Wetting Transition

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May 5, 1998

Abstract

In the presence of a wall a binary mixture may exibit a new phase transition, the wetting transition. We start with the analysis of dew (a liquid drop on a surface), discuss the mean field theory describing its equilibrium, observe phase transitions of the first and second order, mention impurities and long-ranged van der Waals forces, note the physical equivalence of dew to magnetic domain, report that we live in the upper critical dimension, and consider an unusual critical exponent, continuously depending on the dew's parameters.

1 The wetting transition

(Here we follow closely a review of P.G. de Gennes [1])

A liquid/vapor interface L/V, in the vicinity of a solid S may exibit either a finite equilibrium contact angle θ_e (partial wetting) or a strictly vanishing contact angle (complete wetting). There may exist a particular temperature T_w at which we switch from one regime to the other. This is called the wetting transition temperature.

Unfortunately, the L/V/S systems are usually not convenient for studies of this wetting transition. To change significantly the interfacial energies γ_{ij}, we would have to scan a rather broad temperature range. To maintain the L/V equilibrium then requires that one work at high pressures. Because of these practical difficulties, all current studies on T_w have been carried out with the other three-phase equilibria, where temperature variations are feasible and have more spectacular effects on the interfacial energies. The two main examples are solid/liquid A/liquid B, free surface/liquid A/liquid B, where A and B are two coexisting phases of a binary mixture with a certain critical consolute temperature T_c. It turns out, that in such case, the interfacial energy vary considerably when we consider the broad vicinity of T_c (typically a 30° interval). This makes experimentation much simpler.

Two typical examples of the wetting transition have been observed by Pohl and Goldburg (1982) [2] and Moldover and Schmidt (1983) [3]. The former considered a system of two liquid phases (A,B) (litidine water mixtures) against common glass (S). The technique is based on capillary rise and allows for a plot of $\cos\theta_e$ as a function of temperature. Below the certain temperature $T = T_w$, $\cos\theta_e = 1$, while above $T = T_w$, $\cos\theta_e$ decreases (with nearly constant slope). The latter experiment was carried out with A,B=alcohol+fluorocarbon mixtures, S=free surface. Macroscopic measurements of the contact angle indicated a wetting transition at $T_w = 311K$, and complete wetting (by the floururich phase) in the interval between T_w and $T_c = 363K$. At $T = T_w$ the measurements of the thickness e of the flourocarbon film showed a finite jump of $e(T)$.

Two questions arise: is the wetting trasition a phase transition? What is the order of this transition? The answer to the first question is yes. Before answering the second question let us resort to the theory of contact lines in thermodynamic equilibrium.

2 Angles and energies: the Young condition. Complete wetting: the special features.

When a small liquid droplet is put in a contact with a flat solid surface, two distinct equilibrium regimes may be found : partial wetting with a finite contact angle θ_e, or complete wetting ($\theta_e = 0$) [Figs. 1]. In cases of partial wetting we are dealing with three phases which are in contact at the contact line L: the solid S, the liquid L and the corresponding equilibrium vapor V. Each interface has a certain free energy per unit area γ_{sl}, γ_{sv} and γ_{lv} (the latter, for simplicity, will simply be called γ).

These parameters describe adequately the energy content of the interfaces far from L. In the vicinity of L, the structure is much more complex [Fig.2]. There is a "core region" around the nominal position of L, where the complications occur. It is possible, however, to relate θ_e to the far field energies γ_{ij} without any knowledge of the core. This was one of the (many) discoveries of the British scientist Thomas Young (1773-1829).

The basic idea is to write that, in equilibrium, the energy must be stationary with respect to any shift (dx) of the line position. In such a shift (a) the bulk energies are unaffected (since the pressure is the same in the liquid and in the vapor); (b) the core is unaffected - it is simply translated. Calculating the changes of areas we come up with the condition:

$$\gamma_{sv} - \gamma_{sl} - \gamma cos\theta_e = 0. \tag{1}$$

Equation (1) gives $\cos\theta_e$ as a function of interfacial energies. The special case

$$\gamma = \gamma_{sv} - \gamma_{sl} \tag{2}$$

leads to $\cos\theta_e = 1$ or $\theta_e = 0$ (complete wetting). At the first sight the situation appears to be exceptional. However, it is not, because $\gamma_{sl} + \gamma$ can never be larger than γ_{sv} (in thermodynamic equilibrium). Otherwise the free energy of the interface could be lowered by intercalating a liquid film of macroscopic thickness and the true γ_{sv} would be equal to $\gamma_{sl} + \gamma$, i.e., we would have complete wetting. However in nonequilibrium case a solid/vapor interfacial energy γ_{so} can be larger than $\gamma_{sl} + \gamma$. The difference

$$S = \gamma_{so} - \gamma_{sl} - \gamma \tag{3}$$

is called the spreading coefficient. The importance of S was first recognized by Cooper and Nuttal (1915) in connection with the spraying of insecticides on leaves. Large positive values of S favour the spreading of a liquid.

3 The Cahn model. Mean field theory.

The theoretical description of wetting transition was proposed by Cahn in 1977 [4]. We will follow his arguments.

(a) The liquid-solid interface can be described by the continous liquid number density $\rho(z)$ which varies smoothly as a function of distance z from the wall. This seems to be most adequate at temperatures close to T_c. The hope is that most of variations of $\rho(z)$ will take place over distances comparable to correlaton length ξ and this distance is larger than the intermolecular distance a in the liquid when $T \approx T_c$.

