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An interface potential approach to capillary condensation in a rectangular groove

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Abstract. Using an interfacial potential approach we study capillary condensation within an infinitely long rectangular fissure in an otherwise planar surface. We demonstrate how the groove fills sharply, but continuously, with the wetting liquid as the chemical potential and temperature are varied. This is contrasted to the situation for an infinitely deep slit, where the transition is first order.

1. Introduction

Although the wetting transition on planar substrates is well understood (Dietrich 1988, Charvolin *et al* 1990), much less is known for situations where the substrate geometry is more complicated. Therefore in this paper we study the shape of the liquid profile within a wetting geometry around a simple substrate inhomogeneity, an infinitely long rectangular fissure in an otherwise planar surface. We demonstrate how the groove fills sharply, but continuously, with the wetting liquid as the chemical potential and temperature are varied. This is in contrast to the situation for an infinitely deep groove when the capillary condensation transition is first order (Evans 1990).

The interface potential we shall employ includes terms resulting from the surface tension of the interface, the chemical potential difference between liquid and gas and fluid–fluid and fluid–substrate interactions of the non-retarded van der Waals form. It can be derived by minimizing a density functional expression for the grand canonical potential within the sharp kink approximation, that is within the subspace of piecewise constant density profiles (Dietrich 1988).

In section 2 we show how the interface free energy can be minimized in coordinates appropriate to the slit geometry to give a differential equation for the height of the interface above the substrate. This can be solved numerically and the results are presented in section 3 as a function of the aspect ratio of the groove and the thermodynamic parameters. Comparison is made to a slit of infinite depth in section 4. Section 5 provides a conclusion in which the results are summarized and related to previous work. A discussion is given of the validity of the interface potential approach.

2. Interface potential approach for a rectangular groove

Our aim is to study the profile of the wetting layer in a rectangular groove of finite width and depth, but infinite length, embedded in a plane, as shown in figure 1. The

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function l_s which defines the substrate surface is a step function

$$l_s(x) = \begin{cases} 0 & \text{if } |x| \geqslant D/2 \\ -qD & \text{if } |x| < D/2 \end{cases} . \tag{1}$$

Hence D is the slit width and q the ratio of its depth to its width.

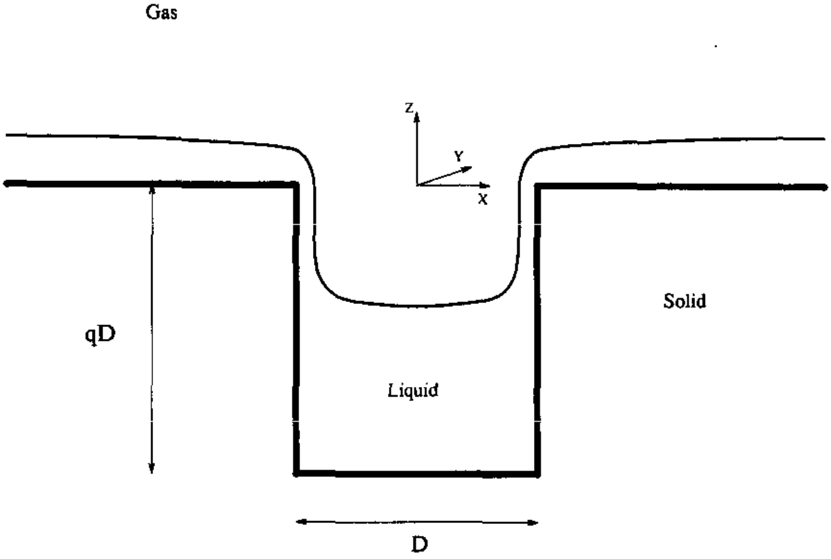

Figure 1. Rectangular groove of width D and depth qD. The origin is chosen to be at the level of the plane, at an equal distance from each edge of the well. The x and y axes lie in the plane perpendicular and parallel to the groove respectively.

