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The Sullivan model for the wetting transition in a closed system

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Abstract. The wetting transition in a closed system is analytically discussed based on the Sullivan model. The wetting transition is first order for the finite system, while it becomes of second order for the infinite one. In addition, the temperature T_w of the wetting transition becomes lower as the separation of the two walls decreases.

1. Introduction

The wetting transition has received much attention recently [1]. A variety of models has been studied from different points of view. When the Sullivan model is taken, the problem of wetting phenomena is equivalent in the mathematical expression to the dynamics of a classical particle in a conservative potential [2]. An obvious advantage of this model and its generalization is that the analytical method could be used in the discussion [3]. This model was also used to discuss the wetting phenomena in fluid mixtures [4].

In the modern version of van der Waals theory for fluids the interaction between the molecules is split into two parts [5]. The strong short-range repulsion is expressed by a hard-core molecular reference system, while the weak attraction is treated as a perturbation. The thermodynamic potential Ω can then be written as

$$\Omega = \int d^3r [f_h(\rho, T) - (\mu - \Phi(\mathbf{r}))\rho(\mathbf{r})] + \frac{1}{2} \int d^3r \int d^3r' \chi'(|\mathbf{r} - \mathbf{r}'|)\rho(\mathbf{r})\rho(\mathbf{r}') \quad (1)$$

where μ , T , and $\rho(\mathbf{r})$ are the chemical potential, the temperature, and the local density of the fluid, respectively. $f_h(\rho, T)$ is the Helmholtz free energy of the hard-core system, $\Phi(\mathbf{r})$ corresponds to the attraction of the wall on the fluid, and $\chi'(|\mathbf{r} - \mathbf{r}'|)$ to the weak attractive force between the fluid molecules. Much attention has until now been focused on the wetting transition in an open system, where the chemical potential μ , the pressure p , and the temperature T of the fluid are all fixed. However, the wetting transition in closed systems has hardly been discussed. It is clear that the famous Moldover–Cahn experiment is carried out in a system where the total number N of particles is fixed [6]. Monte Carlo simulations are often made for given N and volume. In this paper we consider a theoretical model of the wetting transition in a closed system. The results are qualitatively in agreement with the molecular dynamics simulation [7].

To simplify the problem we consider a system with two parallel walls at $x = 0$ and $x = H$, respectively [8]. The system is assumed to be homogeneous in both y and z directions, so we have that the density of fluid per unit of area

$$\rho(x) = \rho(\mathbf{r})$$

and that

$$\Phi(x) = \Phi(r) \quad \chi(|x|) = \int \int dy dz \chi'(|r|).$$

The Helmholtz free energy per unit area is

$$F = \int_0^H dx [f_h(\rho, T) + \rho(x)\Phi(x)] + \frac{1}{2} \int_0^H dx \int_0^H dx' \chi(|x - x'|)\rho(x)\rho(x'). \quad (2)$$

For a system with given N , T , and H , which stands for the volume of the system, the equilibrium state is determined by minimalization of the Helmholtz free energy F with the constrained condition

$$N = \int_0^H dx \rho(x) \quad (3)$$

that is

$$\frac{\delta(F - \mu N)}{\delta\rho} = 0 \quad (4)$$

where μ stands for the undetermined coefficient. When the Sullivan model [2] is used, we have that

$$\Phi(x) = -\epsilon(e^{-x} + e^{x-H}) \quad (5)$$

and that

$$\chi(|x - x'|) = -\frac{\alpha}{2}e^{-|x-x'|}. \quad (6)$$

Here $\Phi(x)$ and $\chi(|x - x'|)$ have the same range of action, which is chosen to be the unit of length. Substituting equation (2) into equation (4) we obtain that

$$\mu_h(x) - \mu + \Phi(x) + \int_0^H dx' \chi(|x - x'|)\rho(x') = 0 \quad (7)$$

where $\mu_h = \partial f_h / \partial \rho$ is the chemical potential of the hard-core system. Since we have chosen the Sullivan model by equations (5) and (6), the non-linear integral equation (7) could be simplified as an ordinary differential equation

