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Wetting on a spherical surface

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It is shown in the framework of the Cahn model [J. Chem. Phys. **66**, 3667 (1977)] that the wetting layer, which forms on a spherical surface, always has a finite thickness $l \sim \ln R$ where R is the radius of a sphere. The temperature T_w of a first-order wetting transition is higher in a spherical geometry than in a flat one. The shift of the transition temperature T_w is proportional to $\ln R/R$ for large R.

It was argued by Cahn in his pioneering paper[1] that if two critical phases α and β are in contact with a third noncritical phase γ, which forms a flat wall, one can expect, at coexistence conditions, a wetting transition at some temperature T_w below the critical temperature T_c. At T_w the contact angle θ becomes equal to zero, which means that one of the critical phases intrudes between the wall and the other critical phase, forming a layer of macroscopic thickness l. In the Cahn model, l grows infinitely when the α-β coexistence line is approached above T_w, and it is found that $l \sim -\ln|\Delta\mu|$, where $\Delta\mu$ is the departure of the chemical potential from its coexistence value.

There has been much of literature on wetting phenomena since Cahn's discovery (for recent reviews, see Refs. 2–4). While much is known about wetting in the presence of a flat wall, only recently has more attention been devoted to wetting on curved surfaces.[5,6]

In this paper we are concerned with wetting of a sphere by a liquid in the context of the Cahn mean-field theory.[1] It is a simple observation that if a wetting layer is to form on a spherical surface it cannot be infinitely thick. This is because of the Antonoff rule for the solid-vapor ($\gamma_{s\text{-}v}$), solid-liquid ($\gamma_{s\text{-}l}$), and liquid-vapor ($\gamma_{l\text{-}v}$) surface tensions which reads

$$A_R \gamma_{s\text{-}v} = A_R \gamma_{s\text{-}l} + A_{R+l} \gamma_{l\text{-}v}, \tag{1}$$

where A_R and A_{R+l} are the areas of spheres with the radii R and $R+l$, respectively. Equation (1) can be satisfied only if l is finite. For large R, one has

$$\gamma_{s\text{-}v} \cong \gamma_{s\text{-}l} + \gamma_{l\text{-}v} \left[1 + \frac{2l}{R} \right] , \tag{2}$$

where $\gamma_{s\text{-}v}$, $\gamma_{s\text{-}l}$, $\gamma_{l\text{-}v}$, and l are generally functions of R and $l/R \to 0$ as $R \to \infty$, as we must recover the case of a flat wall $\gamma_{s\text{-}v}^{\infty} = \gamma_{s\text{-}l}^{\infty} + \gamma_{l\text{-}v}^{\infty}$. It follows immediately from Eq. (2) that the wetting temperature should shift upwards for a finite R. In this paper we shall be mainly interested in the asymptotic, large-R behavior of various quantities.

We consider the surface part of the grand thermodynamic potential Ω_s as a functional of the density profile $\rho(r)$

$$\Omega_s\{\rho\} = 4\pi \int_R^{\infty} \left[\omega(\rho) - \omega(\rho_b) + \tfrac{1}{2} L \left(\frac{d\rho}{dr} \right)^2 \right] r^2 dr + 4\pi R^2 \Phi(\rho_s) , \tag{3}$$

where $\omega(\rho) = f(\rho) - \mu\rho$, f is the free-energy density, $\rho_b = \rho(r=\infty)$, and we assume that the vapor is the bulk phase; L is a constant. $\Phi(\rho_s)$ is the contribution to the surface energy due to the interaction between the fluid and the spherical surface and has a form of a contact potential[2]

$$\Phi(\rho_s) = -h_1 \rho_s + \tfrac{1}{2} a_1 \rho_s^2 , \tag{4}$$

where $\rho_s = \rho(r=R)$. Depending on the values of parameters h_1 and a_1, wetting by liquid or drying by vapor of first or second order can occur in a flat geometry.[2] We confine ourselves to the situation when the parameters, h_1, a_1 give a first-order wetting transition. The minimization of Eq. (3) with respect to $\rho(r)$ leads to the Euler-Lagrange equation

$$\frac{d^2\rho}{dr^2} + \frac{2}{r}\frac{d\rho}{dr} - \frac{1}{L}\frac{\partial \Delta\omega}{\partial \rho} = 0 , \tag{5}$$

where $\Delta\omega = \omega(\rho) - \omega(\rho_b)$, together with the boundary conditions

$$\left. \frac{d\rho}{dr} \right|_{r=R} = \frac{1}{L}\Phi'(\rho_s) = \frac{1}{L}(-h_1 + a_1\rho_s) , \qquad \rho(r=\infty) = \rho_v . \tag{6}$$

Equation (5) can be considered as an equation of motion where ρ plays the role of a dynamical variable and r plays the role of time. $\Delta\omega(\rho)$ can be regarded as an external potential. The second term in Eq. (5) introduces a friction, with the friction coefficient decreasing like the inverse of time r. The energy is not conserved and an extra work is needed to move the particle against friction forces.

