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Does the longer-range wall potential in generalized Sullivan models favour a first-order wetting transition?

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Abstract. The discussion based on the generalized Sullivan models for the wetting transition has until now argued that the longer-range wall potential tends to favour a first-order wetting transition. The present paper, however, proposes an analytically derived counter-example

Since Moldover and Cahn verified experimentally the existence of the wetting transition [1] in 1980 the theory on the wetting transition has been developed rapidly [2]. This kind of phase transition can be roughly described as follows. Consider a system of fluid which is located at the coexistence line of phases A and B (for instance, gas and liquid), coming into contact with a solid wall. Assuming that phase B fills the space far from the wall, and that the presence of the wall favours phase A, a phase-A film would form close to the wall. The state where the phase-A film has macroscopic thickness is called the completely wet state, while the state where phase-A film has only microscopic thickness is called the partially wet state. As the temperature increases along the A–B coexistence line up to a critical value T_w the state of the system can transform from a partially wet state to a completely wet state. This kind of phase transition is called the wetting transition. The wetting transition can be discussed using van der Waals theory. In the modern van der Waals theory [3] the interaction between molecules is split into two parts. The reference system is taken to be a hard-core system with a short-range repulsion, while the weak long-range attractive force is treated as a small perturbation.

Let us consider a system which consists of a simple fluid and a solid wall. For simplicity, we assume that the wall is represented by a plane located at $x = 0$, the fluid fills the half-space $x > 0$, and the system is uniform at the y and z direction. The Helmholtz surface free energy then reads

$$\sigma_s = \int_0^\infty \mathrm{d}x \{f_h(\rho_h(x)) - [\mu - \Phi(x)]\rho(x) + p\} + \frac{1}{2}\int_0^\infty \mathrm{d}x \int_0^\infty \mathrm{d}x' \chi(|x - x'|)\rho(x)\rho(x') \tag{1}$$

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where μ and p are the chemical potential and the pressure of the fluid, respectively, $\rho(x)$ is the density profile, $f_h(\rho(x))$ is the free-energy density of the hard-core system, and $\chi(|x-x'|)$ and $\Phi(x)$ are the intermolecular and wall potentials, respectively. The equilibrium state of the system would be decided by minimizing the free energy σ_s, i.e.,

$$\delta\sigma_s/\delta\rho(x) = 0$$

which gives the result that

$$\mu_h(\rho(x)) - \mu + \Phi(x) + \int_0^\infty dx'\,\chi(|x-x'|)\rho(x') = 0. \tag{2}$$

Here $\mu_h = (\partial f_h/\partial\rho)_T$ is the chemical potential of the hard-core system. Because of the non-linear dependence of the chemical potential on ρ, it is very difficult to solve the integral equation (2). To simplify this non-linear equation Sullivan chose [4,5]

$$\chi(|x|) = -\tfrac{1}{2}\alpha e^{-|x|} \tag{3}$$

and

$$\Phi(x) = -\epsilon e^{-x} \tag{4}$$

so that the integral equation (2) could be transformed into a second-order ordinary differential equation. The special choice of (3) and (4) defines the famous Sullivan model. The discussion based on this model shows that it displays only a second-order wetting transition. It is well known that the wetting transition in a real system could also be of first order. For this reason several generalizations of this model have been proposed.

For a simple fluid there are at least three ways to generalize the Sullivan model. The assumption (3) is maintained, while the expression (4) is modified in these three cases. Tarazona and Evans take [6]

$$\Phi(x) = -\epsilon e^{-\beta x} \tag{5}$$

to replace the assumption (4). They performed a numerical calculation on this model, followed by several analytical and numerical works by other authors [7–9]. The choice $\beta = 1$ led back to the Sullivan model itself. It is very clear that a smaller value of β leads to a longer-range of the wall force. Hauge and Schick proposed another expression [10]

$$\Phi(x) = -\epsilon e^{-x} - \epsilon_\beta e^{-\beta x} \qquad \beta \ll 1 \tag{6}$$

