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The effect of surface fields on the phase transitions of a confined fluid

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Abstract. By means of a dynamics approach, the phase transition of a simple fluid confined by two different adsorbing walls is investigated using the van der Waals theory. For partial wetting situations, we recover the recent results for second-order phase transitions at the critical wall separation. In particular, we study the effect of surface fields on the phase behaviour and phase transitions of the fluid.

Recently considerable attention has been focused on the behaviour of fluids confined in narrow pores or capillaries [1]. Most theoretical studies have been concerned with the nature of phase equilibria of fluids (or magnets) between parallel plates (slits) that exert equal or opposing surface fields [2-15]. For the former system, the main features of the phase diagram are rather well understood [1, 3]. The best known example of a phase transition is that of capillary condensation: bulk two-phase coexistence is shifted from chemical potential $\mu = \mu_{\text{sat}}$ for wall separation $H = \infty$, to $\mu < \mu_{\text{sat}}$ for finite H . In particular, the bulk critical temperature $T_{c,b}$ is shifted to $T_{c,h}$, according to finite-size scaling, $T_{c,b} - T_{c,h} \simeq H^{-1/\nu}$, where ν is the correlation length critical exponent of bulk fluid. For opposing surface fields, however, the phase equilibria of the confined fluid can be very different from that for equal fields [8]. If the surface field ϵ_1 (or ϵ_2) is such that critical wetting (or drying) occurs at a single wall at a transition temperature T_w , then phase coexistence for finite wall separation H is restricted to temperature $T < T_{c,h} < T_w$ (so-called partial wetting situation). In the temperature range $T_{c,b} > T > T_w$ (the so-called complete wetting situation), there is no phase coexistence for finite wall separation, instead, there is a single soft mode. This phase has unusual properties, e.g., the existence of an exponentially large transverse correlation length $\xi_{\parallel} \sim e^H$ for systems with short-range forces in $d \geq 3$. The critical point shift $T_w - T_{c,h} \sim H^{-1/\beta_s}$, where β_s is the critical exponent that describes the growth of the wetting film at a single wall.

In this work, we intended to study the effects of competitive wall fields on the phase behaviour and on the order of the phase transition of a fluid in planar slits with different wall fields. In their recent paper, Parry and Evans [8] investigated, within the Landau framework, the phase behaviour of an Ising magnet between opposing plates. In a partial

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wetting situation ($T < T_{c,h} < T_w$ or $\epsilon_m - \varphi/2 < \epsilon_1, \epsilon_2 < \epsilon_m + \varphi/2$, see below), there exists a critical wall separation H_0 . For $H > H_0$ two distinct stable phases coexist while for $H \leq H_0$ there is a single phase. The transition at H_0 is the second-order transition. In their paper they were not concerned with how the phase transition is affected by the slight change of the surface fields. When the surface fields of the plates are changed very slightly from their opposing values, is the phase behaviour different from that of the system for opposing surface fields, and how is the phase transition affected by the change of the surface fields? To answer these questions, we consider a simple fluid confined by two different adsorbing walls. We present, within the van der Waals framework, analytic results concerning the phase equilibria. The result of the presence of the coexistence between two confined phases and the accompanying criticality in the partial wetting situation is recovered here in detail and the discussion is put in a rather different way from that in [8]. Our discussion is based on the dynamics approach, which has been proved extremely powerful in studying the order of the wetting transition [16–19]. In this approach, the wetting problem of a simple fluid can be transformed into a problem in classical dynamics.

In the zeroth-order van der Waals theory, the interfacial free energy functional $\gamma[\rho(x)]$ is of the form [20]

$$\gamma[\rho(x)] = \int_0^H [f_h(\rho(x)) + (\Phi(x) - \mu)\rho(x) + p] dx + \frac{1}{2} \int_0^H \int_0^H dx dx' \chi(|x-x'|)\rho(x)\rho(x') \quad (1)$$

where μ is the chemical potential, f_h is the Helmholtz free energy density of a uniform hard-sphere fluid, $\chi(|x|)$ is the attractive part of the fluid–fluid potential, $\Phi(x)$ is the total solid–fluid potential, H is the wall separation, and p is the equilibrium pressure in the fluid. The equilibrium density profile $\rho(x)$ now should be given by the condition $\gamma[\rho(x)] = \text{minimum}$, which leads to the equation

$$\mu = \mu_h[\rho(x)] + \Phi(x) + \int_0^\infty dx' \chi(|x-x'|)\rho(x') \quad (2)$$

where $\mu_h = \partial f_h / \partial \rho$ is the chemical potential of a hard-sphere fluid. We choose the following potentials [20]:

$$\chi(|x-x'|) = -(\alpha/2)e^{-|x-x'|} \quad \Phi(x) = -\epsilon_1 e^{-x} - \epsilon_2 e^{x-H} \quad (\epsilon_1 \neq \epsilon_2, 0 \leq x \leq H). \quad (3)$$