$$\frac{d^2\mu_h}{dx^2} = \mu_h - \mu - \alpha\rho \equiv -\frac{dV}{d\mu_h} \quad (8)$$

with

$$V(\mu_h) = -\frac{1}{2}(\mu_h - \mu)^2 + \alpha(p_h - p) \quad (9)$$

where $p_h = -f_h + \mu_h\rho$ is the pressure of the hard-core system, while p is the pressure of the fluid. According to equation (8) the wetting problem could be equivalent to the classical motion of a particle in the conservative potential V , where μ_h acts the role of 'coordinate' of the particle, while x the 'time'. We shall use the dynamical language in what follows.

In this paper we adopt the ideal lattice gas model for the hard-core system, because it gives for $\rho(\mu_h)$ the simplest possible representation

$$\rho(\mu_h) = \left[1 + \exp\left(-\frac{\mu_h}{k_B T}\right) \right]^{-1}. \quad (10)$$

When $\mu = -\alpha/2$ the potential is symmetric about the axis $\mu_h = 0$. For high temperature (above $T_c = \alpha/4k_B$) the potential $V(\mu_h)$ has only one maximum, and this situation corresponds to the low-density homogeneous phase of the fluid. For low temperature (below T_c), however, $V(\mu_h)$ has two maxima, and one minimum between them. With such a temperature the fluid is at two-phase coexistence. T_c is called the critical temperature. The maximum of $V(\mu_h)$ at $\mu_h = -\phi_0 < 0$ and $\mu_h = \phi_0 > 0$ are called the gas peak and liquid peak, respectively, where ϕ_0 is the positive root of the equation

$$\phi_0 = \frac{\alpha}{2} \tanh \frac{\phi_0}{2k_B T}.$$

When $\mu \neq -\alpha/2$, however, the potential $V(\mu_h)$ is not symmetric about the axis $\mu_h = 0$, and the heights of its two peaks might be different. Denoting the positions of the gas peak and liquid peak as ϕ_g and ϕ_l , respectively, we may calculate the gas density ρ_g and liquid density ρ_l through equation (10). The pressure of the gas phase is [5]

$$p = p_h(\rho_g) - \frac{1}{2}\alpha\rho_g^2. \quad (11)$$

We define a parameter $\lambda \geq 0$ such that

$$\lambda^2 = -\frac{d^2 V(\phi_l)}{d\mu_h^2}. \quad (12)$$

It could be proven that

$$\lambda^2 = 1 - \frac{2\phi_l}{e^{\phi_l} - e^{-\phi_l}} \leq 1.$$

This parameter is important in the analytical discussion. A more physical definition for this parameter is that

$$\lambda^2 = \frac{(\partial p / \partial \rho)_T}{(\partial p_h / \partial \rho)_T} \Big|_{\rho=\rho_l}.$$

Besides, $1/\lambda$ gives roughly the width of the liquid-gas interface.

The boundary conditions for solving the differential equation (8) could also be obtained from equation (7). These conditions are

$$\frac{d\mu_h(0)}{dx} = \mu_h(0) - \mu - 2\epsilon \quad (13)$$

and

$$\frac{d\mu_h(H)}{dx} = -\mu_h(H) + \mu + 2\epsilon. \quad (14)$$

We may obtain from equation (8) the 'mechanical energy' conservation

$$\frac{1}{2} \left(\frac{d\mu_h}{dx} \right)^2 + V(\mu_h) = C$$

where C is the total energy of the particle. From this conservation condition we have that

$$\frac{d\mu_h}{dx} = v\sqrt{2(C - V)} \quad (15)$$

where $v = \text{sign}(d\mu_h/dx)$. Hence the time that the particle must take to move from the initial state i to the final state f , i.e., the distance between the two parallel walls, is