which means that a longer-range wall potential is attached to the Sullivan potential. Besides this, Piasecki and Hauge gave the third generalization [11,12]

$$\Phi(x) = -\epsilon e^{-x} - \epsilon_0\theta(x_0 - x). \tag{7}$$

With ϵ and ϵ_0 given, a larger value of x_0 correspods to a longer-range force. With $x_0 = 0$ the potential (7) comes back to the Sullivan model itself, hence the force range of the third generalization *cannot be shorter* than that of the Sullivan model. The wall potentials considered in this paper are all of exponential form, often called 'short-range potentials'. On the contrary, the term 'long-range potential' is often used for potentials with power-law tails, which will not be discussed here. Discussion on all these generalized Sullivan models led to a common conclusion:

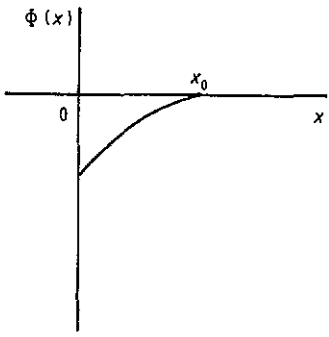

Figure 1. The wall potential for the model under consideration. A small value of γ implies a larger x_0, and so a longer-range force.

Proposition 1. A longer-range force favours a first-order wetting transition.

Is proposition 1 a conclusion of the starting point (1) or is it dependent on the special choice (5), (6), and (7)? The motivation of the present paper is to give a clear answer to this question.

Let us consider the following choice of wall potential (see figure 1):

$$\Phi(x) = \begin{cases} -\epsilon(\mathrm{e}^{-x} - \mathrm{e}^{-x_0}) & \text{if } x < x_0 \\ 0 & \text{if } x > x_0. \end{cases} \tag{8}$$

Denoting

$$\gamma = 1/x_0 \tag{9}$$

one has that a smaller value of γ corresponds to a larger x_0, which means a force of longer range. In contrast to the model (7), we have that the force range of (8) *cannot be longer* than that of the Sullivan model, since the longest case $x_0 \to \infty$ in (8) corresponds to the Sullivan model. According to proposition 1 we would only expect a second-order wetting transition for model (8). We will discuss this model with the purpose of re-examining proposition 1.

Substituting (3) into the integral equation (2), and differentiating with respect to x, one obtains the result that

$$\frac{\mathrm{d}\mu_\mathrm{h}}{\mathrm{d}x} + \frac{\mathrm{d}\Phi}{\mathrm{d}x} + \frac{\alpha}{2}\int_0^\infty \mathrm{d}x'\,\mathrm{e}^{-|x-x'|}\rho(x')[\theta(x-x') - \theta(x'-x)] = 0. \tag{10}$$

Differentiating the above equation once more with respect to x we have

$$\frac{\mathrm{d}^2\mu_\mathrm{h}}{\mathrm{d}x^2} = \mu_\mathrm{h} - \mu - \alpha\rho + \Phi - \frac{\mathrm{d}^2\Phi}{\mathrm{d}x^2}. \tag{11}$$

By using (8) we can rewrite the above equation as

$$\frac{\mathrm{d}^2\mu_\mathrm{h}}{\mathrm{d}x^2} = \begin{cases} \mu_\mathrm{h} - \mu - \alpha\rho + \epsilon\mathrm{e}^{-1/\gamma} & \text{if } x < 1/\gamma \\ \mu_\mathrm{h} - \mu - \alpha\rho & \text{if } x > 1/\gamma. \end{cases} \tag{12}$$

Noting that the integral terms in the left-hand sides of (2) and (10) are continuous functions of x, we have at both sides of the point $x = 1/\gamma$ the connective conditions

$$\mu_h(x = 1/\gamma + 0) = \mu_h(x = 1/\gamma - 0) \tag{13}$$

and

$$\frac{d\mu_h(x = 1/\gamma + 0)}{dx} - \frac{d\mu_h(x = 1/\gamma - 0)}{dx} = \epsilon e^{-1/\gamma}. \tag{14}$$