The substrate is immersed in a fluid close to two-phase coexistence at a reduced temperature $t = (T_c - T)/T_c$, where T_c is the temperature of the bulk critical point. The chemical potential, relative to its value at two-phase coexistence, $\Delta\mu$, is chosen such that the gas phase is preferred. The substrate–fluid interaction is defined so that the substrate attracts the fluid atoms. Hence a layer of liquid forms on the substrate. The liquid–gas interface can either follow the contours of the well, a situation preferred by the chemical potential contribution to the free energy, or ignore the well to minimize the interfacial area and the associated surface tension. We study the transition between these states as a function of $\Delta\mu$, t and q.

We work within the approximation that there is a sharp interface at a distance $l(\boldsymbol{r})$ from the substrate surface. One can reasonably assume that the interface position depends only on the x coordinate, $l(\boldsymbol{r}) \equiv l(x)$, because the system is invariant with respect to translations along the y axis (see figure 1). In terms of $l(x)$ the interfacial free energy per unit length along the slit is taken to be (Dietrich 1988)

$$\Omega_I[l(x)] = \int_{-\infty}^{\infty} \left\{ \sigma\sqrt{1 + \left(\frac{\mathrm{d}l}{\mathrm{d}x}\right)^2} + \Delta\tilde{\mu}\,[l(x) - l_s(x)] \right\} \mathrm{d}x + \omega[l(x)]. \tag{2}$$

The first term is the free energy of the interface itself—the surface area of the interface multiplied by the liquid–gas surface tension, σ. The second contribution to the free energy results from absorbing a given volume of the thermodynamically unfavourable liquid phase. The difference in number densities between the two phases has been subsumed into the chemical potential

$$\Delta\tilde{\mu} = (n_\mathrm{l} - n_\mathrm{g})\Delta\mu. \tag{3}$$

The final term models the interatomic interactions. In the case where both fluid–fluid and fluid–substrate interaction potentials are of the non-retarded van der Waals form, $1/r^6$, this can be written as

$$\omega[l(x)] = \frac{12A}{\pi}\int_{\mathrm{gas}}\int_{\mathrm{substrate}} \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|^6}\mathrm{d}\boldsymbol{r}'\mathrm{d}\boldsymbol{r} \tag{4}$$

where A is the Hamaker constant. The integral over the substrate can be carried out analytically for a rectangular groove giving

$$\omega[l(x)] = \int_{-\infty}^{\infty}\int_{l(x)}^{\infty} V(x,z)\mathrm{d}z\,\mathrm{d}x \tag{5}$$

where

$$V(x,z) = -2A\left\{\frac{1}{z^3} + \frac{1}{4}\left[f\left(x+\frac{D}{2},z\right) - f\left(x-\frac{D}{2},z\right)\right]\right\} \tag{6}$$

with

$$f(s,z) = g(s,z+qD) - g(s,z) \tag{7}$$

and

$$g(u,v) = \frac{-u^2v^2 - 2u^4 - 2v^4}{u^3(u^2+v^2)^{1/2}v^3}. \tag{8}$$

The last term in equation (6) is clearly due to the presence of the well. For a planar substrate, $q \to 0$, $V(x,z)$ reduces as expected to the potential of a single wall

$$V_{\mathrm{planar}}(z) = -\frac{2A}{z^3}. \tag{9}$$

Note that we require a positive Hamaker constant to correspond to the case where a liquid layer forms upon the substrate.

Minimization of the functional (2) with respect to $l(x)$ leads to the Euler–Lagrange equation

$$\frac{\mathrm{d}^2 l}{\mathrm{d}x^2} - \frac{1}{\sigma}\left[1+\left(\frac{\mathrm{d}l}{\mathrm{d}x}\right)^2\right]^{3/2}\{V(x,l(x)) + \Delta\tilde{\mu}\} = 0. \tag{10}$$

The Hamaker constant A, the number density difference $\Delta n = n_\mathrm{l} - n_\mathrm{g}$, and the interfacial tension σ all vanish at the critical point. We adopt the customary power-law temperature dependence

$$\sigma \sim \sigma_0 t^{\mu} \tag{11}$$

$$\Delta n \sim \Delta n_0 t^{\beta} \tag{12}$$

$$A \sim A_0 t^{\beta}. \tag{13}$$

We will take the three-dimensional values for the exponents, $\mu = 1.264$ and $\beta = 0.328$ (Fisher and Chen 1985).