The positive parameters α and ϵ_1, ϵ_2 are measures of the strength of the attractive fluid–fluid and solid–fluid potentials, respectively. With the above choice of $\Phi(x)$ and $\chi(|x|)$, the integral equation (2) can be reduced to a second-order differential equation for $\mu_h(\rho(x))$:

$$d^2 \mu_h / dx^2 = \mu_h - \mu - \alpha \rho(x) \equiv -dV/d\mu_h \quad (4)$$

where

$$V(\mu_h) = -\frac{1}{2}(\mu_h - \mu)^2 + \alpha(p_h - p) \quad (5)$$

and $p_h = -f_h + \mu_h \rho$ is the pressure of a uniform hard-sphere gas. For concreteness we adopt the lattice-gas model for $p_h(\rho)$ and $\mu_h(\rho)$:

$$p_h(\rho) = -k_B T \ln(1 - \rho) \quad (6)$$

$$\mu_h(\rho) = k_B T \ln[\rho/(1 - \rho)] \quad (7)$$

where k_B is Boltzmann's constant. For subcritical temperature, $\alpha > \alpha_c \equiv 4k_B T$, and $V(\mu_h)$ has two 'hills', as shown in figure 1. The 'gas hill' located on left is denoted by $\mu_h = \varphi_g$, while the 'liquid hill' on the right by $\mu_h = \varphi_l$, and we have $V(\varphi_g) = 0$. Moreover, if $\mu = -\alpha/2 = \mu_{\text{sat}}$, the function $V(\mu_h)$ has two equal maxima at $\mu_h = \varphi_0$ and $-\varphi_0$ and a minimum at $\mu_h = 0$, where φ_0 is the positive root of the equation

$$\varphi_0 = (\alpha/2) \tanh(\varphi_0/2k_B T). \quad (8)$$

At this value of μ , bulk coexistence between gas and liquid occurs. Two boundary conditions attached to equation (4) are

$$-(d\mu_h/dx)|_{x=0} = \mu_h[\rho(0)] - \mu - 2\epsilon_1 \quad (9)$$

and

$$-(d\mu_h/dx)|_{x=H} = \mu_h[\rho(H)] - \mu - 2\epsilon_2. \quad (10)$$

Equation (4) can be seen as the equation of motion describing a classical particle moving in the conservative potential (5). Its first integral gives the conservation law of mechanical energy

$$\frac{1}{2}(d\mu_h/dx)^2 + V(\mu_h) = W \quad (11)$$

where W is the total energy, independent of x , whose value depends on μ , T and H . Solving for the 'velocity' $\dot{\mu}_h \equiv d\mu_h/dx$ we have

$$d\mu_h/dx = \pm[2(W - V)]^{1/2}. \quad (12)$$

The dynamical trajectories of equation (12) in the $\dot{\mu}_h - \mu_h$ diagram are called energy condition lines. When $\epsilon_1 = \epsilon_m \equiv -\mu/2 = \alpha/4$ or $\epsilon_2 = \epsilon_m$, the boundary condition line (9) or (10) passes through the origin of the $\dot{\mu}_h - \mu_h$ plane of figure 2. The wall separation H , or in the dynamical language, the time taken by a particle in going from the initial state i to the final state f is given by

$$H = \int_i^f \frac{d\mu_h}{\nu[2(W - V)]^{1/2}} \quad (13)$$

where $\nu = \pm 1$, depending on the direction of the 'velocity'. It can be proved, from equations (1), (2), (3), (9) and (10), and with the help of the technique employed by Sullivan [21], that the interfacial free energy is given by

$$\gamma = -WH/\alpha - (1/\alpha)(\epsilon_1^2 + \epsilon_2^2 - 2\epsilon_1\epsilon_2 e^{-H}) + S/\alpha \quad (14)$$

where

$$S = \frac{1}{2}[\mu_h(0) - \mu - 2\epsilon_1]^2 + \frac{1}{2}[\mu_h(H) - \mu - 2\epsilon_2]^2 + \int_{\mu_h(0)}^{\mu_h(H)} \nu[2(W - V)]^{1/2} d\mu_h \quad (15)$$