(b) The forces between solid and liquid are of the short range ($\sim a$) and can be described by simple adding of energy $\gamma_c(\rho_s)$ at the solid surface. Here $\rho_s = \rho(z = 0)$ and

$$\gamma_c = \gamma_0 - \gamma_1\rho_s + \frac{1}{2}\gamma_2\rho_s^2 + ... \tag{4}$$

Here γ_1 describes an attraction of the liquid by the solid and γ_2 - a certain reduction of the liquid/liquid attractive interactions near the surface: a molecule lying on the surface interacts with the less number of molecules than it would in the bulk. However, the Cahn approach doesn't impose any limitations on the form of $\gamma_c(\rho_s)$. Here it is also worth emphasizing that γ_c is not all the interfacial energy. Another counterpart γ_d comes from the distortions in the profile $\rho(z)$.

(c) Nonhomogenuous statistics of the liquid can be treated by a mean-field theory. The expression for γ_d is given by

$$\gamma_d = \int \Psi(z) dz \tag{5}$$

$\Psi(z)$ is the free-energy-excess that is due to inhomogeneity in the region of the interface, that is

$$\Psi(z) = \psi(z) - \psi(\rho_{l/v}, T) = \psi(z) - \psi^{l/v} \tag{6}$$

Here $\psi(z)$ is the true free energy density for one-component system, $\rho_{l/v}$ and $\psi^{l/v}$ mean the density ρ_l and the Helmholtz free-energy density ψ_l of the bulk phase L on the L-side, while on the V-side they mean ρ_v and ψ^v. If we take

$$\psi(z) = \psi(\rho(z), T) \tag{7}$$

(as was done by number of autors [6]), the minimisation of energy will lead to a density profile that is a step function at all temperatures, and to vanishing of the surface tension. This happens, because we are missing in (7) an extra term penalizing inhomogeneous behaviour of the density profile and introducing a characteristic length on the fluid. It is interesting that the theory was given such a form already by van der Waals [7] (1893), Landau and Lifshitz's theory of magnetic domain (1935) [8] is equivalent, and the theory has been reformulated and extended by Cahn and Hillard (1958) [9].

In the simplest version of the theory Ψ is given by

$$\Psi(z) = \frac{1}{2} L \left(\frac{d\rho}{dz}\right)^2 + W(\rho, T) \tag{8}$$

see, e.g. [10]. Here

$$W(\rho, T) = F(\rho, T) - \rho\mu - P \tag{9}$$

F is the free energy density of the bulk liquid, μ its chemical potential, P its pressure. The values of μ and P correspond to the exact coexistence of liquid and vapor. In fact, W is nothing but Landau energy of the system. At fixed temperature $W(\rho)$ has two minima of equal height ($W = 0$) for the two equilibrium densities $\rho = \rho_l$ and $\rho = \rho_v$. The general outlook of $W(\rho)$ is scetched at figure 3. A detailed discussion these questions one can find in the book by J.S. Rowlinson and B. Widom [5].

4 Two types of wetting transition.

Now we have all we need for tackling the problem in a standard way. Thus, first of all we minimise the total free energy γ_{total}:

$$\gamma_{total} = \gamma_d + \gamma_c(\rho_s) \tag{10}$$

Once done, one obtains two conditions: one - in the bulk and another on the solid surface.

$$\frac{1}{2}L\left(\frac{d\rho}{dz}\right)^2 = W(\rho) \tag{11}$$

$$\gamma_c'(\rho_s) - L\rho'(0) = 0 \tag{12}$$

The eqn.(11) was obtained by integrating along z and eliminating the constant of integration (as it can be seen from considering the point $\rho = \rho_l$). Modify (12) with the help of (11)

$$-\gamma_c'(\rho_s) = [2LW(\rho_s)]^{\frac{1}{2}} \tag{13}$$

Substitute (11) into (8) and (5):

$$\gamma_d(\rho_s, \rho_b) = \int_{\rho_b}^{\rho_s} [2LW(\rho)]^{\frac{1}{2}} dz \tag{14}$$

Equation (14) allows for the direct calculation of the distortion energy γ_d. Equation (13) determines the surface density ρ_s and leads to the graphical construction of fig. 4. Here, for simplicity, we have chosen the specific form of γ_c proposed in (4).

If the slope (γ_2) is small, the condition (13) may give four roots for ρ_s.

Two of them correspond to a maximum of free energy and, thus, are unstable. We find a competition between a state of low ρ_s ($\rho_s = \rho'$) describing a nearly "dry" solid in contact with vapor ($\rho = \rho_v$) and a state of high ρ_s ($\rho_s = \rho'' > \rho_l$) describing a wet solid in contact with liquid. The energies of these two states are

$$\gamma_{sv} = \gamma_d(\rho_v, \rho') + \gamma_c(\rho'), \quad \gamma_{sl} = \gamma_d(\rho_l, \rho'') + \gamma_c(\rho''). \tag{15}$$

The liquid/vapor interfacial energy γ can be derived from the same analysis:

$$\gamma = \gamma_d(\rho_v, \rho_l) \tag{16}$$

Discuss the spreading coefficient S, see (3).

Fortunately, S has a simple graphical interpretation on fig.4: $S = S1 - S2$ is the difference of the two shaded areas. (One can easily check it using (14), (15), (16).)

Let us trace the changes as we vary the temperature, see figs. 5.

(a) $T << T_c$. The difference $\rho_l - \rho_v$ is large, $S2 > S1$. Hence, $S < 0$, i.e. $\cos\theta_e$ is finite. We have partial wetting in this regime.

(b) When we rise temperature, the difference $S1 - S2$ decreases and vanishes at some temperature T_w. Here $S = 0$ and $\theta_e = 0$.