The parameters σ_0, Δn_0 and A_0 are material dependent. For a typical liquid–gas system, sulphur hexafluoride adsorbed on silica, $A_0 \sim 4 \times 10^{-22}$ J, $\sigma_0 \simeq 0.05$ J m^{-2} and $\Delta n_0 \simeq 10^{28}$ m^{-3} (Moldover 1985). The qualitative behaviour of the differential equation (10) is not affected in any radical manner by the choice of the amplitudes σ_0 and Δn_0, as we will see below.

It is convenient to introduce the scaled variables

$$L \equiv l/D \tag{14}$$

$$X \equiv x/D. \tag{15}$$

The differential equation (10) then becomes

$$\frac{\mathrm{d}^2 L}{\mathrm{d}X^2} - \frac{1}{t^{\mu-\beta}}\left[1 + \left(\frac{\mathrm{d}L}{\mathrm{d}X}\right)^2\right]^{3/2} \{c_1 V(L, X) + c_2 \Delta\mu\} = 0 \tag{16}$$

where we have defined the coefficients

$$\begin{aligned} c_1 &= A_0/\sigma_0 D^2 \\ c_2 &= D\Delta n_0/\sigma_0. \end{aligned} \tag{17}$$

The substrate potential is now given by

$$V(X, L) = -2\left\{\frac{1}{L^3} + \frac{1}{4}\left[f\left(X + \frac{1}{2}, L\right) - f\left(X - \frac{1}{2}, L\right)\right]\right\} \tag{18}$$

with

$$f(s, L) = g(s, L + q) - g(s, L). \tag{19}$$

The function $g(u, v)$ remains as given in equation (8).

The profiles $L(X)$ of the gas–liquid interface are the solutions of the differential equation (16) subject to two boundary conditions. For a planar substrate L is independent of X and we require that far away from the cleft

$$\left[\frac{\mathrm{d}L}{\mathrm{d}X}\right]_{|X| \gg 1} = 0. \tag{20}$$

By symmetry a second boundary condition is

$$\left[\frac{\mathrm{d}L}{\mathrm{d}X}\right]_{X=0} = 0. \tag{21}$$

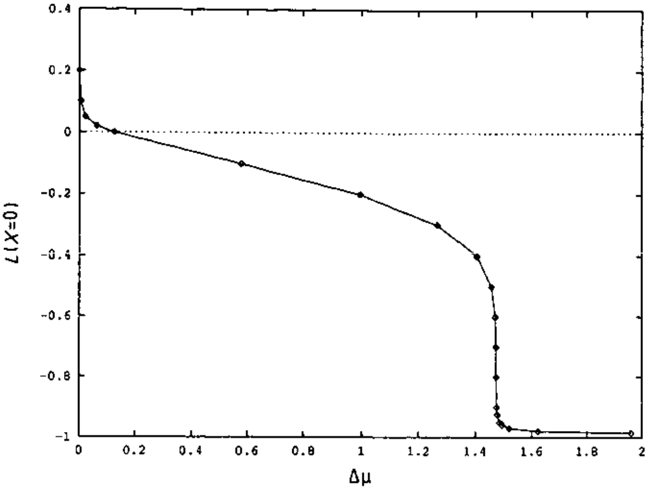

Figure 2. Reduced thickness L of the liquid layer at $X = 0$ against the chemical potential difference $\Delta\mu$ for a square well, $q = 1$. The abscissa unit is 10^{-25} J. The parameter values are $t = 0.005$, $c_1 = 3 \times 10^{-8}$, $c_2 = 10^{23}$ J^{-1}.