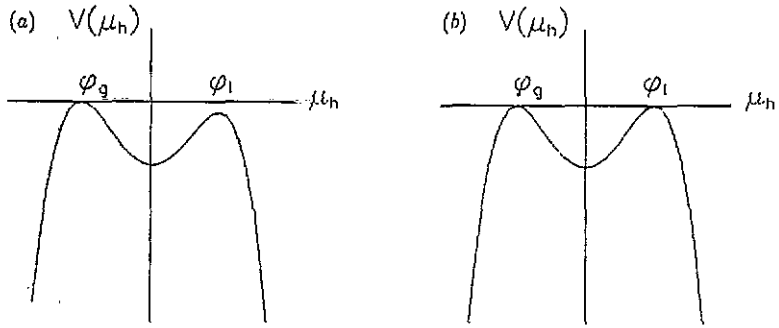


Figure 1. A qualitative feature of $V(\mu_h)$: (a) $\mu < -\alpha/2$, and (b) $\mu = -\alpha/2$. ($\varphi_1 = \varphi_0$, $\varphi_g = -\varphi_0$).

is the area, in the $\dot{\mu}_h-\mu_h$ diagrams of figure 2, enclosed by the energy condition line, the boundary condition lines, and the μ_h axis.

Several dynamical solutions of the equation of motion (4) consistent with the boundary conditions may exist. In such cases, the physically relevant solution is that which carries the smallest free energy. In the following, we will find these solutions and compare the corresponding free energies. In this way the order of the phase transition will be determined.

First, we specialize in the case where $\mu = -\alpha/2$. In this case there exist coexisting gas and liquid phases in the bulk. The full curves in figure 2(a) refer to the energy condition lines with different ‘energy’ W , while the full lines refer to the initial condition line l_0 and the final condition line respectively. For the single-wall situation, one could find that the crossover between the two different wetting situations is located at $\epsilon_1 = \epsilon_m + \varphi_0/2$. In fact, for $\epsilon_1 > \epsilon_m + \varphi_0/2$, the intersection between the initial condition line and μ_h axis is at $\mu_h > \varphi_0$, which corresponds to the complete wetting situation (corresponding temperature $T > T_w$). For $\epsilon_m - \varphi_0/2 < \epsilon_1 < \epsilon_m + \varphi_0/2$, the intersection is in the region $-\varphi_0 < \mu_h < \varphi_0$, which corresponds to the partial wetting situation ($T < T_w$). It is straightforward to prove that the transition from partial to complete wetting states is the critical wetting transition, which coincides with the result in the original Sullivan model of the wetting transition.

More specifically we consider the partial wetting situation in which the two walls exert opposing surface fields:

$$\epsilon_1 = \epsilon_m + \delta \quad \epsilon_2 = \epsilon_m - \delta \tag{16}$$

with $0 < \delta < \varphi_0/2$. We make use of an analytical method, rather than the graphical construction used by the authors of [8], to describe the phase behaviour as illustrated in figure 2 and figure 3, and the phase transitions between different wetting states. Now the boundary conditions (9) and (10) become

$$(d\mu_h/dx)|_{x=0} = \mu_h(0) - 2\delta \tag{17}$$

and

$$-(d\mu_h/dx)|_{x=H} = \mu_h(H) + 2\delta. \tag{18}$$

For a given potential $V(\mu_h)$ and δ , an energy condition line L and the initial condition line l_0 may have two intersections, or one point of tangency, or no intersections, as shown in figure 2. Substituting equation (17) into equation (11), we find