(c) At $T > T_w$, S is positive. As previously mentioned this regime is unobservable in thermal equilibrium. Instead of building up a liquid/vapor interface with $\rho = \rho'$, the system creates a macroscopic film wetting the surface and giving a total surface energy $\gamma_{sl} + \gamma$. Thus, we keep $\theta_e = 0$ (complete wetting). Ultimately, at higher temperatures ($T \sim T_c$) only one stable root is left, corresponding to a solid/liquid interface.

Now we are ready to address the questions posed at the end of section 1. Is it a phase transition and what is its order? In this scenario at T_w the free energy jumps from one minimum ($\rho_s = \rho'$) to another ($\rho = \rho''$). Therefore this is a phase transition of the first order. An experimentalist would have said it long ago refering to the finite jump of film's thickness observed in experiments of Moldover and Schmidt. He would have also plotted $\cos\theta_e$ versus temparature and pointed out a finite slope at the point ($T = T_w$) where the graph intersects $\cos\theta_e = 1$.

However, it may occur that the the slope of $-\gamma_c'(\rho_s)$ is large and at all temperatures there is the only root ρ_s, see fig. 6.

(a) At low temperatures $\rho_s < \rho_l$, and we can construct two density profiles corresponding to two physical situations: one profile where $\rho(z)$ decreases from ρ_s to ρ_v which describes S/V interface. Another profile corresponds to S/L interface and $\rho(z)$ increases from it's surface value ρ_s to ρ_l. One can see that our "area rule" reveals that the spreading coefficient S is negative. Consequently, one observes partial wetting.

(b) At temperatures higher than T_w there is only the possibility of S/L interface. Here the density decreases from ρ_s to ρ_l.

One can infer that this is a phase transition of the second order.

5 Role of long-ranged forces. Impurities.

In the last section we have stated the existence of second order wetting transitions. They are rather rare for the reasons we will briefly mention below. However they have stimulated a considerable theoretical effort. Besides, one can look at this problem as a study of phase transitions of systems with boundaries or surfaces (i.e., in fact, all real systems). We will return to detailed discussion of second order wetting transitions from this point of view in the section 6.

We have described the short-range forces by introducing the potential $\gamma_c(\rho_s)$. However in certain situations long-ranged forces – mainly van der Waals forces (VW) for organic liquids or double layer forces for water – become relevant. Consider a liquid film of thickness dzeta covering a solid. When its thickness is large, VW term may become dominant. Then agonist VW forces (see, e.g. [11]) bear repulsive energy and tend to thicken the film. A possible situation is sketched at figure 7. When VW terms gives an energy equal to that of macroscopic film γ_{sv}, the system jumps by a first order transition from the $\zeta = \infty$ to $\zeta = \zeta_1$.

A similar description can be given for water solutions against an ionizable surface. Whenever the Debye screening κ_d^{-1} is larger than L/V interface thickness,the repulsive term dominates the behaviour of the film at large distances and the energy plot is qualitatively similar to the preceeding one. The transition temperature is shifted to a lower value and the transition becomes of the first order.

Long range forces can also induce a flourishing variety of transition phenomena. Quite a few of them are described and referenced at the review of de Gennes [1]. I would like to mention two of them.

It is incorrect to assume exponential tail for the L/V interface when the interactions between molecules in the fluid become long range. The $(\nabla\rho)^2$ expansion in (8) becomes invalid. What happens when it breaks down? A first attempt to answer this question is due to Sullivan (1979) [12]. He chose a pair interaction

$$U(r_{ij}) = -\frac{\alpha}{4\pi r_{ij}} e^{\gamma_1 r_{ij}} \tag{17}$$

and the solid/molecule interaction within the same range γ_1^{-1} ,

$$V(z_i) = -\epsilon_w e^{-\gamma_1 z_i} \tag{18}$$

Sullivan found a simple solution of complete integral mean-field equation for this special choice without assuming a "gradient square" expansion. He obtained some interesting results. For instance, high ϵ_w led θ_e to decrease with T (as it is in Cahn theory), while at low ϵ_w, θ_e decreases with T. His wetting transitions were of the second order, but later works with the same model led to first-order transitions.

It is clear, though, that this artificial potential is not adequate to study the order of the transition. It cuts down the interactions much more vigorously than expected VW forses decrease ($\sim z^{-2}$). It is more instructive to keep realistic VW interactions, carrying out numerical calculations. Such calculation have found transitions that were constantly of the first order. Further analysis showed that, though the second order transitions are not completely ruled out, they occur under conditions so stringent that they have never been observed in numerical calculations.

It is also a must to mention the dramatic effects that chemical contaminations may have on the wetting phenomena (for references see, again, [1]).

6 Second order transition: detailed discussion. The domain of validity of mean field theory. The upper critical dimension. Correlations. Gaussian fluctuations. Critical exponents.

Here we will discuss the domain of validity of mean field theory describing the critical wetting. We will concentrate on the wetting transition of the second order close to the consolute point T_c of binary flid mixture, i.e. the case when $t = (T - T_c)/T$ is small. Then one can proceed with the standard expansion for Landau energy at small T, rather than with the function $W(\rho, T)$. The presence of the wall has two effects on the L/V mixture: (i) the semiinfinite geometry of the system changes the interactions experienced by the molecules of the surface layer. This may be taken into account by an incremental surface temperature field c localized on the surface of the wall. (ii) The preferential adsorption of one component of the mixture induces a difference in the chemical potential of the two components on the surface. This can be cast by introducing a local chemical potential h_1 on the surface. One can see that at small t this approach is equivalent to the consideration above (sections 3,4).

