 - \alpha)}{J^*(1 + \alpha)} \Gamma_1^2 e^{-2\alpha t'_0} + \frac{\beta(1 - \beta)}{J^*(1 + \beta)} \Gamma_3^2 e^{-2\beta t'_0}. \tag{C3}$$

Here the superscript ' denotes quantities in the transition point and

$$J^* \equiv J + \alpha\Gamma_{10}(\Gamma_{11} - \Gamma_{21}) + \beta\Gamma_{30}(\Gamma_{31} - \Gamma_{41}).$$

Obviously (C3) requires that h'_0 and J^* have the same sign.

Inserting (C3) into (24) gives

$$\begin{aligned} H'_1 = \Gamma_{10}(1 - \alpha)[1 + (\alpha/J^*)\Gamma_{10}\Gamma_{21}]e^{-\alpha t'_0} \\ + [\beta(1 - \beta)/J^*(1 + \beta)]\Gamma_{21}\Gamma_{30}^2(1 + \alpha)e^{(\alpha - 2\beta)t'_0} \end{aligned}$$

$$\begin{aligned} H'_2 = \Gamma_{30}(1 - \beta)[1 + (\beta/J^*)\Gamma_{30}\Gamma_{41}]e^{-\beta t'_0} \\ + [\alpha(1 - \alpha)/J^*(1 + \alpha)]\Gamma_{41}\Gamma_{10}^2(1 + \beta)e^{(\beta - 2\alpha)t'_0}. \end{aligned}$$

For large t'_0 , we have $H'_1 \sim e^{(\alpha-2\beta)t'_0}$, $H'_2 \sim e^{-\beta t'_0}$. Cancelling t'_0 yields (26).

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