$$C = -2V(\xi) - (\xi - 2\delta)^2 \tag{19}$$

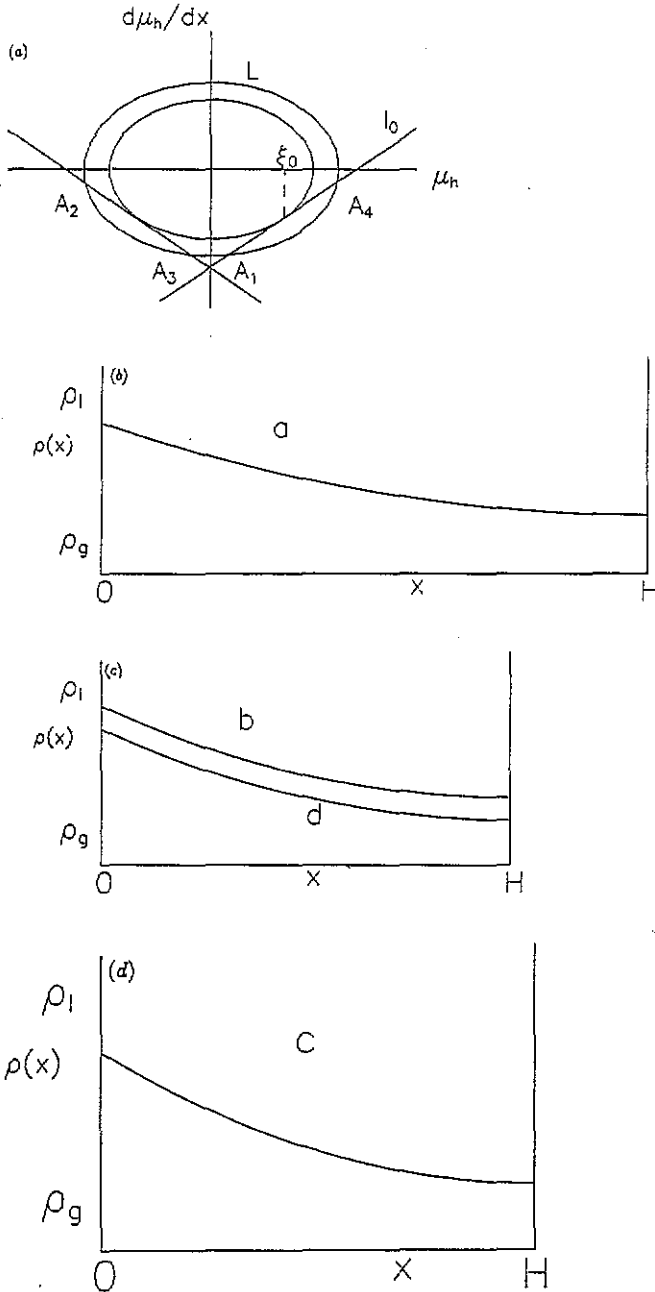


Figure 2. (a) The relations between energy condition lines L and initial condition line l_0 in the $\mu_h - \dot{\mu}_h$ plane for opposing surface fields. (b), (c) and (d) related schematic profiles corresponding to four different states. See the text for details.

where $C = -2W$, $\xi = \mu_h(0)$. With a fixed δ , the variation of C can alter the position of the energy condition line, so the locations of the intersections between the energy condition line and the initial condition line vary. As a result, the value of ξ will be changed. Therefore, ξ is the function of C , or, equivalently, C is the inverse function of ξ . When the energy

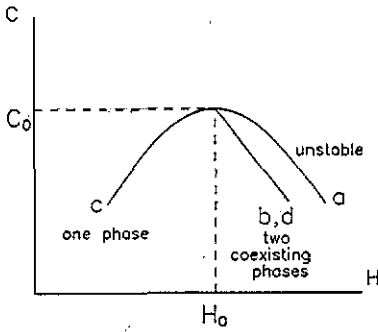


Figure 3. The dependence of C on H near $C = C_0$ for opposing surface fields. A second-order phase transition occurs at $H = H_0$.

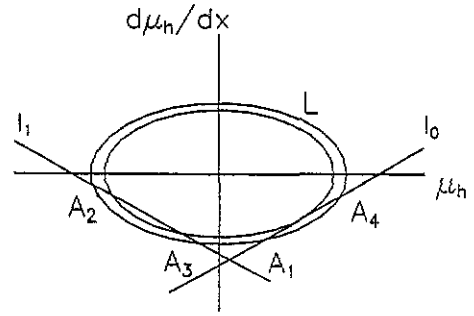


Figure 4. The relations between energy condition lines L and initial condition line l_0 , as well as the final condition line l_1 in the $\mu_h - \mu_h$ plane for $\Delta > 0$; see the text for details.

condition line is tangential to the initial condition line, C takes its maximum value, and the corresponding ξ is denoted by ξ_0 . From the condition $\partial C / \partial \xi = 0$ at $\xi = \xi_0$ it follows that

$$[dV(\xi)/d\xi]_{\xi_0} + (\xi_0 - 2\delta) = 0. \tag{20}$$

Expanding C about ξ_0 , we get

$$C = C_0 + C_2(\xi - \xi_0)^2 + C_3(\xi - \xi_0)^3 + \dots \tag{21}$$

where

$$C_2 = -[d^2V(\xi)/d\xi^2]_{\xi_0} - 1 \tag{22}$$

$$C_3 = -\frac{1}{3}[d^3V(\xi)/d\xi^3]_{\xi_0} \tag{23}$$

etc. For $\xi > 0$, we can obtain from equation (13) that

$$\frac{H}{2} = \int_0^\xi \frac{d\mu_h}{[-2V(\mu_h) - C(\xi)]^{1/2}} \tag{24}$$

which can also be expanded near ξ_0

$$H/2 = H_0/2 + h_1(\xi - \xi_0) + h_2(\xi - \xi_0)^2 + \dots \tag{25}$$

where

$$h_1 = [\partial(H/2)/\partial\xi]_{\xi_0} = 1/(2\delta - \xi_0) \tag{26}$$

$$h_2 = \frac{1}{2}[\partial^2(H/2)/\partial\xi^2]_{\xi_0} = 1/2(2\delta - \xi_0)^2 + C_2J \tag{27}$$

