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Capillary condensation in binary Sullivan fluid mixtures confined between two parallel walls

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Abstract. The Sullivan model is adopted for the interaction parameters of fluid–fluid and wall–fluid potentials in binary mixtures. The capillary condensation in ‘two-coexisting-phases’ and ‘three-coexisting-phases’ open systems confined between two parallel walls is studied analytically by a dynamical approach. The result shows that not only a first-order but also a continuous transition is possible. The two systems studied in the present paper have no apparent difference in their wetting behaviours, and their phase diagram constructed in terms of the two components of the wall–fluid potential is a segment of an ellipse.

1. Introduction

A detailed study of the wetting transition in a one-component system with a single flat substrate has been given [1], including the analytical [2, 3] and numerical work [4]. For systems that are confined between two parallel walls, only a few treatments for open systems [5] and closed systems [6] exist. An analytical study of binary fluid mixtures in a limited space has not yet been performed, although there has been a numerical work on capillary condensation in binary fluids [7]. Thus a systematic treatment on such problems analytically is necessary.

The previous studies reveal that the substrate plays an essential role in determining the wetting behaviours of binary fluid mixtures [8], such as the order of the transition and the phase diagram of the wetting state. Naturally, we are convinced that an added substrate may provide more phenomena, especially in the limit of a small separation between the two walls. This consideration motivated us to carry out the investigation in the present paper.

Capillary condensation is a phenomenon that occurs when a fluid in a dilute state changes into a condensed state in a narrow slit [5]. In one-component systems, extensive studies have been dedicated to investigation of adsorption, desorption and capillary phenomena in a confined space with variables such as temperature, pressure, wall separation and chemical potential [9]. In our approach, all the thermodynamical quantities mentioned above are fixed (in equilibrium); only the wall–fluid force is allowed to vary. We wish to show how the wetting film develops and what the order of capillary condensation is in a simple and idealized model. The Sullivan [2] model is adopted for our binary fluid mixture confined between two parallel walls. It provides a possible way for us to deal with the problem

analytically, since all the interaction potentials (fluid–fluid and fluid–substrate) have an exponential form with the same range. After some algebra, we can transform the typical thermodynamical issue of the wetting transition into a dynamical version that describes the motion of a classical particle in a conservative potential, where the time corresponds to the thickness of wetting film, and a change in the trajectory refers to a transition of the wetting state. This approach has been successfully used in a series of previous studies [3, 6, 8, 10] on which the present paper is based.

For the wetting problem studied here, the corresponding dynamical potential may have two peaks γ and λ but not necessarily of the same height [11] (coexistence of two phases), or three peaks γ , δ and β (coexistence of three phases). The total time that the particle spends in its travel must be H , corresponding to the value of the distance between the two parallel walls. The particle cannot arrive at the right-hand summit of the peak as in the case $H = \infty$ [8]; instead it may stop at some lower point P near the peak which is defined by the total energy of the particle. The turning point should be determined by the time $t = H/2$ where its velocity is zero, because the initial and final conditions require that the route is symmetric back and forth; this means that only one phase intrudes into the slit in this case. When the fluid–wall potentials vary, exchange of two phases in the slit corresponds to capillary condensation and it may be first order or second order. However, another kind of trajectory is also possible when the particle starts to move near one peak and ends near the other peak, still keeping the duration H ; this means that the two walls are wetted by two different phases separately and the profile of the fluid is asymmetric about the two walls. Unfortunately, in this case, the trajectory expansion method developed in [8] fails because the reference trajectory (a route connecting the two peaks concerned) is not known as a prerequisite; so we cannot obtain an analytical result for this case; instead we have to study the problem with the help of numerical calculation. The result shows that this kind of trajectory corresponds to a state with a higher free energy than the PQ route; so it can be neglected in the study.

Our analytical approach is carried out by expanding the dynamical potential around the peak, which is correct only within a small range. This approximation restricts the validity of our analytical result and the derived separatrix in the phase diagram is effective only for a small segment of ellipse (see figures 3 and 4 later), which means that the two walls cannot be adsorbed too much in our model.

The present paper is organized as follows. Section 2 gives a dynamical description for the surface free energy of binary fluid mixtures confined between two parallel walls. Section 3 studies the capillary behaviours of the systems with the coexistence of two phases and with the coexistence of three phases. The last section gives some discussion on related problems.