$$H = \int_i^f \frac{d\mu_h}{v\sqrt{2(C - V)}} \quad (16)$$

Denoting by $n = N/H$ the average density of the fluid, we obtain from equations (3) and (15) that

$$nH = \int_i^f \frac{d\mu_h}{v\sqrt{2(C - V)}} \quad (17)$$

The most interesting range for the values of n in the investigation of the wetting transition is $\rho_g < n < \rho_l$. Otherwise, if $n < \rho_g$ (or $n > \rho_l$) the space between the two walls will obviously be occupied by gas (or liquid) phase, and no phase transition could take place. In fact, in order to make the wetting transition in the system possible, we should assume the value of n to be distinctly different from both ρ_g and ρ_l .

Now we have completely formulated the problem. For given α , T , ϵ , H , and n , we may (at least, in principle) obtain the chemical potential μ and the 'mechanical energy' C from equations (16) and (17), and then the pressure p and the free energy F . If more than one pair of values of μ and C were obtained from equations (16) and (17), the equilibrium state of the system would be that one with the smallest free energy F .

2. The Helmholtz free energy

Sullivan proved [2] that the free energy of an infinite open system is connected to an area in the $d\mu_h/dx - \mu_h$ space, which is that between the dynamical trajectory, the initial condition line, and the μ_h axis. In a similar way we can prove that the free energy (2) for the equilibrium state may be expressed by

$$F = \frac{1}{\alpha} [S - 2\epsilon^2(1 - e^{-H}) - CH] + \mu nH - pH \quad (18)$$

where

$$S = \frac{1}{2} [\mu_h(0) - \mu - 2\epsilon]^2 + \frac{1}{2} [\mu_h(H) - \mu - 2\epsilon]^2 + \int_i^f v\sqrt{2(C - V)} d\mu_h \quad (19)$$

which is the area in the $d\mu_h/dx - \mu_h$ space, confined by the two boundary condition lines and the trajectory of the particle. Denoting $\lim_{H \rightarrow \infty} S$ by S_0 , we may prove (see the appendix) that

$$S = S_0 + (C - \alpha nm + \alpha \Delta p)H + S_1 \quad (20)$$

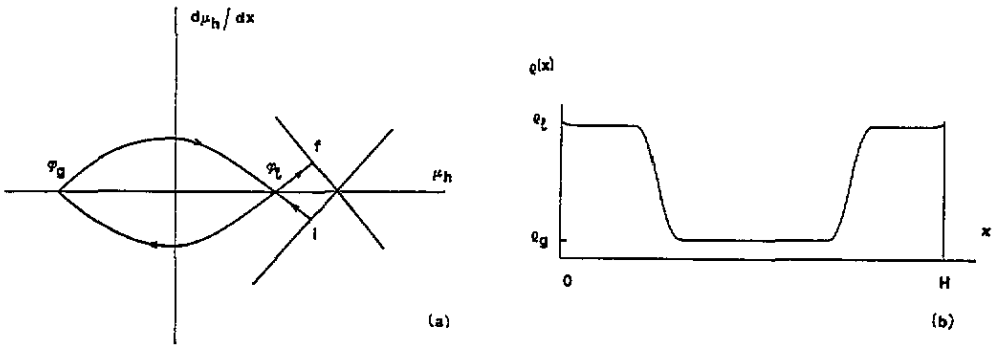


Figure 1. The completely wet state. The system is assumed to be infinite ($H \rightarrow \infty$). (a) The trajectory in the $d\mu_h/dx - \mu_h$ space. (b) The density profile of the fluid between two walls. This profile is symmetric about $H = \frac{1}{2}$.

where

$$S_1 = \int_H^\infty (C - \alpha n m + \alpha \Delta p) dH \tag{21}$$

$$m = \mu + \frac{\alpha}{2} \tag{22}$$

and

$$\Delta p = p - p_\infty. \tag{23}$$

Equation (18) could, by using equation (20), be rewritten as

$$F = F_0 + \frac{1}{\alpha}(S_0 + S_1) \tag{24}$$

where

$$F_0 = - \left(p_\infty + \frac{1}{2} \alpha n \right) H - \frac{2}{\alpha} \epsilon^2 (1 - e^{-H}). \tag{25}$$

For given values of α , T , H , n , and ϵ , the value of F_0 is determined, hence the minimum of F is specified by the minimum of $S_0 + S_1$.