For our subsequent analysis, we assume $\Delta\mu = 0$ and following special form for $\Delta\omega(\rho)$

$$\Delta\omega(\rho) = \begin{cases} \tfrac{1}{2} L \lambda_v^2 (\rho - \rho_v)^2 & \text{for } \rho < \rho_m, \\ \tfrac{1}{2} L \lambda_l^2 (\rho - \rho_l)^2 & \text{for } \rho > \rho_m, \end{cases} \tag{7}$$

where $\rho_m = \rho_v + (\lambda/2\lambda_v)(\rho_l - \rho_v)$ is the point where the two parabolas cross each other forming a cusp. The two coefficients λ_v^2, λ_l^2 are proportional to the inverse of the vapor and liquid compressibility, respectively. This is quite a good approximation in the region of the two minima of $\Delta\omega$, thus in the region important for the wetting phenomena. It breaks down when the temperature is too close to the bulk critical temperature. This type of approximation can also be found either in the context of the Cahn theory[7] or in the context of the Sullivan theory.[8] With the assumed form of $\Delta\omega(\rho)$, Eq. (5) becomes linear and easy to solve. The general solution is a linear combination of $\exp(\pm\lambda_{v,l}r)/r$. There are two possibilities:

I. For all r, $\rho(r) < \rho_m$. Then the solution of Eq. (5), satisfying the boundary conditions, has the following form:

$$\rho^{\mathrm{I}}(r) = \rho_v + \frac{h_1 - a_1\rho_v}{L\lambda_v(1+1/\lambda_v R)}\frac{R}{r}\exp[-\lambda_v(r-R)] \ , \tag{8}$$

where $\rho_s^{\mathrm{I}} = \rho^{\mathrm{I}}(R)$ must be less than ρ_m. The solid-vapor surface tension is given by

$$\begin{aligned}\gamma_{s\text{-}v}^{\mathrm{I}} &= \Omega_s\{\rho^{\mathrm{I}}\}/4\pi R^2 \\ &= \tfrac{1}{2}L\lambda_v(\rho_s^{\mathrm{I}} - \rho_v)^2\left(1 + \frac{1}{\lambda_v R}\right) + \Phi(\rho_s^{\mathrm{I}}) \ .\end{aligned} \tag{9}$$

II. The profile $\rho(r)$ passes through ρ_m at some point $r = r_0$. The continuity conditions at r_0 for $\rho(r)$ and its derivative must be satisfied; hence

$$\rho^{\mathrm{II}}(r) = \begin{cases} \rho_v + \frac{1}{2}(\rho_l - \rho_v)\dfrac{\lambda r_0}{\lambda_v r}\exp[-\lambda_v(r-r_0)] & \text{for } r > r_0, \\ \rho_l - \dfrac{(\rho_l - \rho_v)}{2\lambda_1 r}\{(1+\lambda r_0)\exp[\lambda_l(r-r_0)] - \exp[-\lambda_l(r-r_0)]\} & \text{for } R < r < r_0, \end{cases} \tag{10}$$

where

$$\frac{2}{\lambda} = \frac{1}{\lambda_v} + \frac{1}{\lambda_l} \ .$$

We interpret r_0 as the location of the liquid-vapor interface. By substituting Eq. (10) into Eq. (6), we arrive at the equation for r_0:

$$\left(1 + \frac{1}{\lambda_l R} + \frac{a_1}{\lambda_l L}\right)u^2 - 2\left(1 + \frac{a_1}{\lambda_l L}\right)\varkappa R u + (1+\lambda r_0)\left(1 - \frac{1}{\lambda_l R} - \frac{a_1}{\lambda_l L}\right) = 0 \ , \tag{11}$$

where

$$u = \exp[\lambda_l(r_0 - R)]$$

and

$$\varkappa = \frac{h_1 - a_1\rho_l}{L(\rho_l - \rho_v)(1 + a_1/\lambda_l L)} \ .$$