2. Surface free energy for an n -component mixture

Suppose that an n -component fluid mixture with a chemical potential μ_i and a density ρ_i ($i = 1, 2, \dots, n$) is confined in a space with two parallel adsorbing walls located at $x = 0$ and $x = H$ and is homogeneous in the y, z directions. The system is in contact with a reservoir of fluid at temperature T and chemical potential μ_i . So the total number of particles in our system is not conserved (open system). The modern van der Waals theory [12] gives the lowest-order surface free energy in this system:

$$\sigma\{\{\rho_i(x)\}\} = \int_0^H dx \left[f_H(\{\rho_i(x)\}) - [\mu_i - \Phi_i(x) - \bar{\Phi}_i(x)]\rho_i(x) + p \right]$$

$$+ \frac{1}{2} \int_0^H \int_0^H dx dx' \rho_i(x) \chi_{ij}(x-x') \rho_j(x') \quad (1)$$

where a summation over 1 to n is implied for the repeated indices, H is the separation between the two parallel walls, x is the distance from the left-hand wall, f_H is the Helmholtz free energy density for the hard-core system, $\Phi_i(x)$ is the left-hand wall potential, $\bar{\Phi}_i(x)$ is the right-hand wall potential, p is the equilibrium pressure and χ_{ij} is the attractive intermolecular potential integrated over lateral dimensions. The equilibrium state is determined by $\delta\sigma/\delta\rho_i = 0$:

$$\mu_i = \mu_{Hi}(x) + \Phi_i(x) + \bar{\Phi}_i(x) + \int_0^H dx' \chi_{ij}(x-x') \rho_j(x') \quad (2)$$

where $\mu_{Hi} = \partial f_H / \partial \rho_i$. Dividing equation (1) by $k_B T$, using equation (2) and inserting $f_H = \mu_{Hi} \rho_i - p_H$, we have

$$\sigma / k_B T = I + J \quad (3)$$

where

$$I \equiv \frac{1}{k_B T} \int_0^H dx [p_H - p + \frac{1}{2}(\mu_i - \mu_{Hi})\rho_i] \quad J \equiv \frac{1}{2} \frac{1}{k_B T} \int_0^H dx (\Phi_i + \bar{\Phi}_i)\rho_i.$$

The Sullivan model in binary fluid mixtures behaves as

$$\begin{aligned} \Phi_i &= -\epsilon_i \exp(-x) & \bar{\Phi}_i &= -\epsilon_i \exp[-(H-x)] \\ \chi_{ij}(x-x') &= -\frac{1}{2} \alpha_{ij} \exp(-|x-x'|). \end{aligned}$$

Introducing the quantities

$$\begin{aligned} t = x & \quad \xi_i = \frac{\mu_{Hi}}{k_B T} & A_{ij} &= \frac{\alpha_{ij}}{k_B T} & M_i &= \frac{\mu_i}{k_B T} & r_H &= \frac{p_H}{k_B T} \\ r = \frac{p}{k_B T} & \quad E_i = \frac{\epsilon_i}{k_B T} & K_i(x) &= \frac{1}{k_B T} \int_0^H dx' \chi_{ij}(x-x') \rho_j(x') \end{aligned}$$

and matrices

$$\begin{aligned} \mathbf{E} &= (E_i)_{n \times 1} & \mathbf{K} &= (K_i)_{n \times 1} & \mathbf{A} &= (A_{ij})_{n \times n} & \mathbf{R}(x) &= (\rho_i(x))_{n \times 1} \\ \mathbf{P} &= -\frac{1}{2} \int_0^H dx' \exp(-x') \mathbf{R}(x') & \mathbf{Q} &= -\frac{1}{2} \int_0^H dx' \exp[-(H-x')] \mathbf{R}(x'). \end{aligned}$$

Here the subscripts $n \times 1$ and $n \times n$ represent matrices of n rows and one column and of n rows and n columns, respectively. The real symmetry matrix \mathbf{A} has a total number n of real eigenvalues A_i and there exists a real orthogonal matrix \mathbf{C} which diagonalizes \mathbf{A} like $\mathbf{C}\mathbf{A}\mathbf{C}^+ = \mathbf{A}^0$ with $\mathbf{A}^0 = (A_i \delta_{ij})_{n \times n}$. So the matrix $\mathbf{T} = \tau\mathbf{C}$ causes $\mathbf{T}\mathbf{A}\mathbf{T}^+ = \mathbf{I}^0$, where the matrix $\tau = (A_i^{-1/2} \delta_{ij})_{n \times n}$ and \mathbf{I}^0 is the unit matrix. It can easily be shown that $\mathbf{K}(0) = \mathbf{A}\mathbf{P}$, $\mathbf{K}(H) = \mathbf{A}\mathbf{Q}$; so

$$J = \mathbf{E}^+(\mathbf{P} + \mathbf{Q}) = \frac{1}{2} \mathbf{e}^+ [\mathbf{TK}(0) + \mathbf{TK}(H)]$$

where $\mathbf{e} = 2\mathbf{TE} = (e_i)_{n \times 1}$ is the wall potential matrix and \mathbf{e}^+ is its transposed matrix. From equation (2) we have

$$\mathbf{m}(x) - \frac{1}{2}\mathbf{e}\{\exp(-x) + \exp[-(H-x)]\} + \mathbf{TK}(x) = 0 \quad (4)$$