3. The wetting transition in an infinite system

When $H \rightarrow \infty$, we have that $S_1 \rightarrow 0$, and the equilibrium state of the system is determined by minimization of S_0 . If there is only one wall in the system, it would be the same as the original Sullivan model. The state of the system could be completely wet, or partially wet, depending on whether the parameter ϵ is larger or smaller than the value of $\phi_0/2 + \alpha/4$. For the system we are considering the situations could be a little more complicated, because there are two walls. Since the two walls are exactly the same, i.e., the strengths ϵ of the wall potential are equal to each other, the two boundary condition lines must intersect at a point $\mu_h = \mu + 2\epsilon$ on the μ_h axis. The state of the system could be completely wet, or partially wet, or completely dry, depending on whether the parameter $\epsilon > \epsilon_1$, or $\epsilon_2 < \epsilon < \epsilon_1$, or $\epsilon < \epsilon_2$, where

$$\epsilon_1 = \frac{\phi_0}{2} + \frac{\alpha}{4} \quad \epsilon_2 = -\frac{\phi_0}{2} + \frac{\alpha}{4}. \tag{26}$$

When $\epsilon > \epsilon_1$, as shown in figure 1, the trajectory from the initial state *i* to the final state *f* must pass through the liquid peak, the gas peak, and the liquid peak again. That means that both walls are wet. We call the state completely wet.

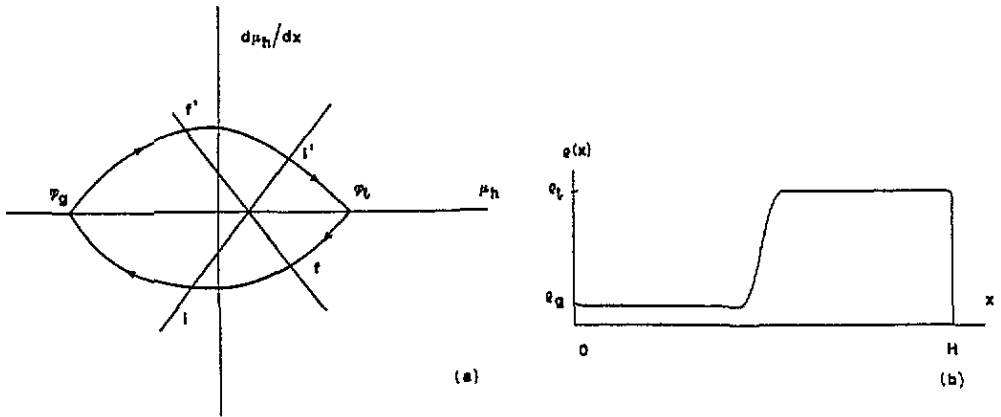


Figure 2. The incompletely wet state for the case $H \rightarrow \infty$. (a) The trajectory in the $d\mu_h/dx-\mu_h$ space. (b) The density profile of the fluid. This profile is antisymmetric around $H = \frac{1}{2}$ only when the two boundary lines in (a) happen to pass through the origin, i.e., $\epsilon/\alpha = \frac{1}{4}$.

When $\epsilon_2 < \epsilon < \epsilon_1$, as shown in figure 2, we find that there are four possible trajectories from the initial line (*i* or *i'*) to the final line (*f* or *f'*) with different free energy:

- (a) *i*-gas-liquid-*f*;
- (b) *i'*-liquid-gas-*f'*;
- (c) *i*-gas-liquid-gas-*f'*;
- (d) *i'*-liquid-gas-liquid-*f*.