Speaking the magnetic language, one can say that the effect of the wall is described by the surface temperature c and the surface magnetic field h_1. If the bulk boundary conditions far from the wall favour one phase (for instance down-spins), and if h_1 is positive then, at sufficiently low temperature, a layer of up-spins with a finite thickness (determined by h_1, c and t) may "partially wet" the surface.

We will focus our attention on the behaviour near a critical point M of the critical wetting line OA ($h = 0$) of figure 8.

Consider a Landau-Ginzburg-Wilson Hamiltonian A ($\equiv \beta H$) in d dimentions for a one component order parameter $\Phi(z; \rho_1, ..., \rho_{d-1})$ below T_c (here $\rho_1, ..., \rho_{d-1}$ - degrees of freedom parallel to the wall; as we prefer to speak in magnetic terms it cant lead to a misunderstanding):

$$\begin{aligned} A &= \int_{z>0} d^d x \left\{ \frac{1}{2}(\nabla\Phi)^2 + \frac{t}{2}(\Phi^2 - M^2) + \frac{g}{4!}(\Phi^4 - M^4) \right\} + \\ &+ \int d^{d-1}\rho \left\{ \frac{1}{2}c\Phi^2(0,\boldsymbol{\rho}) - h_1\Phi(0,\boldsymbol{\rho}) - \left[\frac{1}{2}cM^2 - h_1 M\right] \right\} \end{aligned} \tag{19}$$

in which M is the bulk sponateous magnetization($M = \left(\frac{-6t}{g}\right)^{1/2}$ - at the mean field level). In fact the effective Hamiltonian (19) is ill-defined: $\nabla\Phi$ will have in general a δ-function at $z = 0$ and the product $\theta(z)(\nabla\Phi)^2$ is not defined. We shall regularize it by restricting ourselves to order parameter which satisfies the boundary condition

$$\left.\frac{\partial\Phi}{\partial z}(z,\boldsymbol{\rho})\right|_{z=0_+} = c\Phi(0,\boldsymbol{\rho}) - h_1. \tag{20}$$

(One can easily check that in this class of functions the surface term in the variation of the Hamiltonian is vanishing). The standard procedure of finding stationary points of A will lead to the situation discussed in the section 4. In magnetic terms the second order transition occurs at some temperature $T_w(h_1, c)$ defined by

$$t_w = T_w/T_c - 1 = -\frac{gh_1^2}{6c^2} \tag{21}$$

When t reaches t_w ($T < T_w$) the thickness of the wetting layer z_0 diverges:

$$z_0 \sim \frac{1}{\sqrt{-2t_w}} \ln \frac{1}{(T_w - T)}. \tag{22}$$

See figures 9. When $T < T_w$ the mean field profile is given by

$$\Phi_c(z) = -M \tanh\left[\sqrt{\frac{-t}{2}}(z - z_0)\right] \tag{23}$$

The additional surface tension of the interface $\delta\gamma$, due to its binding to the wall near T_w behaves as

$$\delta\gamma \sim -\gamma_0 (T_w - T)^2 \tag{24}$$

In order to characterize the correlations we go beyond the mean field level and consider gaussian fluctuations. The standard procedure [13] gives a correlation length in directions parallel to the wall:

$$\xi_{||} = \frac{\xi_0}{(T_w - T)} \tag{25}$$

This interesting result is in contrast with the usual $\nu = 1/2$ mean field law. This wetting transition corresponds to a restoration of a broken symmetry: in the infinite system translational symmetry would leave the location of the interface undetermined (the parameter z_0) in (23) would be arbitrary). The low modes which translate and distort the interface would be gapless. In the semiinfinite geometry the wall breaks translational invariance: long wavelength fluctuations of the interface are suppressed at low temperatures by the wall. However at T_w, the energy-entropy balance for the interface favours a liberation of the interface; z_0 becomes arbitrary and translational invariance is restored.

Physically, the restoraton of translational invarience is responsible for the interaction of nonsingular modes which modifies the self-coupling (or effective interactions) of the long-wave modes and these effective interactions vanish as $(T_w - T)^2$! As a consequence the upper critical dimension is *three*, i.e. a three-dimensional bulk liquid with a two-dimensional interface[13]. (A naive calculation taking into account the singular modes only would lead to a conclusion that the upper critical dimension is five!) Therefore one would expect corrections to the above mean field theory results sufficiently close to T_w.

To study these corrections Brezin et al. have constructed an interface displacement model for $(d-1)$-dimensional interface. Clear, that it is of the most interest for $d = 3$. (For $d = 2$ it is possible to solve it exactly, though). Its analysis gave a rise to a very unusual critial exponent, whose value depends continuously on the parameter $\omega = k_B T_w / 4\pi\xi_b^2\gamma$ (where ξ_b is the *bulk* correlation length) [14].

For $0 < \omega < \frac{1}{2}$ we find instead of (25)

$$\xi = \xi_0 |t|^{-\nu}, \qquad \nu = (1-\omega)^{-1}, \tag{26}$$

while for $\frac{1}{2} < \omega < 2$,

$$\begin{aligned} \xi &= \xi_0 |t|^{-\nu} [\ln(\frac{1}{|t|})]^{-\tilde{\nu}}, \\ \nu &= (\sqrt{2} - \sqrt{\omega})^{-2}, \\ \tilde{\nu} &= [1 + (\omega/8)^{\frac{1}{2}}]\nu \end{aligned} \tag{27}$$

and for $\omega > 2$,

$$\xi \sim \exp[c_1 |t|^{-1} ln(1/|t|)], \tag{28}$$

where c_1 is a constant.