where $\mathbf{m}(x) = (m_i)_{n \times 1}$ is the coordinates matrix of the corresponding classical particle and

$$m_i = T_{ij}(\xi_j - M_j). \quad (5)$$

From the equivalence of equation (2) and the dynamical equation of the particle given by

$$\ddot{m}_i + \partial U / \partial m_i = 0 \quad (6)$$

we can easily derive that the conservation of energy is expressed by the first integral

$$\frac{1}{2}\dot{m}_i\dot{m}_i + U = C \quad (7)$$

where $U = r_H - r - \frac{1}{2}m_i m_i$ is the dynamical potential and C is the total energy of the particle [13]; so $\partial U / \partial m_i = \partial r_H / \partial m_i - m_i$.

Replacing $\mathbf{TK}(0)$, $\mathbf{TK}(H)$ in J by equation (4) yields

$$J = \frac{1}{2}\mathbf{e}^+[\mathbf{e}(1 + \exp(-H)) - \mathbf{m}(0) - \mathbf{m}(H)].$$

The transformed I takes the form

$$I = - \int_0^H dx \left(r_H - r - \frac{1}{2}(\xi_i - M_i) \frac{\partial r_H}{\partial \xi_i} \right)$$

where we have used the relation $\rho_i = \partial r_H / \partial \xi_i$. Equation (5) gives $\partial m_s / \partial \xi_i = T_{si}$; so $\rho_i = (\partial r_H / \partial m_s) T_{si}$. Thus $I = - \int_0^H [C - \frac{1}{2}\dot{m}_i\dot{m}_i + \frac{1}{2}\dot{m}_i\dot{m}_i] dx$. After some algebraic calculations, we obtain the matrix form as

$$I = \int_0^H (\dot{\mathbf{m}}^+ \dot{\mathbf{m}} - C) dx - \frac{1}{2}[\mathbf{m}^+(H)\dot{\mathbf{m}}(H) - \mathbf{m}^+(0)\dot{\mathbf{m}}(0)]$$

where H corresponds to the total time that the particle spends. Differentiating equation (2) with respect to $x (= t)$ and taking $t = 0$ and $t = H$, one obtains the initial and final conditions of the particle's motion:

$$\dot{\mathbf{m}}(0) = \mathbf{m}(0) - \mathbf{e} \quad \dot{\mathbf{m}}(H) = -\mathbf{m}(H) + \mathbf{e}. \quad (8)$$

Equation (3) becomes

$$\sigma / k_B T = \frac{1}{2}(\mathbf{e}^+ \mathbf{e}) \exp(-H) + S_0 - HC$$

where $S_0 = \sigma_0 / k_B T - \frac{1}{2}(\mathbf{e}^+ \mathbf{e})$ represents the area of an n -dimensional hypersurface in $(n+1)$ -dimensional space $(\sqrt{-v}, m_1, m_2, \dots, m_n)$ and

$$\frac{\sigma_0}{k_B T} = \int_0^H \dot{\mathbf{m}}^+(x)\dot{\mathbf{m}}(x) dx + \frac{1}{2}[\dot{\mathbf{m}}^+(0)\dot{\mathbf{m}}(0) + \dot{\mathbf{m}}^+(H)\dot{\mathbf{m}}(H)]. \quad (9)$$

It can easily be proved that $(\partial / \partial C)(\sigma_0 / k_B T) = H$; so the surface free energy (1) is separated into two independent contributions:

$$\sigma / k_B T = S_\infty + \Delta S \quad (10)$$

where S_∞ is the free energy when $H = \infty$ in S_0 ; it doubles the single-wall expression (2.17) in [10] because the two walls are identical and each contributes an equal amount to the free energy. The latter term

$$\Delta S = \int_H^\infty C dH + \frac{1}{2}(\mathbf{e}^+ \mathbf{e}) \exp(-H) \quad (11)$$

is the modification to the free energy when H is finite, which corresponds to a correlation effect of the two walls. For an infinite separation $H = \infty$, ΔS vanishes.

3. Capillary condensation

In the dynamical description [10], a classical particle moving in the potential U can be written in ideal lattice gas model as

$$U = \ln[1 + \exp(\xi_1) + \exp(\xi_2)] - r - \frac{1}{2}(m_1^2 + m_2^2) \tag{12}$$

where

$$\begin{aligned} \xi_1 &= \sqrt{\frac{1}{2}(A' + B')m_1} - \sqrt{\frac{1}{2}(A' - B')m_2 + M'} \\ \xi_2 &= \sqrt{\frac{1}{2}(A' + B')m_1} + \sqrt{\frac{1}{2}(A' - B')m_2 + M'} \end{aligned}$$

are two components of chemical potentials; here A' and B' are intermolecular potentials between the same kind and between different kinds, respectively, and M' is the chemical potential in equilibrium (chosen equal for the two components in our treatment for simplicity). The initial and final conditions (8) and the first integral (7) of equation (6) define the initial and final curves in the plane (m_1, m_2) ; they coincide with each other completely. We call them the *boundary line* L as shown in figure 1. The permitted motion of the particle starts at a point Q on the curve L , moves towards a peak of potential (12), stops at a certain position P and returns back along the same route so as to keep the total time H . Because of the symmetry of equation (6) with respect to the transformation $t \rightarrow H - t$, only half the route up to the time $H/2$ needs to be considered.