It is obvious that state (a) is equivalent to (b) where the liquid wets one wall but not the other. We call this state incompletely wet (or incompletely dry). In state (c) the liquid wets neither of the two walls, which we call completely dry, while (d) corresponds to completely wet. The equilibrium state of the system should be that with the minimum free energy *F*. It is easy to find that the states (c) and (d) correspond to a larger S_0 , and so also to a larger *F*. Hence the equilibrium state is (a), or equivalently, (b). The system is the incompletely wetting one.

When $\epsilon < \epsilon_2$ the liquid wets neither of the two walls, i.e., it is the completely dry state, as shown in figure 3.

Summarizing the above discussion we obtain that

$$\text{the state is } \begin{cases} \text{completely wet} & \text{when } \epsilon > \epsilon_1 \\ \text{incompletely wet} & \text{when } \epsilon_2 < \epsilon < \epsilon_1 \\ \text{completely dry} & \text{when } \epsilon < \epsilon_2. \end{cases} \quad (27)$$

If one calculates carefully the free energy it will be found for $\epsilon \simeq \epsilon_1$ that

$$S_0(\epsilon) = S_0(\epsilon_1) + \frac{4\lambda}{1 + \lambda}(\epsilon - \epsilon_1)^2 \quad \text{for } \epsilon > \epsilon_1$$

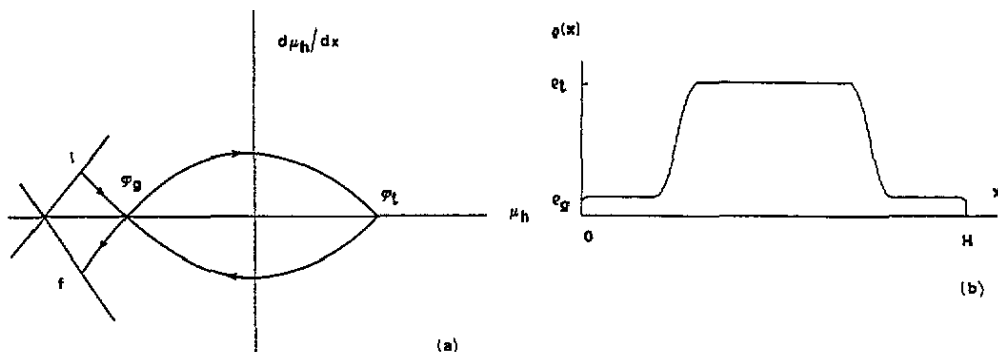


Figure 3. The completely dry state for $H \rightarrow \infty$. (a) The trajectory in the $d\mu_h/dx-\mu_h$ space. (b) The density profile of the fluid. This profile is symmetric about $H = \frac{1}{2}$.

and

$$S_0(\epsilon) = S_0(\epsilon_1) - \frac{4\lambda}{1-\lambda^2}(\epsilon - \epsilon_1)^2 \quad \text{for } \epsilon < \epsilon_1.$$

We may see that both S_0 and $dS_0/d\epsilon$ are continuous, but $d^2S_0/d\epsilon^2$ is not. Hence at $\epsilon = \epsilon_1$ (or for the same reason at $\epsilon = \epsilon_2$) both the free energy F and $\partial F/\partial\epsilon$ are continuous while $\partial^2 F/\partial\epsilon^2$ is discontinuous. That means that the phase transitions are of second order.

In the experiment it is easier to control the temperature than the strength of the wall potential, so it is interesting to see the dependence of the state on the temperature. Equation (26) is then rewritten as

$$\frac{\epsilon_1}{\alpha} = \frac{1}{2}\rho_l(T_w) \quad \frac{\epsilon_2}{\alpha} = \frac{1}{2}\rho_g(T_w) \tag{28}$$

which means that the phase transition takes place at

$$0 \leq \frac{\epsilon}{\alpha} \leq \frac{1}{2}. \tag{29}$$

The structure of the parameter space is sketched in figure 4. When the wall potential is repulsive ($\epsilon/\alpha < 0$) the system is always in the completely dry state. When the attractive strength of the wall potential is very strong so that $\epsilon/\alpha > \frac{1}{2}$, however, the state of the system is always completely wet. In both the above cases no phase transition takes place. In the investigation of the wetting transition the interesting case is the weakly attractive wall potential with parameter values in region (29).