3. Numerical results

The first question we want to address is: when will the well fill as coexistence is approached? A natural measure of the coverage is the thickness of the liquid film in the middle of the well $L_0 \equiv L(X = 0)$. To construct the curve $L_0(\Delta\mu)$ we solved the differential equation (16) with a variable stepsize, fourth-order Runge–Kutta method. For low coverage the variable $L(X)$ changes rapidly near the edges of the well, $X = \pm 1/2$. It is the necessity of obtaining an accurate profile in this treacherous corner region that renders the adaptive stepsize necessary. The general procedure is as follows. We fix L_0, and, for a given $\Delta\mu$, calculate a profile that satisfies the equation (21). We then tune the parameter $\Delta\mu$ until the profile satisfies the boundary condition (20). The tuning of $\Delta\mu$ for low coverage within the groove is quite demanding, while for high coverage it is much quicker.

A typical result of the numerical calculations for the groove is shown in figure 2. We find that the curve $L_0(\Delta\mu)$, albeit very steep at the transition from an empty to a full slit, is continuous and single-valued. The planar thickness far from the groove, which follows immediately from equation (10),

$$L^{\text{planar}} \sim \frac{l^{\text{planar}}}{D} = \frac{1}{D}\left(\frac{2A}{\Delta n \Delta\mu}\right)^{1/3} \tag{22}$$

varies very little in the crossover region. The thickness of the thin film forming on the walls of the well is of order of the planar thickness. If $\Delta\mu$ is larger than the crossover value, then $L_0 \approx L^{\text{planar}} - qD$. When $\Delta\mu \to 0$, the expected behaviour $L_0 \approx L^{\text{planar}} \sim (\Delta\mu)^{-1/3}$ is recovered.

We worked within the interval $10^{-4} \leqslant t \leqslant 10^{-1}$. Typical values for the width of the slit were $2.5 \times 10^{-8} \leqslant D \leqslant 5 \times 10^{-7}$ m. For a fixed reduced temperature t, and a fixed depth to width factor q, the shape of $L_0(\Delta\mu)$ depends on the ratio

$$\frac{c_2}{c_1} = \frac{D^3 \Delta n_0}{A_0} \tag{23}$$

where c_1 and c_2 are the coefficients appearing in the differential equation (16). The larger the ratio c_2/c_1, the steeper the jump in $L_0(\Delta\mu)$. The jump becomes less pronounced for smaller values of the reduced temperature t.

For a fixed reduced temperature t, and a fixed ratio c_2/c_1, the jump is sharper for a larger q. In the limit $q \to \infty$ the change in coverage must become discontinuous as confirmed by figure 3.

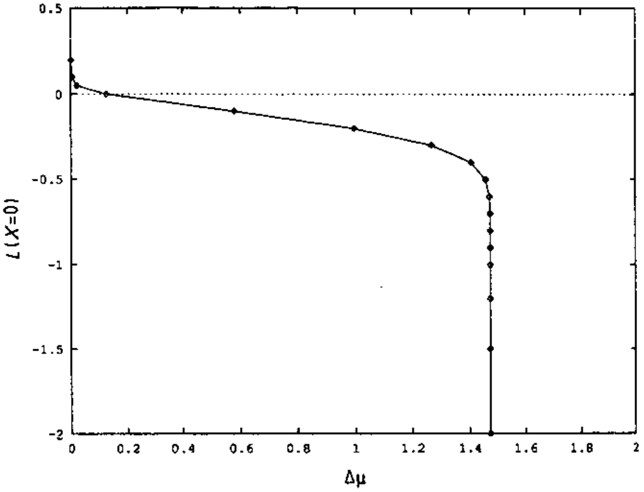

Figure 3. Reduced thickness L of the liquid layer at X=0 against the chemical potential difference $\Delta\mu$ for an infinitely deep groove, $q \to \infty$. The abscissa unit is 10^{-25} J. The parameter values are $t = 0.005$, $c_1 = 3 \times 10^{-8}$, $c_2 = 10^{23}$ J^{-1}.

