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Thermally activated dynamics of capillary condensation

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Abstract. This paper is devoted to the thermally activated dynamics of capillary condensation. We present a simple model which enables us to identify the critical nucleus involved in the transition mechanism. This simple model is then applied to calculate the nucleation barrier from which we can obtain information on the nucleation time. We present a simple estimation of the nucleation barrier in slab geometry both in the two-dimensional case and in the three-dimensional case. We extend the model to the case of rough surfaces which is closer to the experimental case and allows comparison with experimental data.

1. Introduction

When two surfaces are brought together in a condensable vapour near saturation, a first-order phase transition from gas to liquid occurs at small gap width provided that the liquid wets the solid substrate, i.e. has a contact angle smaller than 90° . Macroscopic considerations predict that the condensation occurs for distances between the solid surfaces H less than a critical distance H_c obeying

$$\Delta\rho \Delta\mu \simeq 2(\gamma_{SV} - \gamma_{SL})/H_c \quad (1)$$

where $\Delta\rho = \rho_l - \rho_g$ is the difference between the bulk densities of the liquid and the gas and $\Delta\mu = \mu_{sat} - \mu$ is the (positive) undersaturation in chemical potential, with μ_{sat} the chemical potential at bulk coexistence [1]. If the gas is assumed to be close to ideal, then

$$\Delta\mu \approx k_B T \ln(P_{sat}/P_{vap}) = k_B T \ln(1/RH)$$

where RH is the so-called relative humidity. At standard ambient conditions, for water ($\gamma_{LV} = 72 \text{ mJ m}^{-2}$, $\rho_L \approx 3 \times 10^{28} \text{ m}^{-3}$, $RH = 40\%$), we obtain $H_c \approx 2 \text{ nm}$. Capillary condensation is usually invoked to interpret adsorption isotherms of gases in mesoporous media [2]. This transition is now well documented, both from the experimental [3–5] and theoretical points of view [6, 7].

On the other hand, the problem of the *dynamics* of the transition has received very little attention. Experimentally, only indirect information on the dynamics is available in the literature. Experimental studies of capillary condensation using the surface force apparatus

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(SFA) technique systematically show an important hysteresis in the interaction force between two substrates when the separation of the surfaces is first decreased and then increased. This large hysteresis indicates the strong metastability of the gas phase when $H < H_c$, which persists over macroscopic times. Recent experiments with a SFA have studied the growth of the liquid meniscus after the nucleation [8], but no attention has been given to the nucleation time. Experiments measuring the cohesion inside divided materials may provide indirect information on the dynamics of the transition too [9, 11, 12]. Theoretically, lattice-gas simulations showed that the (topologically equivalent) drying transition occurs via the creation of ‘tubes’ connecting the two wetting films [13].

Going beyond these results, a theory proposing a mechanism for the dynamics of the capillary condensation is still needed.

In the following, we propose to calculate the shape and the corresponding energy of the critical nucleus. First, a simplified model in the slab geometry based on a macroscopic approach will be considered. The macroscopic description is expected to give only a qualitative picture of the mechanism but has the advantages of rendering calculations tractable and of capturing the essential features of the physics involved. We shall moreover focus on the problem of the estimation of the energy barrier to nucleation of a liquid bridge. Secondly, we show how the natural roughness of the surfaces on a nanometric scale can be taken into account in the dynamics of the transition. Applications to the adsorption kinetics in a granular medium will be discussed.

2. The slab geometry

In a first step, we restrict our attention to a system confined between two perfectly smooth and flat solid surfaces, and in contact with a reservoir of temperature T and chemical potential μ .

Let us consider the situation in which planar liquid films of varying thickness e ($e < H/2$) develop on both solid surfaces. Following Evans *et al* [6, 14], the grand potential of the system may be written as

$$\Omega = -p_V V_V - p_L V_L + 2\gamma_{SL} A + 2\gamma_{LV} A \quad (2)$$

where V_V (V_L) is the volume of the gas (liquid) phase and A is the surface area. Using $V_L = 2Ae$, $V_V = A(H - 2e)$ and $p_V - p_L \simeq \Delta\rho \Delta\mu$, one gets

$$\Delta\omega(e) \equiv \frac{1}{A}(\Omega - \Omega(e = 0)) = \Delta\rho \Delta\mu 2e. \quad (3)$$