4. The wetting transition in the finite system

When the separation of the two walls H is finite, we have to solve equations (16) and (17) for C and m . This can be done approximately.

When $m \simeq 0$ the values of ϕ_g , ϕ_l , and λ are of the order of m , and are shown to be irrelevant to the results. From $\partial p/\partial\mu = \rho$ we know that

$$\Delta p = \rho_g m + O(m^2) \tag{30}$$

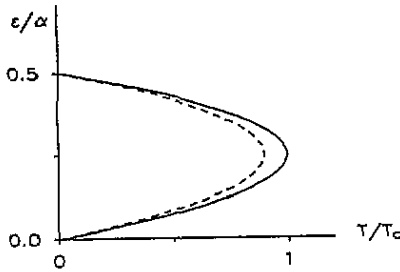


Figure 4. The structure of the parameter space. The solid line represents the case of $H \rightarrow \infty$ and the dashed line a finite H . These boundaries are symmetric between wetting and drying due to the special choice of equation (10).

so that equation (21) becomes

$$S_1 = \int_H^\infty [C - \alpha(n - \rho_g)m]dH. \tag{31}$$

Equation (11) gives that $V(\phi_g) = 0$, and then we have

$$V(\phi_1) = 2m\phi_0 + O(m^2). \tag{32}$$

In order to calculate the volume integral (16) we expand the mechanical potential V at ϕ_g

$$V(\mu_h) \simeq V_0 - \frac{\lambda^2}{2}(\mu_h - \phi_g)^2 \tag{33}$$

where $V_0 = V(\phi_g) = 0$. Assuming that the particle arrives at $\mu_h(a)$ when $x = a$ and at $\mu_h(b)$ when $x = b$, and that $\phi_g < \mu_h(b) < \mu_h(a)$ and $C = V(\mu_h(b)) < V_0$, we have

$$-2(C - V_0) = \lambda^2[\mu_h(b) - \phi_0]^2.$$

Hence the integral

$$I = \int_{\mu_h(a)}^{\mu_h(b)} \frac{d\mu_h}{\sqrt{2(C - V(\mu_h))}} \simeq \frac{1}{\lambda} \ln \frac{\sqrt{2(C - V_0) + \lambda^2 h^2} + \lambda h}{\sqrt{2|C - V_0|}} \tag{34}$$

where

$$h = \mu_h(a) - \phi_0. \tag{35}$$

Equation (34) is also correct for $C > V_0$ if we take $\mu_h(b) = \phi_g$. As we use equation (34) in the present work the parameters C and m are always of the order of h^2 or higher, so the equation could be written as

$$I \simeq \frac{1}{\lambda} \ln \frac{\sqrt{2}\lambda h}{\sqrt{|C - V_0|}}. \tag{36}$$

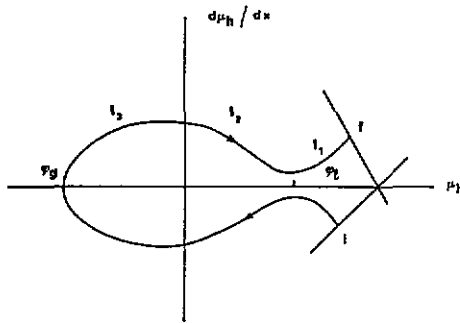


Figure 5. The calculation of the completely wet state for a finite H .

This result can also be used in the vicinity of the liquid peak.