Because of our choice of the parameters h_1, a_1 corresponding to wetting by the liquid in a flat geometry, we have $\varkappa > 0$ in the interesting range of temperatures $T > T_w^\infty = T_w(R = \infty)$. Equation (11) can have up to three solutions for r_0. One of them gives $u < 1$, and the second one does not give a proper asymptotic behavior for large R, in that sense that $l(R) = r_0 - R$ does not diverge as $R \to \infty$. We interpret that solution as belonging to the unstable branch of Ω_s. We do not analyze Eq. (11) in detail here as we are only interested in the asymptotic limit of $\lambda_l R \gg 1$ and $\varkappa R \gg 1$. In this limit there always exists one stable solution

$$u \cong 2\varkappa R - \frac{\lambda(1 - a_1/\lambda_l L)}{2\varkappa(1 + a_1/\lambda_l L)} - \frac{2\varkappa}{\lambda_l(1 + a_1/\lambda_l L)} \ , \tag{12}$$

for which

$$r_0 \cong R + \frac{1}{\lambda_l}\ln(2\varkappa R) \ , \tag{13}$$

where we have included only the leading terms. It follows immediately from Eq. (13) that the thickness of the wetting film $l(R)$ diverges logarithmically. Having the solution for r_0, we are able to analytically calculate the surface tension $\gamma_{s\text{-}v}^{\mathrm{II}} = \Omega_s\{\rho^{\mathrm{II}}\}/4\pi R^2$. In all calculations of surface tensions we keep only the leading terms proportional to $\ln R/R$ and $1/R$. We find that

$$\gamma_{s\text{-}v}^{\mathrm{II}}(R) = \gamma_{s\text{-}l}(R) + \gamma_{l\text{-}v}(R)\left(1 + \frac{2\ln(2\varkappa R)}{\lambda_l R}\right) \ , \tag{14}$$

where

$$\gamma_{s\text{-}l}(R) = \tfrac{1}{2}L\lambda_l(\rho_s^l - \rho_l^l)^2\left(1 + \frac{1}{\lambda_l R}\right) + \Phi(\rho_s^l) \ , \tag{15}$$

$$\rho_s^l = \rho_l + \frac{h_1 - a_1\rho_l}{\lambda_l L(1 + 1/\lambda_l R) + a_1} \ , \tag{16}$$

$$\gamma_{l\text{-}v}(R) = \gamma_{l\text{-}V}^\infty(1 - 2\delta/R) \text{ with } \delta = -1/\lambda \ . \tag{17}$$

The surface density ρ_s^l corresponds to the profile similar in shape to $\rho^{\mathrm{I}}(r)$ but with $\rho_b = \rho_l$. The expression for $\gamma_{s\text{-}l}(R)$ is exact, but it is understood that it should be expanded up to the order $1/R$ before substitution into Eq. (14). For some range of temperatures there is a competition between the profiles $\rho^{\mathrm{I}}(r)$ and $\rho^{\mathrm{II}}(r)$. The wetting temperature $T_w(R)$ is the temperature at which $\gamma_{s\text{-}v}^{\mathrm{I}}(R) = \gamma_{s\text{-}v}^{\mathrm{II}}(R)$. For higher temperatures, $\gamma_{s\text{-}v}^{\mathrm{II}} < \gamma_{s\text{-}v}^{\mathrm{I}}$ and the generalized Antonoff rule holds. Eventually, when the temperature is high enough, the inequality $\rho_s^{\mathrm{I}} < \rho_m$ can be no longer satisfied and $\rho^{\mathrm{II}}(r)$ becomes the only stable profile. Each of the surface tensions $\gamma_{s\text{-}v}^{\mathrm{I}}$, $\gamma_{s\text{-}l}$, $\gamma_{l\text{-}v}$ can be expressed as a sum of its value for $R = \infty$ (flat geometry) plus some correction term of the order $1/R$. It is worth mentioning that although we do not consider here a free liquid-vapor interface, we are able to extract the dependence of $\gamma_{l\text{-}v}$ on the radius of curvature, since $1/r_0 = 1/(R+l) \sim 1/R$ for large R. In our model $\delta = -1/\lambda < 0$ as usually expected.[9,10]