Two boundary conditions are necessary for determining the solution of the second-order differential equation (12). Assuming that a gas phase fills the space far away from the wall we have a boundary condition that

$$\rho(x \to \infty) = \rho_g \tag{15}$$

where ρ_g is the density of the gas phase. The other boundary condition, which is called the wall condition, could be obtained by putting $x = 0$ in (10) and using (2), that is

$$\frac{d\mu_h(x = 0)}{dx} = \mu_h(x = 0) - \mu - \epsilon(2 - e^{-1/\gamma}). \tag{16}$$

For simplicity we chose the ideal lattice-gas model for the hard-core system, i.e.

$$\rho(\mu_h) = \frac{1}{2}\left[1 + \tanh\left(\frac{\mu_h}{2k_BT}\right)\right]. \tag{17}$$

The above problem of wetting transition is equivalent to the motion of a classical particle in a conservative potential. In fact, putting

$$\xi = \mu_h/(k_BT) \qquad t = x \tag{18}$$

to express the coordinate and the corresponding time of the classical particle, respectively, and denoting

$$E = \epsilon/k_BT \qquad A = \alpha/k_BT \qquad M = (1/k_BT)(\mu + \alpha/2) \tag{19}$$

we can rewrite (12) as

$$\ddot{\xi} = \begin{cases} \xi - (A/2)\tanh(\xi/2) + Ee^{-1/\gamma} - M & \text{if } x < 1/\gamma \\ \xi - (A/2)\tanh(\xi/2) - M & \text{if } x > 1/\gamma. \end{cases} \tag{20}$$

The connective conditions (13) and (14) are then written as

$$\xi(1/\gamma + 0) = \xi(1/\gamma - 0) \tag{21}$$

and

$$\dot{\xi}(1/\gamma + 0) - \dot{\xi}(1/\gamma - 0) = Ee^{-1/\gamma} \tag{22}$$

while the wall condition is written as

$$\dot{\xi}(0) = \xi(0) - M + \tfrac{1}{2}A - E(2 - e^{-1/\gamma}). \tag{23}$$

The equation of motion (20) can also be written as

$$\ddot{\xi} = \begin{cases} -dV'/d\xi & \text{if } t < 1/\gamma \\ -dV/d\xi & \text{if } t > 1/\gamma \end{cases} \tag{24}$$

with the conservative potential

$$V'(\xi) = A\ln(e^{\xi/2} + e^{-\xi/2}) - \tfrac{1}{2}(\xi - M + Ee^{-1/\gamma})^2 + C' \qquad \text{if } t < 1/\gamma \tag{25}$$

and

$$V(\xi) = A\ln(e^{\xi/2} + e^{-\xi/2}) - \tfrac{1}{2}(\xi - M)^2 + C'' \qquad \text{if } t > 1/\gamma \tag{26}$$

Here C' and C'' are constants such that the maximum of the potentials V' and V is zero. In the present paper we restrict ourselves to the case of bulk two-phase coexistence with $M = 0$. When the temperature is below the bulk critical temperature T_c, we have $A > 4$, so the potential $V(\xi)$ has two maxima at $\xi = \pm\phi$, with $\phi > 0$ determined by

$$\phi = \tfrac{1}{2}A\tanh(\phi/2). \tag{27}$$

The fluid density profile in the wetting picture corresponds to a trajectory of the classical particle in the ξ–$\dot{\xi}$ phase space. The point $(\phi, 0)$ in phase space is called the liquid point, while the point $(-\phi, 0)$ is called the gas point.

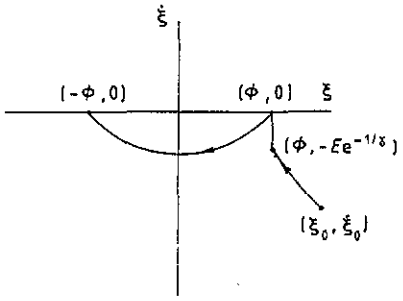

Figure 2. A certain trajectory in phase space. See text for details.