Equations (22), (24) describing the position of the interface and relating $\delta\gamma$ to the correlation length remain valid in the presence of fluctuations. Note, that (26) and (27) both give ν for $\omega \to \frac{1}{2}$. For $\omega \to 2_-$, $\nu \to \infty$. At sufficiently high temperatures (low γ's) the rare fluctuation "touch" the solid surface, and these are the fluctuations responsible for the change in behaviour described by (26) and (27).

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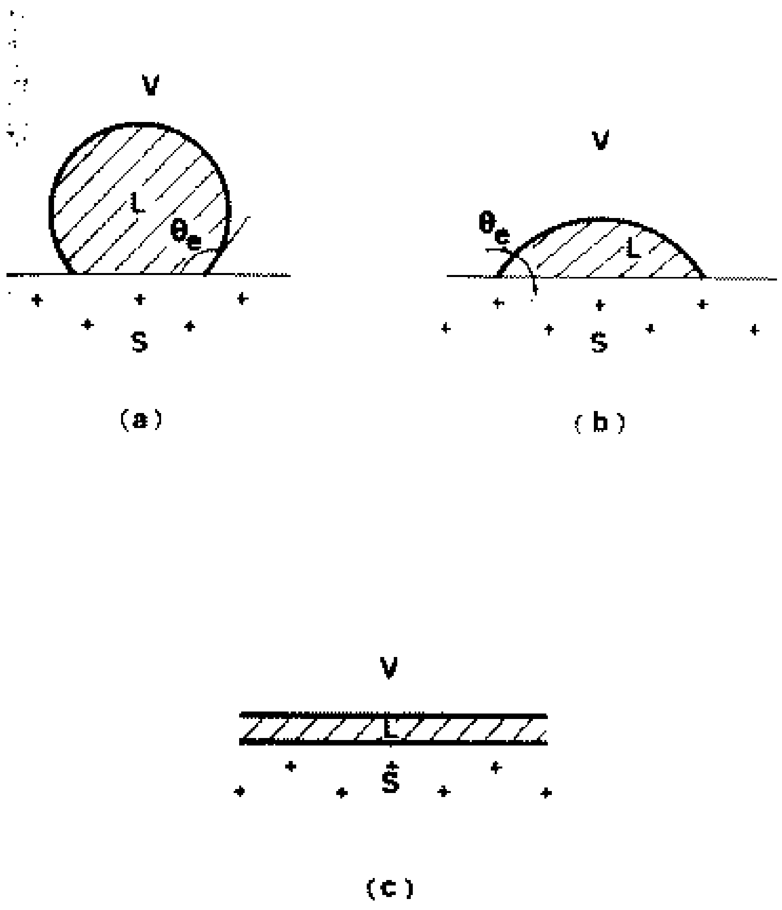

Fig.1. A small droplet in equilibrium over a horizontal surface:
(a) and (b) correspond to partial wetting;
(c) correspond to complete wetting.

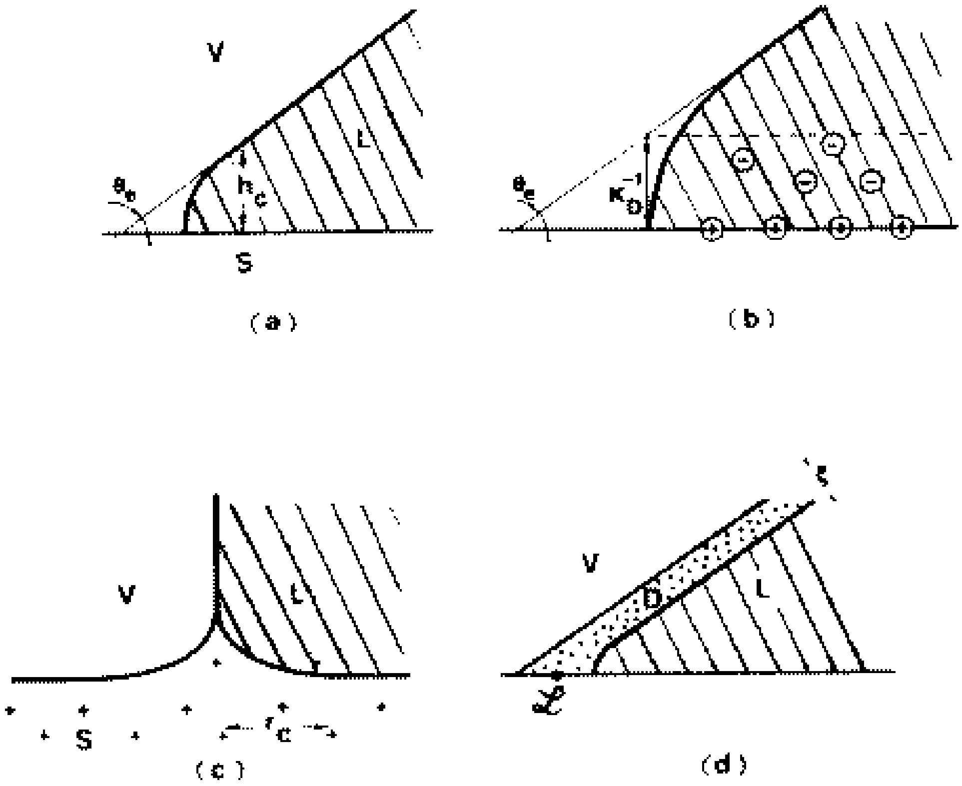

Fig.2. Various types of core structures for the trilple line.
(a) Effect of attractive van der Waals forces.
(b) A charged solid surface wetted by salty wather.
(c) Effect of the finite deformability of the solid.
(d) In the vicinity of a liquid/vapour crutical point, the L/V interface becomes diffuse.