As for the integral (17), the contribution comes mainly from the vicinities of the two peaks. Hence we assume that

$$\rho = \begin{cases} \rho_g & \text{when } \mu_h < 0 \\ \rho_l & \text{when } \mu_h > 0. \end{cases} \quad (37)$$

When $H < \infty$ the results obtained in the last section are changed. In the completely wet case, because of the symmetry of the trajectory, we may write the integrals (16) and (17) as (see figure 5)

$$2(I_1 + I_2 + I_3) = H \quad 2(I_1 + I_2)\rho_l + 2I_3\rho_g = nH$$

where I_1 , I_2 , and I_3 are expressed as

$$I_1 = \int_{\phi_0}^{\mu_h(0)} \frac{d\mu_h}{\sqrt{2(C-V)}} \simeq \frac{1}{\lambda} \ln \frac{\sqrt{2\lambda}h}{\sqrt{C-2m\phi_0}} \quad (38)$$

$$I_2 = \int_0^{\phi_0} \frac{d\mu_h}{\sqrt{2(C-V)}} \simeq \frac{1}{\lambda} \ln \frac{\sqrt{2\lambda}\phi_0}{\sqrt{C-2m\phi_0}} \quad (39)$$

and

$$I_3 = \int_{-\phi_0}^0 \frac{d\mu_h}{\sqrt{2(C-V)}} \simeq \frac{1}{\lambda} \ln \frac{\sqrt{2\lambda}\phi_0}{\sqrt{-C}} \quad (40)$$

with

$$h = \mu_h(0) - \phi_0. \quad (41)$$

It is easy to obtain

$$I_1 + I_2 = k_1 H \quad I_3 = k_2 H \quad (42)$$

where

$$k_1 = \frac{1}{2} \frac{n - \rho_g}{\rho_l - \rho_g} \quad k_2 = \frac{1}{2} \frac{\rho_l - n}{\rho_l - \rho_g} \quad k_1 + k_2 = \frac{1}{2}. \quad (43)$$

Since n is distinctly different from both ρ_g and ρ_l we know that both k_1 and k_2 are distinctly different from zero. Substituting equations (38), (39), and (40) into equation (42) we obtain that

$$C = 0 \quad m = -\lambda^2 h \delta_1. \quad (44)$$

In the calculations here and below we neglect the quantities of orders δ_1^2 , δ_2^2 , or $\delta_1 \delta_2$, where $\delta_i = \exp(-\lambda k_i H)$ for $i = 1, 2$. It could be confirmed that equation (44) is correct for $h < 0$ too. According to equation (33) we have that

$$C = V_0 - \frac{\lambda^2}{2} [\mu_h(0) - \phi_0]^2 + \frac{1}{2} \left[\frac{d\mu_h(0)}{dx} \right]^2.$$

Using the above equation and equation (13) we have

$$h = \frac{2}{1 + \lambda} (\epsilon - \epsilon_1). \quad (45)$$

Substituting equations (44) and (45) into equation (31) we obtain for the completely wet state that

$$S_1 = \frac{8\lambda}{1 + \lambda} \phi_0 (\epsilon - \epsilon_1) \delta_1. \quad (46)$$

In a similar way we can obtain that

$$S_1 = 0 \quad (47)$$

for the incompletely wet state and that

$$S_1 = -\frac{8\lambda}{1 + \lambda} \phi_0 (\epsilon - \epsilon_2) \delta_2 \quad (48)$$

for the completely dry state. These results show that the values of ϵ corresponding to the phase transitions are moved from ϵ_1 and ϵ_2 to

$$\epsilon'_1 = \epsilon_1 - 2(1 - \lambda)\phi_0\delta_1$$

and

$$\epsilon'_2 = \epsilon_2 + 2(1 - \lambda)\phi_0\delta_2$$

respectively. From figure 4 one can see that the transition temperature T_w becomes lower than that for $H \rightarrow \infty$.

Besides, we may see from equations (46), (47), and (48) that the phase transition is of first order instead of second order, since the derivative $dS_1/d\epsilon$ is discontinuous at ϵ'_1 or ϵ'_2 .