Let us consider a certain trajectory in phase space (see figure 2): starting with $(\xi_0, \dot{\xi}_0)$ at $t = 0$, getting to $(\phi, -Ee^{-1/\gamma})$ at $t = 1/\gamma - 0$, jumping to the liquid point $(\phi, 0)$ at $t = 1/\gamma + 0$ and staying there for an 'infinitely' long time, then going to the gas point $(-\phi, 0)$. It is clear that the total energy of this particle at $t = 1/\gamma - 0$ is

$$G = \tfrac{1}{2}E^2e^{-2/\gamma} + V'(\phi). \tag{28}$$

The starting point $(\xi_0, \dot{\xi}_0)$ is then determined by

$$\frac{1}{\gamma} = -\int_{\xi_0}^{\phi} \frac{d\xi}{\sqrt{2[G - V'(\xi)]}} \tag{29}$$

and

$$\dot{\xi}_0 = -\sqrt{2[G - V'(\xi_0)]}. \tag{30}$$

Let us now consider another trajectory close to the previous one. A variation of (24) gives that

$$\delta\ddot{\xi} = -\frac{d^2V'}{d\xi^2}\delta\xi \qquad \text{if } t < 1/\gamma. \tag{31}$$

We solve (31) formally by putting

$$\delta\xi(t) = \delta\xi(0)\exp\int_0^t \mathrm{d}t' K(t').$$

Then

$$K(t) = \delta\dot{\xi}/\delta\xi \tag{32}$$

From (31) and (32), one derives the equation of motion for $K(t)$

$$\dot{K}(t) = -\frac{\mathrm{d}^2V'}{\mathrm{d}\xi^2} - K^2(t) \tag{33}$$

with $V'(\xi)$ determined by (30). We denote

$$\lambda = \sqrt{-\frac{\mathrm{d}^2V(\phi)}{\mathrm{d}\xi^2}} = \sqrt{-\frac{\mathrm{d}^2V'(\phi)}{\mathrm{d}\xi^2}}.$$

which is the inverse of the bulk correlation length [2].

It is easy to prove from equations (25), (26) and (27) that

$$\lambda^2 = 1 - \frac{2\phi}{\mathrm{e}^{\phi} - \mathrm{e}^{-\phi}} \leqslant 1.$$

With a given $K(0)$, the value of $K(t)$ at $t = 1/\gamma - 0$ is determined by (33). We define K_0 such that with the initial value

$$K(0) = K_0 \tag{34}$$

the equation (33) gives exactly that

$$K(1/\gamma - 0) = \lambda \tag{35}$$

at $t = 1/\gamma - 0$. According to the criterion in [9] we have

Second-order wetting transition	if $0 < K_0 \leqslant 1$	
First-order wetting transition	if $K_0 < 0$ or $K_0 > 1$	(36)
Tricricality	if $K_0 = 1$.	

So far, we have in principle sketched the way to predict quantitatively the locus of tricriticality. However, it is not easy to solve the equation of motion (33) for given value of γ_0 analytically. Since the motivation of the present paper is to propose a counter-example to proposition 1, we can consider only the case when $x_0 \gg 1$, i.e. $\gamma \ll 1$. It is not difficult to see from equations (25) and (26) that the difference between V and V' must be very small when $\gamma \ll 1$, so $V'(\xi)$ must have a maximum at some position, say ϕ', close to ϕ. We expand $V(\xi)$ at $\xi = \phi$ as

$$V(\xi) = -\frac{1}{2}\lambda^2(\xi - \phi)^2 + \frac{1}{3!}V_3(\xi - \phi)^3 + \cdots \tag{37}$$

and $V'(\xi)$ at $\xi = \phi'$ as

$$V'(\xi) = V_0' - \frac{1}{2}\lambda'^2(\xi - \phi')^2 + \frac{1}{3!}V_3'(\xi - \phi')^3 + \cdots. \tag{38}$$