with

$$J = \int_0^{\xi_0} \frac{d\mu_h}{2[-2V(\mu_h) - C_0]^{3/2}}. \tag{28}$$

In the appendix, we will prove that

$$\alpha > 4\delta \quad 0 < \xi_0 < 2\delta \quad (29)$$

and

$$C_2 < 0 \quad C_3 > 0 \quad h_1 > 0 \quad h_2 > 0. \quad (30)$$

From equations (21) and (25) it follows that, for given $C < C_0$, there are two values of $H/2$ corresponding to two intersections A_4 and A_1 of the energy condition line L and the initial condition line l_0 , respectively. They are

$$H_+/2 = H_0/2 + (h_1/\sqrt{-C_2})\sqrt{r} + [h_1C_3/2C_2^2 + h_2/(-C_2)]r + \dots \quad (31)$$

and

$$H_-/2 = H_0/2 - (h_1/\sqrt{-C_2})\sqrt{r} + [h_1C_3/2C_2^2 + h_2/(-C_2)]r + \dots \quad (32)$$

with $r = C_0 - C$. From figure 2(a), we note that four solutions exist, all of which are monotonic, corresponding to four distinct states; their profiles are sketched in figure 2(b), (c) and (d). The solution with the smallest H , from A_1 to A_3 , refers to a single phase (denoted by state c), the corresponding wall separation being

$$H_c = 2(H_-/2) = H_0 - (2h_1/\sqrt{-C_2})\sqrt{r} + \dots \quad (33)$$

The second, from A_4 to A_2 , refers to the largest wall separation (denoted by state a), corresponding wall separation being

$$H_a = 2(H_+/2) = H_0 + (2h_1/\sqrt{-C_2})\sqrt{r} + \dots \quad (34)$$

The third and the fourth, from A_1 to A_2 and from A_4 to A_3 , have equal interfacial free energy and therefore constitute coexisting phases (denoted by states d and b), the corresponding wall separation being

$$H_d = H_b = H_+/2 + H_-/2 = H_0 + (h_1C_3/C_2^2 + 2h_2/(-C_2))r + \dots \quad (35)$$

From inequality (30), we find that the coefficients before \sqrt{r} in equation (34) and before r in equation (35) are positive therefore the dependence of C on H near C_0 is of the shape shown in figure 3. As $C \rightarrow C_0$, all four solutions become identical at the critical value H_0 , so the four states have the same interfacial free energy. For $H < H_0$, state c is the only possible state, while for $H > H_0$, we should compare the interfacial free energy of state a and b or d. To this end, differentiating equation (14) with respect to H , we obtain

$$\partial\gamma/\partial H = (1/2\alpha)(C - 4\epsilon_1\epsilon_2e^{-H}) \quad (36)$$

and hence

$$\partial^2\gamma/\partial H^2 = (1/2\alpha)(\partial C/\partial H + 4\epsilon_1\epsilon_2e^{-H}). \quad (37)$$

It is easily seen from equations (36) and (37) that $\partial\gamma/\partial H$ is continuous, but $\partial^2\gamma/\partial H^2$ is discontinuous at $H = H_0$; moreover, the value of $\partial^2\gamma/\partial H^2$ at $H = H_0 + 0$ in state a is

greater than that in state b or d, so the free energy in state a is greater than that in state b or d; consequently, state a is unstable. Thus, for $H > H_0$ two distinct stable phases with equal γ coexist while for $H \leq H_0$ there is a single phase. When H changes from $H < H_0$, passing through $H = H_0$, to $H > H_0$, a second-order phase transition from state c to state b or d takes place.

As demonstrated above, when the plates exert opposing surface fields, the second-order transition occurs at the critical wall separation H_0 . Now we change the surface fields of the plates very slightly from their opposing values, to see how the surface fields affect the order of the transition. To this end, we consider the following surface fields:

$$\epsilon_1 = \epsilon_m + \delta \quad \epsilon_2 = \epsilon_m - (\delta - \Delta) \quad (38)$$

where $\Delta > 0$ is an arbitrarily small constant. Now the initial condition (17) still holds, while the final condition (18) is of the form