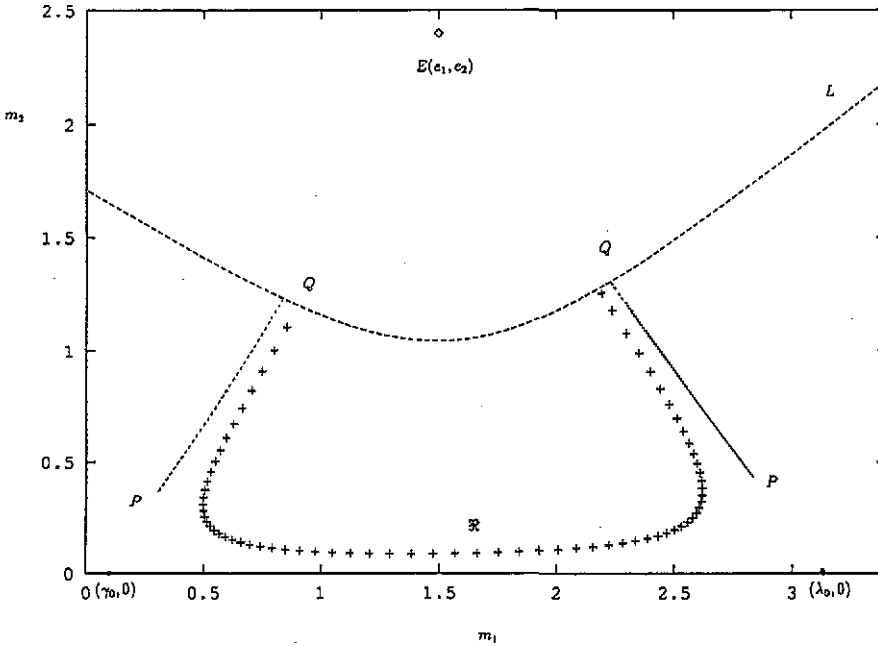


Figure 1. Example of the state in which the phases γ and λ coexist, where L is the boundary line, PQ and R are two kinds of possible trajectory of the particle and where the parameters are $A = 10$, $k = 0.95$, $m_1(0) = 0.839$ (left-hand PQ route), $m_1(0) = 2.233$ (right-hand PQ route), $m_1(0) = 2.179$ (R route) and $C = -0.1$.

3.1. State of two-coexisting-phases

The two-coexisting-phases state is described by two peaks λ and γ of the potential (12) with almost the same height [8]; they are located on axis m_1 as in figure 1. Phase γ has a higher density than phase λ but they have the same contents of the two constituents. If curve L passes near peaks λ and γ , analytical study is possible. Expand (12) near peak γ as

$$U = -\frac{1}{2}a^2(m_1 - \gamma_0)^2 - \frac{1}{2}b^2m_2^2 \quad (13)$$

where $a^2 = -\partial^2U/\partial m_1^2|_\gamma$, $b^2 = -\partial^2U/\partial m_2^2|_\gamma$; here a and b are the principal curvatures at peak γ with coordinates $(\gamma_0, 0)$. Then equation (6) can be solved as

$$m_1 = \gamma_0 + C_1 \exp(at) + C_2 \exp(-at) \quad m_2 = C_3 \exp(bt) + C_4 \exp(-bt) \quad (14)$$

where the coefficients C_1 , C_2 , C_3 and C_4 are related by the conditions $\dot{m}_1(H/2) = \dot{m}_2(H/2) = 0$, which yields $C_2 = C_1 \exp(aH)$, $C_4 = C_3 \exp(bH)$. Here we have taken the total energy of the particle C as negative; so the particle cannot reach the peak of potential (12); it may stop at the lower position P with $U = C$. From equations (7) and (13) we get the trace of point P as an ellipse centred at the peak γ , which is called the *stopping line*. This result is also true for peak λ . The initial condition (8) defines the coefficients in equation (14) as

$$C_1 = (e_1 - \gamma_0)/[(1 - a) + (1 + a) \exp(aH)] \quad C_3 = e_2/[(1 - b) + (1 + b) \exp(bH)].$$