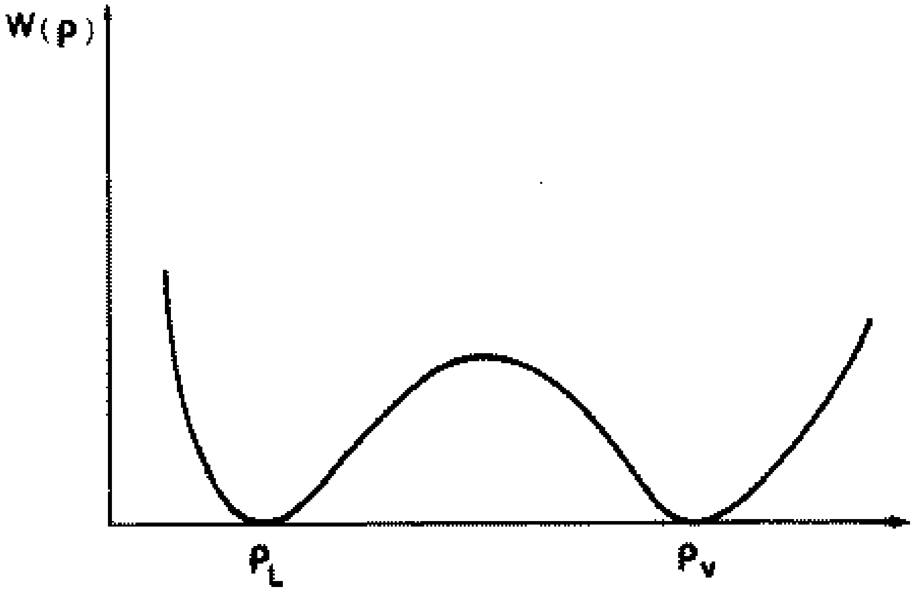

Fig.3. The Landau free energy as a function of density.

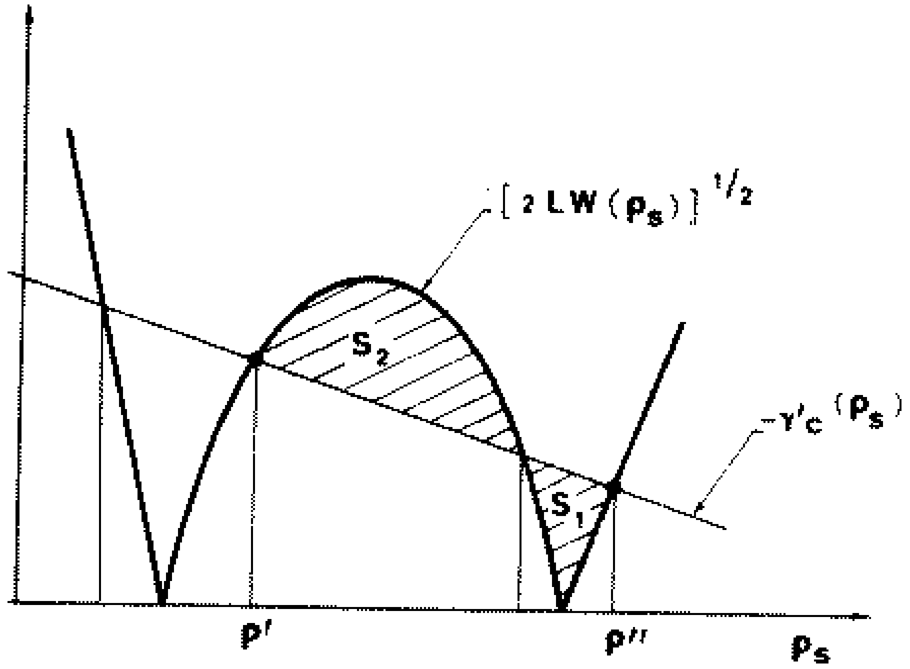

Fig.4. The Cahn construction determing the density at the surface.