$$-(d\mu_h/dx)|_{x=H} = \mu_h(H) + 2(\delta - \Delta). \quad (39)$$

For given potential $V(\mu_h)$, δ and Δ , the phase diagram in the $\dot{\mu}_h - \mu_h$ plane is of the shape shown in figure 4. The full curves in figure 4 refer to the energy condition curves with different value of C the outer corresponds to the smaller value of C . As C changes from large values to small values, the curve moves out. When the curve is tangential to the initial condition line l_0 , there exist two intersections between this energy condition line and final condition line l_1 (for $\Delta > 0$) as illustrated in figure 4. This value of C corresponds to C_0 . For $C > C_0$, there are no intersections between the energy condition curve and the initial condition line; on the other hand, for $C < C_0$, the energy condition curve has two intersections with each boundary condition line. Using a similar technique as applied above, we can obtain four solutions which are illustrated in figure 5 in the $H-C$ plane near $C = C_0$. Now the four distinct states are denoted by a' , b' , c' , d' respectively. Clearly, when $\Delta = 0$, figure 3 is recovered. Thus coexistence of two phases occurs for $H > H_0$ and appropriate criticality occurs at $H = H_0$. When $\Delta \neq 0$, the derivative $\partial C/\partial H$ for states c' and b' at $C = C_0$ is continuous; thus the value of $\partial^2 \gamma/\partial H^2$ is continuous. Hence, there is no phase transition as the state changes from c' to b' . On the other hand, the interfacial free energy of state b' is lower than that of d' and a' as H increases and the interfacial free energies of b' and d' go to the same value as $H \rightarrow \infty$, hence these two states are at coexistence for infinite wall separation. Consequently, the system with $\Delta \neq 0$ is devoid of phase transitions at finite wall separation.

The above discussion refers to the case of $\mu = -\alpha/2$. When $\mu \neq -\alpha/2$ the behaviour of the system is different. The occurrence of criticality corresponds to the case where two boundary condition lines are tangential to the energy condition curve. When the boundary condition line (17) is tangential to curve (11) we have that

$$\eta^2 = -C - 2V(\xi) \quad \eta = -\partial V(\xi)/\partial \mu_h \quad \eta = \xi - 2\delta \quad (40)$$

where (ξ, η) is the point of tangency, with $\xi = \mu_h(0)$ and $\eta = d\mu_h(0)/dx$. When μ increases from $-\alpha/2$ to $-\alpha/2 + d\mu$ both the energy condition line and the boundary condition line move a little. For fixed C we have from the first two equations in (40) that

$$dC = -2d\{V(\xi) + \frac{1}{2}[\partial V(\xi)/\partial \mu_h]^2\} = 0. \quad (41)$$

Noting from equation (4) that $\partial^2 V(\xi)/\partial \mu_h \partial \mu = 1$ we get that $\partial V(\xi)/\partial \mu = \xi + \phi$; here ϕ is a constant. So we have that

$$d\xi = -\{[\xi + \phi + \partial V(\xi)/\partial \mu_h]/\partial V(\xi)/\partial \mu_h(1 + \partial^2 V(\xi)/\partial \mu_h^2)\} d\mu. \quad (42)$$

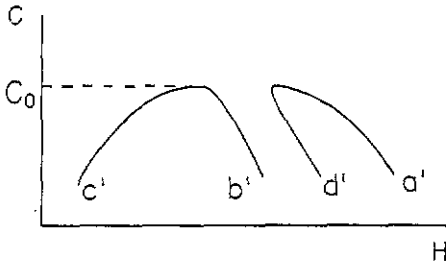


Figure 5. The dependence of C on H near $C = C_0$, with $\Delta > 0$.

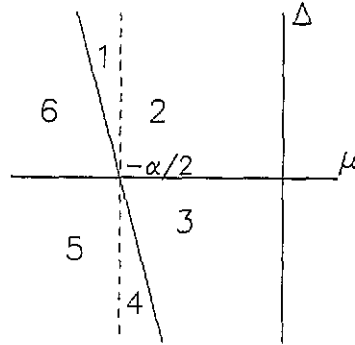


Figure 6. The six regions with different phase behaviours in the μ - Δ plane. Regions 2, 3, 5, 6 are devoid of phase transitions. Regions 2, 3 refer to the 'liquid' state, and 5, 6 to the 'gas' state. In regions 1 and 4 there exist first-order evaporation and condensation transitions respectively. These transitions terminate at the critical point on the full line.