Denoting

$$c = c' - c'' - \tfrac{1}{2}E^2 e^{-2/\gamma} - Ee^{-1/\gamma}\phi'$$

we have from equations (25) and (26) that

$$V(\xi) = -c + Ee^{-1/\gamma}(\xi - \phi') + V'(\xi). \tag{39}$$

Treating $l = Ee^{-1/\gamma}$ as a small parameter, with the help of (37), (38) and (39) we obtain that

$$\begin{aligned} \phi' &= \phi - (1/\lambda^2)l + O(l^2) \\ \lambda' &= \lambda + [V_3/(2\lambda^3)]l + O(l^2) \\ V_3' &= V_3 + O(l). \end{aligned} \tag{40}$$

By using (24) and (28) the equation of motion for $t < 1/\gamma$ can be written as

$$\left(\frac{d^2}{dt^2} - \lambda'^2\right)(\xi - \phi') = -\frac{1}{2}V_3'(\xi - \phi')^2 + \cdots. \tag{41}$$

In the vicinity of $\xi = \phi'$ we may assume that the solution has the following form:

$$\xi(t) = \phi' + ae^{\lambda' t} + be^{-\lambda' t} + \xi_1(t) \tag{42}$$

with a small corrective term $\xi_1(t) = O(a^2, ab, b^2)$. Variation of (42) gives that

$$\begin{aligned} \delta\xi(t) &= e^{\lambda' t}\delta a + e^{-\lambda' t}\delta b \\ \delta\dot{\xi}(t) &= \lambda' e^{\lambda' t}\delta a - \lambda' e^{-\lambda' t}\delta b. \end{aligned} \tag{43}$$

Equation (32) can then be rewritten as

$$K(t) = \lambda' \frac{1 - \eta\exp[2\lambda'(1/\gamma - t)]}{1 + \eta\exp[2\lambda'(1/\gamma - t)]} \tag{44}$$

with $\eta = \exp(-2\lambda'/\gamma)\delta b/\delta a$. Hence we have that

$$K\left(\frac{1}{\gamma}\right) = \lambda' \frac{1 - \eta}{1 + \eta} \qquad K(0) = \lambda' \frac{1 - \eta\exp(2\lambda'/\gamma)}{1 + \eta\exp(2\lambda'/\gamma)}. \tag{45}$$

By using the above results (35) is reduced to

$$\lambda' \frac{1 - \eta}{1 + \eta} = \lambda$$

which, with the help of (40), gives that

$$\eta = \frac{V_3 E e^{-1/\gamma}}{4\lambda^4 + V_3 E e^{-1/\gamma}} \simeq \frac{V_3 E}{4\lambda^4} e^{-1/\gamma} \qquad \text{for } \gamma \ll 1. \tag{46}$$

With the given model of the ideal lattice gas, we obtain from (26) that $V_3 < 0$. In the case of attractive wall E must be positive, so that $\eta < 0$. Note that the absolute value of η is very small as long as $\gamma \ll 1$.

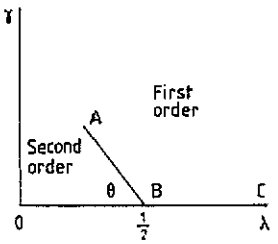

Figure 3. The structure of parameter space. The full line A–B–C is the locus of tricriticality.

Now we can determine the order of the wetting transition according to the criterion (36). The denominator of the fraction in the right-hand side of (44) is zero when

$$\exp(-2\lambda' t) = \frac{4\lambda^4}{-V_3 E}\exp[(1-2\lambda')/\gamma] \qquad \text{for } \gamma \ll 1. \tag{47}$$

For the case $\lambda' < \frac{1}{2}$ the above relation gives $t < 0$, hence $K(t)$ decreases continuously and monotonically in the interval $0 < t < 1/\gamma$. For the case $\lambda' > \frac{1}{2}$, however, as long as γ is sufficiently small, we can always find a value of t_0 in $(0, 1/\gamma)$, such that the denominator of $K(t)$ becomes zero at $t = t_0$, while $K(t) < 0$ for $t < t_0$. Paying attention to the fact that $\lambda = \lambda'$ as $\gamma \to 0$, we arrive at the conclusion that $\lambda > \frac{1}{2}$ always gives a first-order wetting transition as long as $\gamma \ll 0$. It is obvious that $\gamma = 0$ is the Sullivan model itself, and a second-order wetting transition takes place. Hence we know that a section $\frac{1}{2} < \lambda < 1$ of the straight line $\gamma = 0$ in the λ–γ parameter space is a part of the tricritical line.