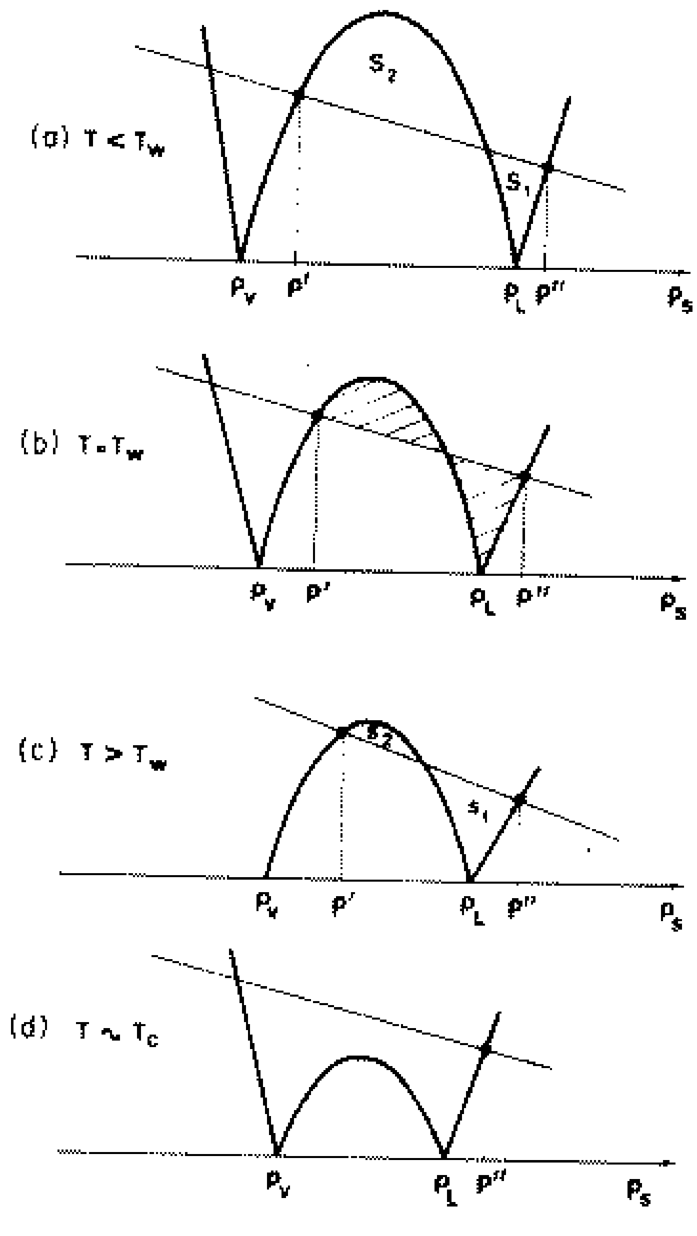

Fig.5. First-order transition from the Cahn construction.