Energy conservation of the particle, at $t = 0$, takes the form

$$C = \frac{1}{2}[\dot{m}_1^2(0) + \dot{m}_2^2(0)] - \frac{1}{2}a^2[m_1(0) - \gamma_0]^2 - \frac{1}{2}b^2m_2^2(0)$$

which defines a relation between the total energy C of the particle and the wall separation H ; so ΔS is obtained from equations (11) and (14):

$$\Delta S = \frac{1}{2}(e_1^2 + e_2^2) \exp(-H) + 2a(e_1 - \gamma_0)^2/(1 + a)[(1 - a) + (1 + a) \exp(aH)] \\ + (-2be_2^2)/(1 + b)[(1 - b) + (1 + b) \exp(bH)].$$

If $H = \infty$, the particle may move towards peak γ and stop at the top; so the solution (14) becomes

$$m_1 = \gamma_0 + C'_2 \exp(-at) \quad m_2 = C'_4 \exp(-bt). \quad (15)$$

The initial condition (8) defines $C'_2 = (e_1 - \gamma_0)/(1 + a)$, $C'_4 = e_2/(1 + b)$; the free energy S_∞ is

$$S_\infty = -\frac{1}{2}(e_1^2 + e_2^2) + a(e_1 - \gamma_0)^2/2(1 + a) + be_2^2/2(1 + b).$$

The total free energy (10) near peak γ is

$$\sigma_\gamma/k_B T = -\frac{1}{2}(e_1^2 + e_2^2)[1 - \exp(-H)] + \alpha_1(e_1 - \gamma_0)^2 + \alpha_2 e_2^2 \quad (16)$$

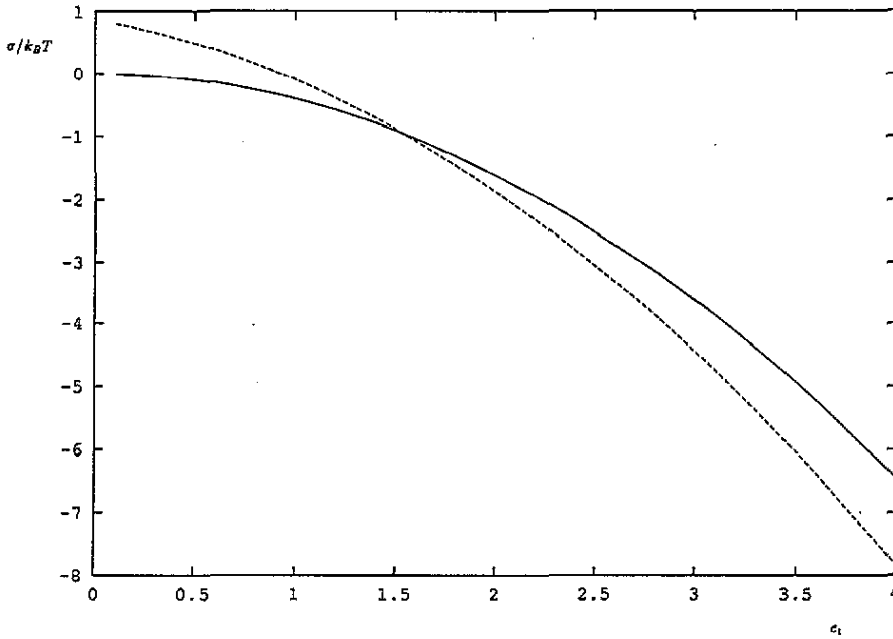


Figure 2. First-order transition in the plane of free energy versus e_1 when e_2 is given, where the parameters are $A = 10$, $k = 0.95$, $H = 4.5$ and $e_2 = 0.01$. The two lines correspond to the free energies of phases γ and λ , respectively.

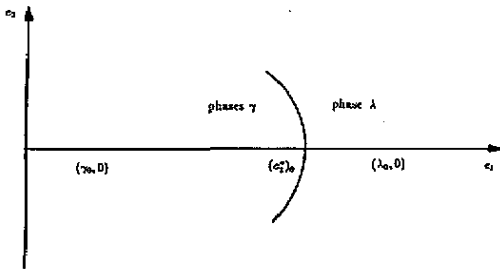


Figure 3. Sketch of the separatrix of the wetting state in the state in which two phases coexist.

where

$$\alpha_1 = [a/2(1+a)][1 - 4/(1-a) + (1+a)\exp(aH)]$$

$$\alpha_2 = [b/2(1+b)][1 - 4/(1-b) + (1+b)\exp(bH)].$$

The same procedure can give the free energy $\sigma_\lambda/k_B T$ near peak λ ; it takes quite the same form as equation (16) with the substitutions $(\alpha_1, \alpha_2) \rightarrow (\beta_1, \beta_2)$, $\gamma_0 \rightarrow \lambda_0$ and $(a, b) \rightarrow (a', b')$, the principal curvatures at the peak λ . Because a, b, a' and b' are all smaller than 1; so $\alpha_1, \alpha_2, \beta_1$ and β_2 are smaller than $\frac{1}{2}$.