As the position of the jump is well defined, it is possible to construct a phase diagram in the $(t, \Delta\mu)$ plane. This is shown in figure 4. The separatrix indicates when the liquid condenses in the groove.

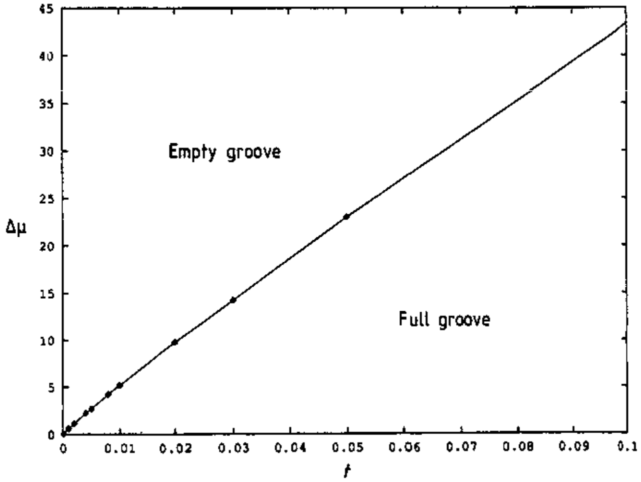

Figure 4. $\Delta\mu$ against t phase diagram for capillary condensation in a square groove, $q = 1$. The ordinate unit is 10^{-25} J. The separatrix gives the value, $(t, \Delta\mu)$, at which the liquid condensate fills the groove. The parameter values are $c_1 = 10^{-7}$ and $c_2 = 5.5 \times 10^{22}$ J^{-1}.

In addition, we have investigated the behaviour of L_0 as a function of t, rather than $\Delta\mu$. We find that the curve $L_0(t)$ is similar to $L_0(\Delta\mu)$. As t increases, L_0 jumps from a low coverage to a high coverage. Again the curve is continuous and single-valued. For completeness we have checked how L_0 behaves as q is varied, for fixed $\Delta\mu$ and t. We find that L_0 increases linearly as q decreases as expected when the interface is bound to the substrate.

We have also evaluated the free energy Ω_I given by equation (2) as a function of $\Delta\mu$. To this end we inserted the profiles that satisfy the Euler–Lagrange equation back into the free energy functional (2) and used the extended Simpson rule to evaluate the integrals.

The result of the integration is displayed in figure 5, where the free energy per unit length of the groove (calculated relative to the background contribution from the planar substrate) is plotted against $\Delta\mu$. The groove free energy exhibits a shoulder corresponding to the crossover region where the groove fills. At the shoulder its derivative, which is a measure of the coverage, undergoes a rapid change. However, as far as we can tell from our numerical data, there is no singularity.

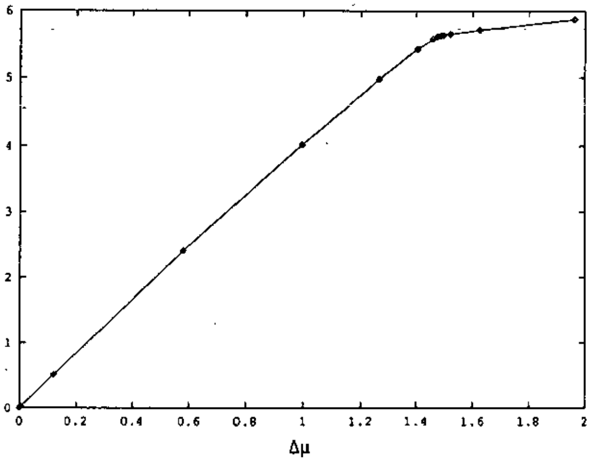

Figure 5. Free energy per unit length of the slit (calculated relative to the background contribution from the planar substrate) as a function of the chemical potential difference $\Delta\mu$ for a square groove, $q = 1$. The abscissa unit is 10^{-25} J and the ordinate unit is 10^{-5} J m^{-1}. The parameter values are $t = 0.005$, $c_1 = 3 \times 10^{-8}$, $c_2 = 10^{23}$ J^{-1}.