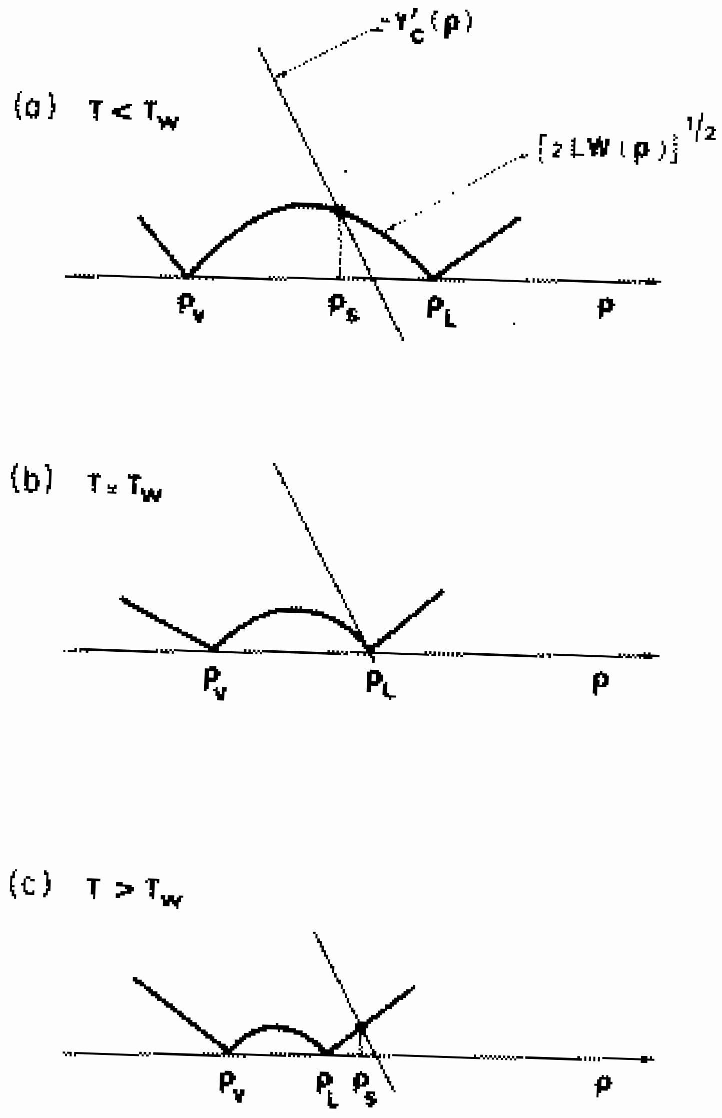

Fig.6. Second-order transition from the Cahn constructio

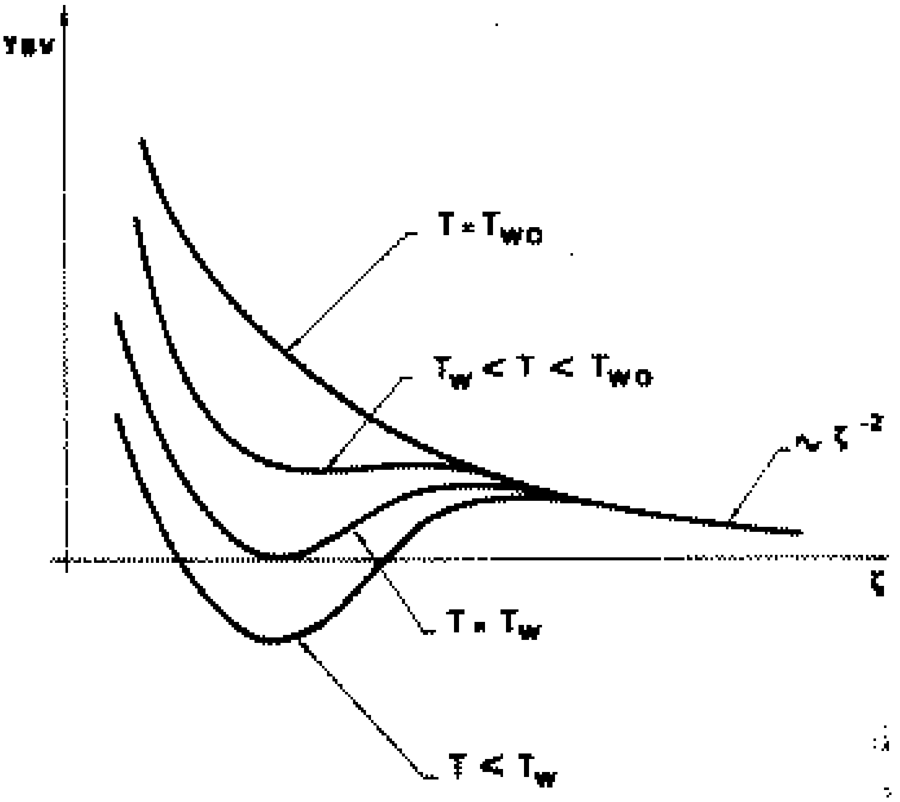

Fig.7. Energy vs thickness with incorporation of long-range van der Waals forces. These forces are assumed to be "agonist" (i.e., they tend to thicken the film). They dominate at long distances.

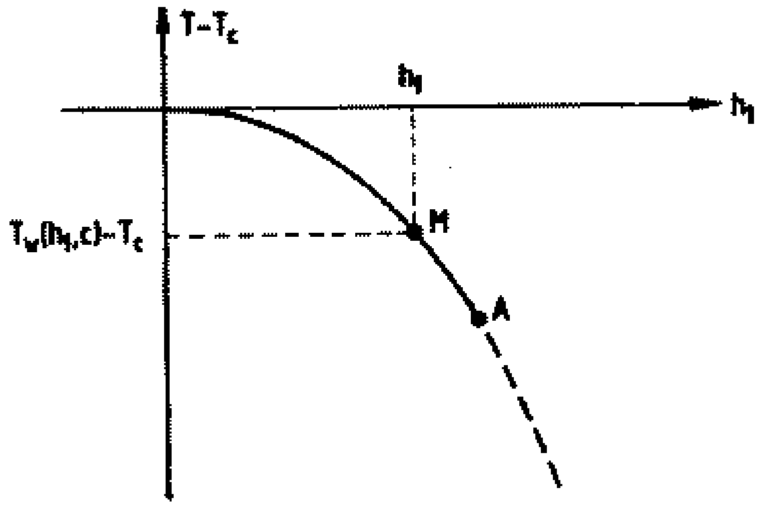

Fig.8. The phase diagram for a fixed given positive c. $h=0_-$.
The line of critical wetting OA corresponds to continuous transitions. The dotted line is the locus of first-order transitions; A is a tricritical point.

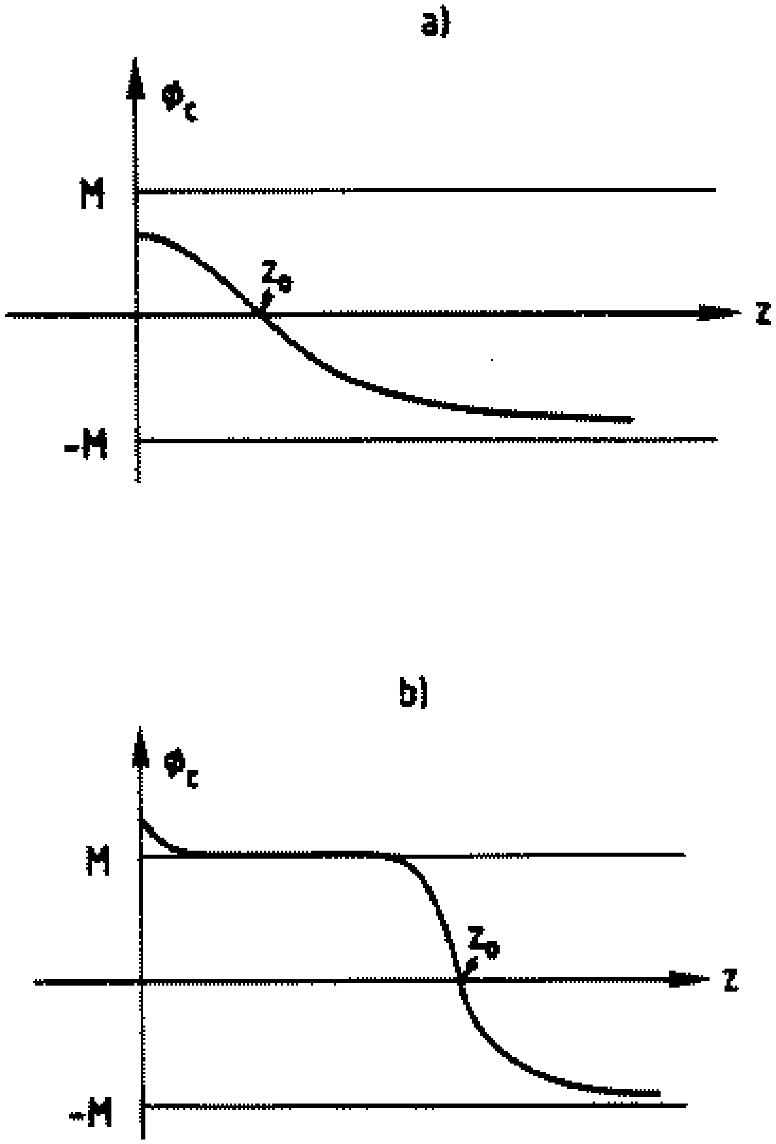

Fig.9.- The mean field profile.
(a) $T < T_w$;
(b) $T_c > T > T_w$: the thickness is proportional to $\ln 1/h_{bulk}$.