If we keep e_2 unchanged, both $\sigma_\gamma/k_B T$ and $\sigma_\lambda/k_B T$ versus e_1 are parabolae in the plane of $(\sigma/k_B T, e_1)$. They intersect at the point $e_1 = e_1^*$ which is determined by

$$\alpha_1(e_1^* - \gamma_0)^2 + \alpha_2 e_2^2 = \beta_1(e_1^* - \lambda_0)^2 + \beta_2 e_2^2. \tag{17}$$

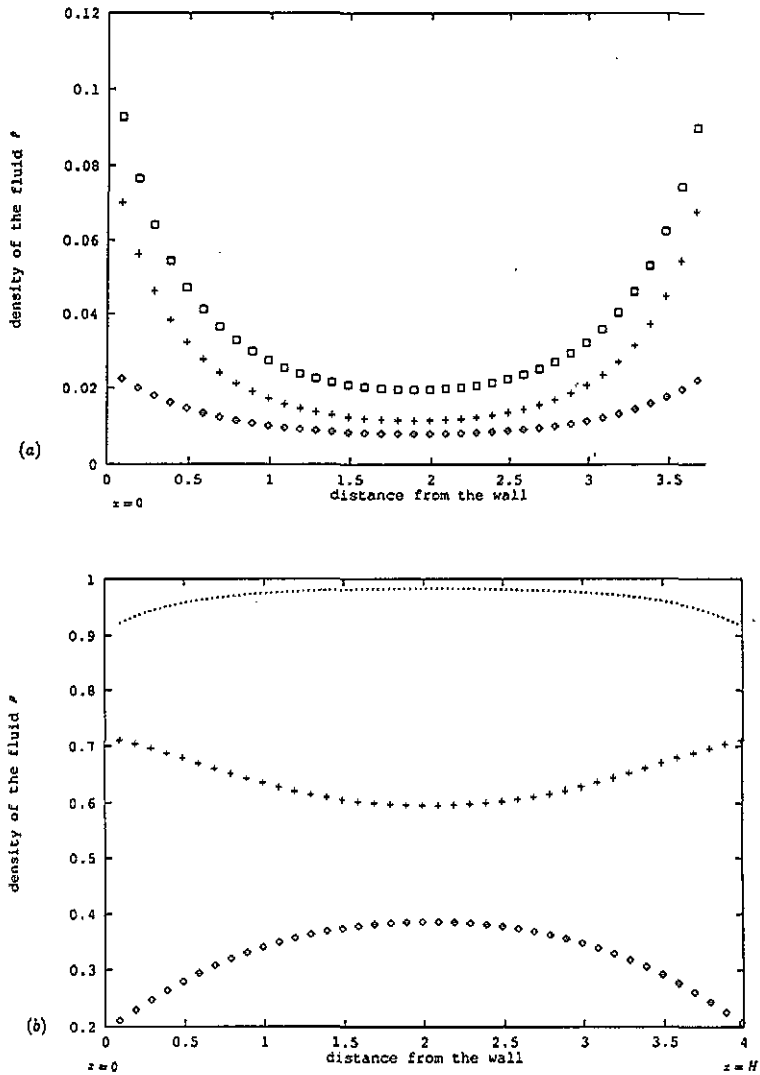


Figure 4. (a) Profile of the density for fluid molecules corresponding to the left-hand PQ route in figure 1, where the parameters are $A = 10$, $k = 0.95$ and $C = -0.1$: \square , profile of the total system; $+$, profile of component 1; \diamond , profile of component 2. (b) Profile of the density for fluid molecules corresponding to the right-hand PQ route in figure 1, where the parameters are $A = 10$, $k = 0.95$ and $C = -0.1$: \cdots , profile of the total system; $+$, profile of component 1; \diamond , profile of component 2. (c) (opposite) Profile of the density of fluid molecules corresponding to the route \mathfrak{R} in figure 1, where the parameters are $A = 10$, $k = 0.95$ and $C = -0.1$: \cdots , profile of the total system; $+$, profile of component 1; \diamond , profile of component 2.