The locus of the tricricality for $\lambda < \frac{1}{2}$ can be calculated by examination on the equation $K(0) = 1$. In this case (45) then gives that

$$\lambda' \frac{1-\exp(2\lambda'/\gamma)\eta}{1+\exp(2\lambda'/\gamma)\eta} = 1. \tag{48}$$

When $\lambda = \frac{1}{2}$ and $\gamma \to 0$ we have $\lambda' = \frac{1}{2}$, so for $\gamma \to 0$ the above equation gives that

$$\exp(2\lambda/\gamma)\eta = -\tfrac{1}{3}.$$

By using (46) we can write the above equation as

$$\frac{\gamma}{\lambda - 1/2} = \frac{2}{-\ln|12V_3E|} \tag{49}$$

When $\lambda \to \frac{1}{2}$ and $\gamma \to 0$ it is easy to obtain from (26) that

$$V_3 = -0.4415 \qquad \phi = 1.3512 \qquad A = 4.5909.$$

Since $\xi(0) = \phi$ and $\dot{\xi}(0) = 0$ the equation (23) gives

$$E = (\phi/2) + (A/4) = 1.8233$$

hence

$$\frac{\gamma}{\lambda - 1/2} \simeq -0.8818 \tag{50}$$

which predicts the direction of the tricritical line at $\lambda = \frac{1}{2}$ and $\gamma = 0$ in parameter space.

Figure 3 shows the structure of parameter space, where the angle $\theta = 41.4°$, and the line A–B–C is the tricritical line. More accurate calculation gives an additional term of order $l = Ee^{-1/\gamma}$ on the right-hand side of (50), which does not influence the angle θ. It is clear that a smaller value of γ, implying a longer range of the wall force, favours a second-order wetting transition instead of a first-order one. When the range of the wall force is *shorter* than that of the Sullivan model the system can still display a *first-order* wetting transition.

The model presented here shows that within the van der Waals framework, starting with the expression of the free energy (1), proposition 1 might not be true. This proposition is indeed correct with the three models (5), (6) and (7). The question as to what kind of wall force favours a first-order wetting transition is still open. In addition, when the fluctuations neglected in the van der Waals theory become important (for instance, the temperature close to the bulk critical temperature T_c, i.e. $\lambda \to 0$), the results may be changed significantly.

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References

[1] Moldover M R and Cahn J W 1980 *Science* **207** 1073
[2] Dietrich S 1988 *Phase Transitions and Critical Phenomena* vol 12 ed C Domb and J Lebowitz (London: Academic)
[3] Hemmer P C and Lebowitz J L 1976 *Phase Transitions and Critical Phenomena* vol 5B ed C Domb and M S Green (London: Academic)
[4] Sullivan D E 1982*Phys. Rev.* A **25** 1669
[5] Sullivan D E 1979 *Phys. Rev.* B **20** 3991
[6] Tarazona D and Evans R 1983 *Mol. Phys.* **48** 799
[7] Aukrust T and Hauge E H 1985 *Phys. Rev.* Lett **54** 1814
[8] Aukrust T and Hauge E H 1987 *Physica* A **143** 54
[9] Ding E J and Hauge E H 1987 *Physica* A **144** 427
[10] Hauge E H and Schick M 1983 *Phys. Rev.* B **27** 4288
[11] Piasecki J and Hauge E H 1987 *Physica* A **143** 87
[12] Aukrust T 1987 *DrIng Thesis* Institute for Theoretical Physics, NTH-Trondheim, Norway