4. An infinitely deep groove

It is of interest to compare the numerical results presented in section 3 to those for an infinitely deep groove, $q \to \infty$ (Evans 1990). We consider two parallel plates at a distance D from each other. When the plates are coated by a liquid film of thickness l, the interfacial free energy per unit area is

$$f_S = 2V_I(l) + 2\Delta\tilde{\mu}l + 2\sigma. \tag{24}$$

where

$$V_I(l) = \frac{A}{l^2} + \frac{A}{(D-l)^2}. \tag{25}$$

The equilibrium thickness is given by

$$\frac{\mathrm{d}V_I}{\mathrm{d}l} + \Delta\tilde{\mu} = 0. \tag{26}$$

When the slit is filled with condensate, the interfacial free energy per unit area is

$$f'_S = \Delta\tilde{\mu} D. \tag{27}$$

Hence the value of $\Delta\mu$ at which the transition occurs is

$$\Delta\mu = \frac{2\sigma + 2V_I(l)}{\Delta n(D - 2l)} \tag{28}$$

where l satisfies equation (26). For a wide slit, where $V_I(l)$ can be approximated by the first term in equation (25), (28) reduces to (Derjaguin 1940)

$$\Delta\mu = \frac{2\sigma}{\Delta n(D - 3l)}. \tag{29}$$

The effect of long-range surface forces is apparent when is compared with the macroscopic Kelvin equation

$$\Delta\mu = \frac{2\sigma}{\Delta n(D - 2l)} \tag{30}$$

obtained by balancing the surface tension and the chemical potential contributions to the free energy.

The transition from a system of two plates coated by two separate liquid layers and a completely filled slit is first order. This can be evidenced by comparing the derivatives of f_S and f'_S at the transition. This is the most striking difference from the results for the finite groove presented in section 3 where the filling transition was found to be abrupt but continuous. The value of $\Delta\mu$ at which the transition occurs is given to within 1% by the modified Kelvin equation (29), for $q \gtrsim 1$.

5. Discussion

We have used an interface potential approach to study capillary condensation within an infinitely long rectangular groove in an otherwise planar substrate. From the results for an infinitely deep groove, section 4, a first-order jump from a low to a high coverage, as coexistence is approached, might have been expected. This would have been signalled by the L_0 against $\Delta\mu$ diagram displaying a loop or capillary spinodal (Evans *et al* 1986).

However, our numerical calculations show that the crossover from a low to a high adsorption is continuous. The transition becomes discontinuous only in the limit $q \to \infty$. The position of the crossover is well approximated by the modified Kelvin equation for $q \gtrsim 1$.

Similar results have been obtained by Robbins *et al* (1991) for a regular array of grooves with $q \leqslant 1$, for a parabolic groove (Darbellay, unpublished) and for a corner geometry (Cheng and Cole 1990). It is worth pointing out that in a study of capillary condensation between neighbouring spheres (Dobbs *et al* 1991) the interfacial potential approach *did* predict a first-order transition giving evidence that the lack of such a transition is not an artifact of the method itself.

The groove is a one-dimensional system. Hence, even if the transition is first order it will be rounded by an amount $\sim \exp(-\sigma q D^2/kT)$ where $\sigma q D^2$ estimates the energy needed to form domain walls between lengths of full and empty slit (Privman and Fisher 1983). The rounding we observed did not obey this functional form. Indeed, a mean-field theory is not expected to predict finite-size rounding.

The interface potential approach itself, although it is the most flexible possibility extant for complicated substrate geometries, must be treated with circumspection. Apart from being a mean field approximation based on density functional theory it relies on a sharp kink approximation for the interface and the replacing of a non-local integral by a local surface tension (Napiórkowski and Dietrich 1992). The latter approximation is known to lead to errors in the tails of the density profiles for a corner substrate (Napiorkowski *et al* 1991).

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