The slopes at $e_1 = e_1^*$ are

$$(\partial\sigma_\gamma/\partial e_1)|_* = 2\alpha_1(e_1^* - \gamma_0) - e_1^*[1 - \exp(-H)]$$

$$(\partial\sigma_\lambda/\partial e_1)|_* = 2\beta_1(e_1^* - \lambda_0) - e_1^*[1 - \exp(-H)].$$

Thus if

$$\alpha_1(e_1^* - \gamma_0) \neq \beta_1(e_1^* - \lambda_0) \tag{18}$$

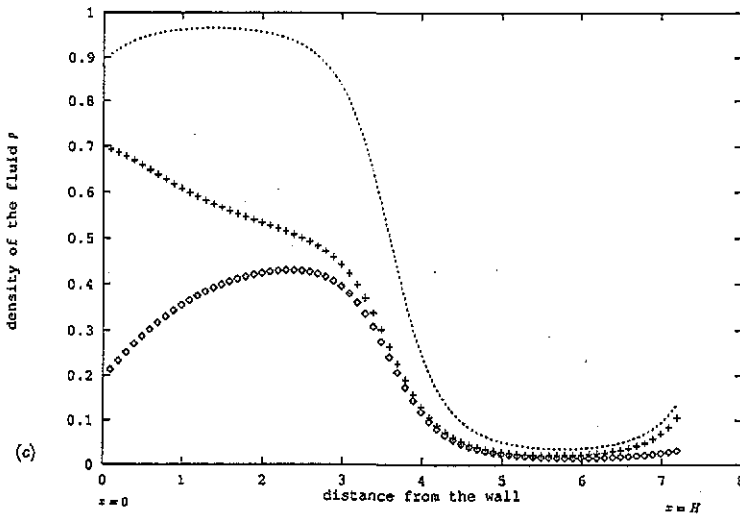


Figure 4. (Continued)

there will be first-order capillary condensation; if

$$\alpha_1(e_1^* - \gamma_0) = \beta_1(e_1^* - \lambda_0) \tag{19}$$

there may be continuous capillary condensation. The corresponding intersecting case of the two parabolae in the $(\sigma/k_B T, e_1)$ plane is shown in figure 2.

The phase separatrix of the wetting state is defined by (17) with the superscript asterisk in e_1^* removed; after some manipulations we have

$$(\alpha_1 - \beta_1)(e_1 + e_1^0)^2 + (\alpha_2 - \beta_2)e_2^2 - \alpha_1\beta_1(\lambda_0 - \gamma_0)^2/(\alpha_1 - \beta_1) = 0 \tag{20}$$

where $e_1^0 = (\beta_1\lambda_0 - \alpha_1\gamma_0)/(\alpha_1 - \beta_1)$. This is an ellipse with the centre $(-e_1^0, 0)$ on the e_1 axis. Owing to the approximate expansions of the potential near peaks γ and λ , the results above are valid only when e_1, e_2 vary within a small range so that the boundary line always passes near the stop line. The separatrix (20) is thus reduced to a small segment of ellipse as shown in figure 3. $(e_1^*)_0$ is determined by equation (20) with $e_2 = 0$, i.e. $(e_1^*)_0 = \gamma_0 + \sqrt{\beta_1}(\lambda_0 - \gamma_0)/(\sqrt{\alpha_1} + \sqrt{\beta_1})$. The region to the right of the separatrix corresponds to a profile of density such as figure 4(a); that to the left refers to a profile such as figure 4(b). For comparison we also give the profiles of trajectory \mathfrak{R} in figure 4(c); they are asymmetrically distributed about the two walls. When e_1 moves from left to right across the separatrix in figure 3, a transition from a gas-like fluid to a liquid-like fluid may occur in this two parallel-plate system; this can be of continuous or discontinuous nature depending on the intermolecular potential (represented by the coefficients $\alpha_1, \alpha_2, \beta_1$ and β_2) or on the separation H between the two walls.

3.2. State of three-coexisting phases

When the potential (12) has three peaks γ, δ and β with (nearly) the same height, we say that the fluid is in a three-coexisting-phases state. Peak γ is located on axis m_1 , whereas peaks δ and β are off axis m_1 but are distributed symmetrically about axis m_1 . Of the

three coexisting phases, γ has the lowest density and the other two constituents have equal contents; δ and β have a higher density but one constituent in phase δ equals the other constituent in phase β and vice versa. Figure 5 shows the position of the three peaks. If the boundary curve L passes near peaks γ and λ , we can adopt the same procedure as in section 3.1 to study the wetting behaviours, because the transformation

$$g_1 = \sqrt{1 - \eta}(m_1 - \delta_1) - \sqrt{\eta}(m_2 - \delta_2) \quad g_2 = \sqrt{\eta}(m_1 - \delta_1) + \sqrt{1 - \eta}(m_2 - \delta_2)$$

can change the coordinate plane (m_1, m_2) into the principal axes coordinates (g_1, g_2) of peak δ , where δ_1, δ_2 are the coordinates of peak δ and $\eta = (\alpha^2 - a^2)/(\alpha^2 - \beta^2)$ is a constant [8]; here

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

and

$$a^2 = (\partial^2 U / \partial m_1^2)|_\delta \quad b^2 = (\partial^2 U / \partial m_2^2)|_\delta \quad c^2 = (\partial^2 U / \partial m_1 \partial m_2)|_\delta.$$

Thus the results in section 3.1 can be used to discuss the wetting behaviours between phases γ and δ if we regard (g_1, g_2) as (m_1, m_2) . The separatrix of the wetting state is shown in figure 6. In this case, the wetting features seem to have no determinate relation to the symmetry of the potential, not like the situation in a single wall [8] where the position of the reference trajectory determines the two-coexisting-phases and three-coexisting-phases states behave quite differently.