Hence the corresponding increment of δ is

$$d\delta = -[(\xi + \phi)/2\partial V(\xi)/\partial \mu_h]d\mu. \tag{43}$$

Similarly, for the other boundary condition line (18) we can find that the increment of δ' is

$$d\delta' = [(\xi' + \phi)/2\partial V(\xi')/\partial \mu_h]d\mu \tag{44}$$

where $\xi' = -\xi$ and $\partial V(\xi')/\partial \mu_h = -\partial V(\xi)/\partial \mu_h$. Consequently the locus of criticality is expressed by

$$\Delta \partial V(\xi)/\partial \mu_h = -\xi(\mu + \alpha/2). \tag{45}$$

The phase behaviour in the μ - Δ plane is illustrated in figure 6, the full line represents the locus of criticality (45), while the broken line corresponds to the bulk first-order phase transition. The angle between the full and broken lines is approximately $\theta = \xi^{-1}\partial V(\xi)/\partial \mu_h$. The parameter space then divides into six regions (see also figure 7 in the μ - H planes). In region 1, where $\Delta > 0$, (see figure 7(a)), when the wall separation H increases, the state of the system first changes continuously from c' to b' (there is no phase transition). For $H \rightarrow \infty$ the value C of state b' is larger than that of state d' . From equation (14) we know that the interfacial free energy γ of the state d' is lower than that of b' , so there must be a transition point H_1 , at which the state undergoes a jump from b' to d' . For large H the state d' corresponds to 'gas' and b' to 'liquid'. The derivative of γ is discontinuous at H_1 . Consequently, the first-order evaporation transition occurs at $H = H_1$, as H changes from $H < H_1$ to $H > H_1$. The transition terminates at the critical point on the full line of figure 6. Coexistence occurs at a shifted bulk field $\mu - \mu_{\text{sat}} = \mu + \alpha/2 < 0$. Similarly, in region 4, where $\Delta < 0$, (see figure 7(c)), the system undergoes a first-order condensation transition from d' to b' as H increases. Coexistence occurs at $\mu - \mu_{\text{sat}} > 0$. Regions 2, 3, 5 and 6, however, are devoid of phase transitions. The regions 2 and 3 refer to the 'liquid' state while regions 5 and 6 refer to the 'gas' state. When $\mu = -\alpha/2$ and $\Delta = 0$, the coexistence

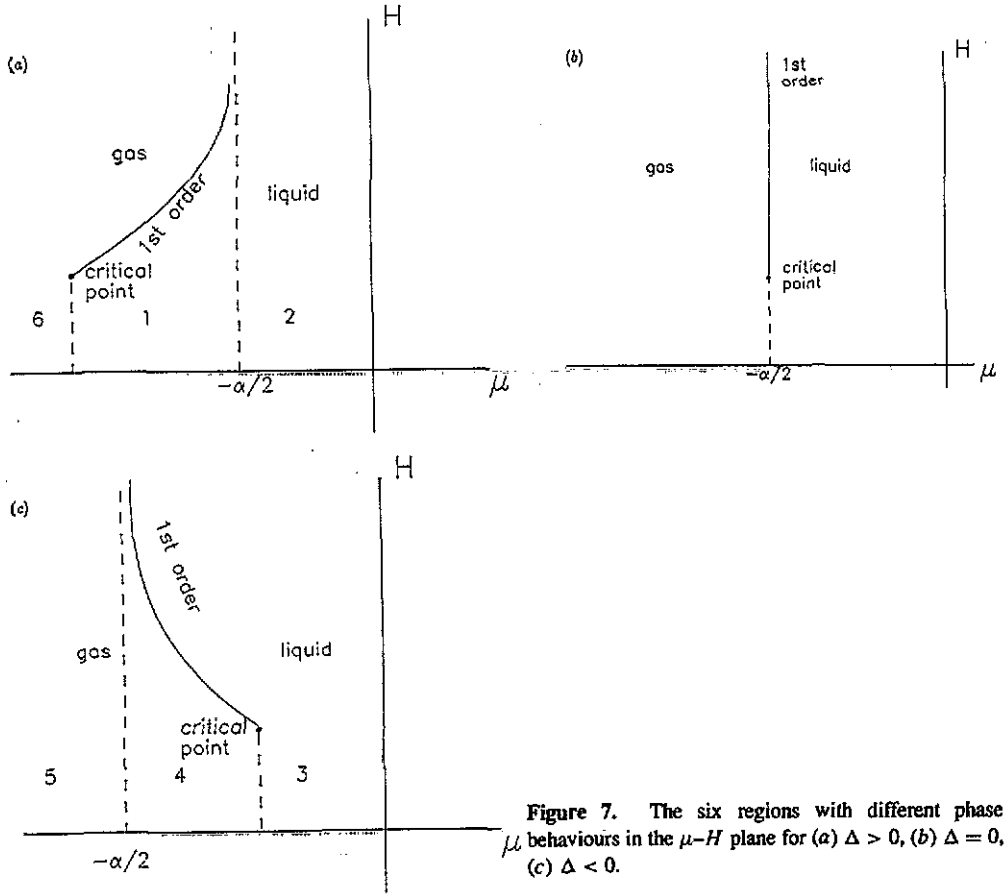


Figure 7. The six regions with different phase μ behaviours in the μ - H plane for (a) $\Delta > 0$, (b) $\Delta = 0$, (c) $\Delta < 0$.

occurs at bulk field $\mu - \mu_{\text{sat}} = 0$ and $H > H_0$, and the accompanying criticality occurs at $H = H_0$ (see figure 7(b)), which coincides with the result of [8].