To calculate the shift of the wetting transition temperature, we leave only the leading term $2\ln(2\varkappa R)/R$ in Eq. (14); hence the equation for $T_w(R)$ reads as follows:

$$\gamma_{s\text{-}v}^{\mathrm{I}\infty}(T_w) = \gamma_{s\text{-}v}^{\mathrm{II}}(R,T_w)$$

$$\cong \gamma_{s\text{-}l}^{\infty}(T_w) + \gamma_{l\text{-}v}^{\infty}(T_w)\left[1+\frac{2l(R,T_w)}{R}\right] , \tag{18}$$

where $T_w(R) = T_w^{\infty} + \Delta T_w(R)$. The expansion around T_w^{∞} gives

$$\frac{\Delta T_w}{T_w^{\infty}} q = \frac{2\gamma_{l\text{-}v}^{\infty}}{R} l(R,T_w^{\infty}) , \tag{19}$$

where

$$q/T_w^{\infty} = [(\partial\gamma_{s\text{-}v}^{\mathrm{I}\infty}/\partial T)_{\mathrm{coex}} - (\partial\gamma_{s\text{-}v}^{\mathrm{II}\infty}/\partial T)_{\mathrm{coex}}]_{T=T_w} . \tag{20}$$

The derivative of $\gamma_{s\text{-}v}^{\infty}$ along the coexistence line is given by

$$(\partial\gamma_{s\text{-}v}^{\infty}/\partial T)_{\mathrm{coex}} = -\eta_s + \Gamma\Delta s/\Delta\rho , \tag{21}$$

where η_s is the surface entropy, Γ stands for the adsorption, and Δs, $\Delta\rho$ are, respectively, the changes of the bulk entropy density and the density at the liquid-vapor transition. It is easy to see that also for the wetting film $(\partial\gamma_{s\text{-}v}^{\infty}/\partial T)_{\mathrm{coex}}$ is finite even though η_s and Γ diverge. The left-hand side of Eq. (19) can be considered as a thermal equivalent of the work that has to be done to build up a wetting film of thickness l. Here one point is worth mentioning. Since it is the presence of a surface potential that curves the liquid-vapor interface and μ corresponds to the bulk liquid-vapor coexistence, we should not expect any total pressure difference. The pressure difference $p = 2\gamma_{1\text{-}v}/R$ occurring in the case of a curved free liquid-vapor interface is here balanced by the pressure difference due to the surface potential.[11]

Formula (19) has been obtained only from the thermodynamics supplemented by the assumption that the corrections to $\gamma_{s\text{-}v}^{\mathrm{I}\infty}$, $\gamma_{s\text{-}l}^{\infty}$, $\gamma_{l\text{-}v}^{\infty}$ are of the order $1/R$ and it should be rather generic. In our model $\Delta T_w \sim \ln R/R$ for large R. For a long-range solid-fluid potential, an algebraic decay of $l(R)/R$ should be expected in three dimensions.

Another interesting quantity is the jump of ρ_s at the bulk liquid-vapor transition. In a flat geometry it is finite and of the order $(\rho_l - \rho_v)$ for $T < T_w^{\infty}$ and zero for $T > T_w^{\infty}$. A curved geometry introduces a weak discontinuity even for $T > T_w(R)$. We find that in our model that discontinuity is given by

$$\Delta\rho_s = \rho_s^{\mathrm{II}} - \rho_s^{l} \cong -\frac{2\gamma_{l\text{-}v}^{\infty}}{(h_1 - a_1\rho_l)\lambda_l R} . \tag{22}$$

A similar problem of wetting on thin cylinders has been studied by Brochard[6] and Levinson, Jouffroy, and Brochard.[5] Our conclusions concerning formation of a finite wetting film are in line with their results. The condition for partial or complete wetting can be expressed in terms of the spreading coefficient $S = \gamma_{s\text{-}v} - \gamma_{s\text{-}l} - \gamma_{l\text{-}v}$. In a flat geometry the wetting transition occurs at $S = 0$ $(\cos\theta = 1)$. However, this is not true in the case of a curved geometry. A wetting film can form on a curved surface if $S > S_c > 0$ (Ref. 6) where S_c is some critical value of the spreading coefficient, and in our model $S_c = 2\gamma_{l\text{-}v}^{\infty} l(R)/R$.

Finally, we would like to notice that there is some analogy between the presented problem and the problem of phase transitions in systems which are limited by two parallel walls, thus, being finite in one direction. Such systems have been recently studied by a few authors.[12-16] In the case of short-range wall-fluid interactions and a first-order wetting transition on a single wall, one finds for a large wall separation D a similar asymptotic behavior, i.e., $l(D) \sim \ln D$ and $\Delta\rho_s(D) \sim 1/D$. We think that this is a rather general manifestation of finite size effects.

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