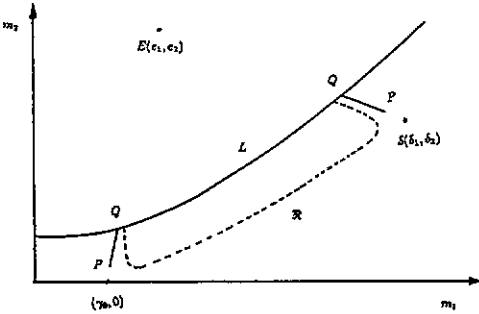


Figure 5. Sketch of the state in which three phases coexist, where L is the boundary line and PQ is a possible trajectory of the particle. Owing to the symmetry of the dynamical potential U about the m_1 axis, only the upper half of the plane is given.

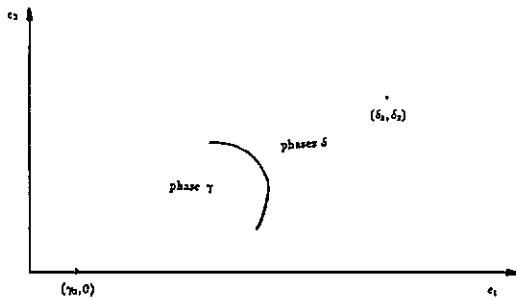


Figure 6. Sketch of the separatrix of the wetting state in the state in which three phases coexist.

The other two phases γ and β have quite the same behaviours as γ and δ because of the symmetry of the dynamical potential (12); moreover, the phases δ and β can also be discussed in the same way; we shall omit these repetitions here.

4. Discussion

Capillary condensation is not the sole phenomenon but a continuous transition is also possible in binary Sullivan fluid mixtures confined in two ideal adsorbing parallel substrates when the fluid-wall potential is varied. The total energy C versus wall separation H in our two-coexisting-phases system can be proved to be monotonic; thus no 'folding relation' like that in a one-component system [5] occurs and consequently no critical point exists. In our discussion, the temperature plays an equivalent role to the fluid-substrate potential; so a similar conclusion as above can also be derived when the temperature is varied; this has been much discussed in the literature. When H increases, one phase increases in thickness and we return to the case of two single-wall systems [8] and the free energy is doubled.

The present study is based on the assumption that the chemical potential M'_1 and M'_2 of the two components are equal, which gives a symmetric potential $U(m_1, m_2) = U(m_1, -m_2)$ [10]. For the general case where $M'_1 \neq M'_2$, the symmetry of U is violated and the analytical study becomes difficult, although we can still adopt the same measures as here. Detailed study goes beyond the scope of our present study.

When the wall-fluid interaction (only for one component) increases (e_1 moves from left to right in the $(\sigma/k_B T, e_1)$ plane), the left-hand PQ route corresponds to the lower free energy and phase γ intrudes into the slit. When e_1 crosses e_1^* , the right-hand PQ route has a favourable free energy, and phase γ appears in the slit. At e_1^* the transition may be first order or second order, depending on the intermolecular interaction or the distance between the two walls, since the coefficients α_1, β_1 in equations (18) and (19) contain two kinds of parameter, i.e. (A, k) and H ; they can lead to capillary condensation. When a continuous transition occurs, the two PQ trajectories do not coincide but their free-energy curves in figure 2(b) are tangents at e_1^* . Like the usual wetting transition where the transition point T_w will shift to T_w' if the substrate potential changes [1], the capillary condensation point e_1^* in our system will also move for different wall potentials e_2 (see figure 3) or for different separations of the slit (included through coefficients $\alpha_1, \alpha_2, \beta_1$ and β_2 ; see equation (17)).

When $H \rightarrow \infty$, one of the two phases γ and λ , e.g. phase γ , fills the bulk; capillary condensation then changes into the usual wetting transition (the film thickness of phase λ on the wall becomes infinite), which can be first order or second order depending on the curvatures of the principal axes [8].

Acknowledgments

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- [12] Hemmer P C and Lebowitz J L 1976 *Phase Transition and Critical Phenomena* vol 5B, ed C Domb and M S Green (London: Academic)
- [13] The total energy C is chosen to be negative so that the dynamical particle cannot bypass the peak in order to satisfy the boundary condition. This restriction is due to the model itself and not our approximation. In the semi-infinite space the total energy C is approaching zero which is ensured by the constant $r = p/k_B T$ in U