The above results indicate that, when the surface fields of the plates change very slightly from their opposing values ($\Delta \neq 0$), the phase behaviour is different, and the location of the condensation or evaporation transition is delicately dependent on the parameter Δ , i.e. the change of the surface fields of the plates, and the shifted bulk first-order transition, might disappear in some parameter range.

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Appendix

In this appendix, we prove the two sets of inequalities (29) and (30), starting from condition

$$2\delta < \varphi_0. \tag{A1}$$

From equation (8), we have

$$\alpha = 2\varphi_0 / \tanh(\varphi_0/2k_B T). \tag{A2}$$

This is a monotonically increasing function of φ_0 . Considering equation (A1), we obtain

$$\alpha > 4\delta / \tanh(\delta/k_B T). \quad (\text{A3})$$

Since $\tanh \delta/k_B T < 1$, we have $\alpha > 4\delta$.

From (20) it follows that

$$\alpha \tanh(\xi_0/2k_B T) = 4\delta. \quad (\text{A4})$$

Comparing (A3) and (A4), we obtain

$$0 < \xi_0 < 2\delta. \quad (\text{A5})$$

This completes the proof of (29).

From (A4) we get

$$\xi_0 = k_B T \ln[(\alpha + 4\delta)/(\alpha - 4\delta)]. \quad (\text{A6})$$

Consequently

$$[d^2 V(\xi)/d\xi^2]_{\xi_0} = -1 + (1/2k_B T)(\alpha^2 - 16\delta^2)/2\alpha \quad (\text{A7})$$

$$[d^3 V(\xi)/d\xi^3]_{\xi_0} = -(\delta/(k_B T)^2)(\alpha^2 - 16\delta^2)/\alpha^2. \quad (\text{A8})$$

From (22), (23) and (A7), (A8) the first two inequalities of (30) can be easily obtained, while the third inequality can be derived from (26).

To prove the last inequality of (30), we first demonstrate

$$C_2 > -2\delta/\xi_0 \quad (\text{A9})$$

that is

$$(\alpha^2 - 16\delta^2)/4\alpha < 2\delta/\ln[(\alpha + 4\delta/\alpha - 4\delta)]. \quad (\text{A10})$$

To prove (A10), we consider the following function

$$f(t) \equiv \ln(t + 1) - t(t + 2)/2(t + 1). \quad (\text{A11})$$

Since $f(0) = 0$, moreover

$$df/dt = -t^2/2(1 + t)^2 < 0 \quad (\text{A12})$$

it follows that, for $t > 0$, $f(t) < 0$. We set

$$t = 8\delta/(\alpha - 4\delta) \quad (\text{A13})$$

which leads to (A10).

In addition, it is necessary to prove that

$$-2V(\mu_h) \geq 2\tilde{V}(\mu_h) \equiv C_0 + (2\delta/\xi_0 - 1)(2\delta\xi_0 - \mu_h^2) \quad (\text{A14})$$

for $0 \leq \mu_h \leq \xi_0$. In fact, if we define $F(\mu_h) \equiv -2V(\mu_h) + 2\tilde{V}(\mu_h)$, it is easy to test $F(\xi_0) = 0$; moreover, when $0 \leq \mu_h \leq \xi_0$

$$dF/d\mu_h = \mu_h\{4\delta/\xi_0 - \alpha/[\mu_h/\tanh(\mu_h/2k_B T)]\}.$$

Noting that (A2) is the monotonically increasing function of φ_0 , we have

$$dF/d\mu_h = \mu_h\{4\delta/\xi_0 - \alpha/[\xi_0/\tanh(\xi_0/2k_B T)]\} = 0$$

where (A4) is used. This completes the proof of (A14). Combining (A14) and (28), we obtain

$$J \leq \int_0^{\xi_0} \frac{d\mu_h}{2[-2\tilde{V}(\mu_h) - C_0]^{3/2}}. \quad (\text{A15})$$

Integrating the right-hand side of (A.15), we have

$$J \leq \xi_0/4\delta(2\delta - \xi_0)^2. \quad (\text{A16})$$

From (A.9) and (A.16), and inequalities $C_2 < 0$ and $J > 0$, it follows that

$$C_2 J \geq -1/2(2\delta - \xi_0)^2. \quad (\text{A17})$$

Applying this result to (27), we obtain the last inequality of (30).

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