5. Conclusions

The wetting transition in the closed system is more complicated than that in the open one. At a certain temperature T below T_c , when the wall potential is very weak both walls are completely dry. As the strength of the wall potential increases the system transfers from the completely dry state to the incompletely wet one. For further increase of the strength the phase transition from the incompletely wet state to the completely wet one takes place. When the separation of the two walls is infinite the phase transition is of second order, while for the finite system it becomes of first order. In this aspect the results we obtain in the present paper are in agreement with those obtained via the molecular dynamics simulations of the cut and shifted Lennard-Jones fluid [7]. However, the simulation world is much more complex [7] and the Sullivan model should be seen as a special case.

If one varies the temperature for a given strength of the wall potential, however, the phase transition might not occur. For repulsive wall potential ($\epsilon/\alpha < 0$ for the Sullivan model), the state of the system would be governed by the walls, i.e., both walls are dry. For strongly attractive wall potential ($\epsilon/\alpha > \frac{1}{2}$ for the Sullivan model), the state of the system is also governed by the walls, i.e., the liquid wets both walls. In both cases there must be two gas-liquid interfaces between two walls, and no phase transition takes place at all. Only for a weakly attractive wall potential ($0 < \epsilon/\alpha < \frac{1}{2}$ for the Sullivan model) does the system undergo the phase transition at a certain temperature T_w below T_c . This temperature becomes lower when the separation H decreases.

We should also mention that the discussion in this paper is restricted to the case of large separation H of the walls. For very small H the approximation (46) is not correct. Besides, the results near the critical point might be changed considerably because fluctuation would play an important role. It should also be emphasized that we consider only the short-range model with plane geometry, so the capillary wave fluctuations are not accounted for properly. The real world possesses power-law dispersion forces which changes the universality class yet again.

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Appendix

When the values of μ , C , or p vary the area S varies also, and we may from equation (19) obtain that [8]

$$\left(\frac{\partial S}{\partial C}\right)_{\mu,p} = [\mu_h(0) - \mu - 2\epsilon] \frac{\partial \mu_h(0)}{\partial C} + [\mu_h(H) - \mu - 2\epsilon] \frac{\partial \mu_h(H)}{\partial C} - [\nu\sqrt{2(C-V)}]_i \frac{\partial \mu_h(0)}{\partial C} + [\nu\sqrt{2(C-V)}]_f \frac{\partial \mu_h(H)}{\partial C} + \int_i^f \frac{d\mu_h}{\nu\sqrt{2(C-V)}}. \quad (A1)$$

By using equations (13), (14), (15), and (16) we find that equation (A1) is simply

$$\left(\frac{\partial S}{\partial C}\right)_{\mu,p} = H.$$

We may obtain similarly that

$$\left(\frac{\partial S}{\partial \mu}\right)_{C,p} = -\alpha n H \quad \left(\frac{\partial S}{\partial p}\right)_{C,\mu} = \alpha H.$$

Hence we have

$$dS = HdC - \alpha n Hd\mu + \alpha Hd p. \quad (\text{A2})$$

When $H \rightarrow \infty$ the particle must stay at the gas peak or the liquid peak for an infinitely long time. That means

$$\mu = -\frac{\alpha}{2} \quad C = 0 \quad p = p_\infty \quad \text{when } H \rightarrow \infty \quad (\text{A3})$$

where p_∞ is determined by equation (11) for the gas phase, and has a similar expression for the liquid. Denoting $\lim_{H \rightarrow \infty} S$ by S_0 , using equations (A2) and (A3) we obtain that

$$S = S_0 + \left[C - \alpha n \left(\mu + \frac{\alpha}{2} \right) + \alpha (p - p_\infty) \right] H + \int_H^\infty \left[C - \alpha n \left(\mu + \frac{\alpha}{2} \right) + \alpha (p - p_\infty) \right] dH \quad (\text{A4})$$

which is the same as equation (20).

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