We note that this description is strictly applicable only to slits with smooth walls, where the fluid–substrate interaction potential depends only on the relative position a fluid molecule with respect to the wall. The discrete nature of the substrate is thus neglected, as was done e.g. by Evans *et al* [14] (see however reference [10]). Note that in the complete-wetting situation, $\Omega(e = 0)$ can be identified with Ω_V , the grand potential of the system filled with the gas phase only. The situation with $e = H/2$ corresponds to the opposite case where the two liquid films merge to fill the pore. The grand potential thus exhibits a discontinuity at $e = H/2$ corresponding to the disappearance of the two liquid–vapour interfaces, and its value is reduced to $2\gamma_{LV}A$. When $e = H/2$, expression (3) must then be replaced by $\Delta\omega(e = H/2) = -\Delta\rho \Delta\mu (H_c - H)$, where H_c is the critical distance defined in equation (1). One may note that the minimum of the grand potential corresponds to a complete filling of the pore by the liquid phase when $H < H_c$, as expected. If we now allow deformation of the interfaces, the corresponding cost has to be added to the grand potential. We assume also a

mirror symmetry of the interfaces, so one finds in this case

$$\Delta\Omega_{tot} = \gamma_{LV} \Delta A_{LV} + \int dS \Delta\omega(e) \quad (4)$$

with $\Delta\Omega_{tot} = \Omega(\{e\}) - \Omega_V$ where $\Delta A_{LV} = A_{LV} - A$ is the excess $L-V$ area. The integration in the last term runs over the solid surface.

2.1. The 2D case

Let us consider first the 2D case. Within the small-slope assumption, i.e. $|de/dx| \ll 1$, $\Delta A_{LV} \simeq \int dx \gamma_{LV} |\nabla e|^2$, extremization of the grand potential leads to the following Euler-Lagrange equation for $e(x)$, where x denotes the lateral coordinate:

$$2\gamma_{LV} \frac{d^2 e}{dx^2} - \frac{d \Delta\omega(e)}{de} = 0. \quad (5)$$

We look for solutions satisfying $e = 0$ and $de/dx = 0$ at infinity. We can choose $e(x=0) = H/2$ to fix the origin. The complete solution, depicted in figure 1(a), can be obtained in the form of parabolic branches with a spatial extent $x_c = \sqrt{HR_c}$ where $R_c = H_c/2$. Let us note that the cusp in the solution for $x = 0$ stems from the discontinuity of $\Delta\omega$ for $e = H/2$ resulting from the assumption of an infinitesimally narrow liquid-vapour interface. Condensation thus occurs through the excitation of short-wavelength fluctuations, in agreement with the simulation results for the drying transition [13]. The corresponding energy of the nucleus (per unit length in the perpendicular direction) can be calculated by integration of equation (4):

$$\Delta\Omega^\ddagger = \frac{4}{3} (\Delta\mu \Delta\rho \gamma_{LV})^{1/2} H^{3/2}. \quad (6)$$

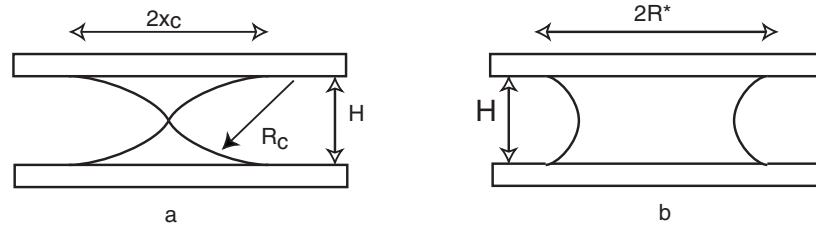


Figure 1. (a) A picture of the critical nucleus for capillary condensation in two dimensions and the perfect-wetting case ($\theta = 0$). The radius of curvature of the meniscus is equal to $R_c = H_c/2$; this is only approximately obeyed within the small-slope assumption. See the text for details. (b) A picture of the critical nucleus in three dimensions and the perfect-wetting case. See the text for details.

It is easy to check that $\Delta\Omega^\ddagger$ corresponds to a saddle point of the grand potential. It is greater than the free energies of both the gas and liquid phases. We just point out that the parabolic solution obtained above is the small-slope approximation to the circle with radius of curvature R_c .

We also mention that the prediction for $\Delta\Omega^\ddagger$ in equation (6) is in agreement with numerical simulation results, obtained using a Landau-Ginzburg model for the grand potential of the system together with a non-conserved Langevin dynamics. Full details of these simulations are given elsewhere [15].

These results can be generalized to the partial-wetting case. The only difference is that the contact angle θ on the surfaces is now non-vanishing and obeys Young's law, $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$. To leading order in H/H_c , one gets [15]

$$\Delta\Omega^\dagger \simeq 2\gamma_{LV} \sin \theta H. \tag{7}$$

2.2. *The 3D case*

The previous approach can now be directly generalized to the 3D case. In fact, maximization of the grand potential, equation (4), leads to two *mechanical equilibrium* conditions: the usual Laplace equation, relating the local curvature κ to the pressure drop $\gamma_{LV}\kappa = \Delta p \simeq \Delta\mu \Delta\rho$; and Young's law, which fixes the contact angle of the meniscus on the solid substrate according to $\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$ (i.e. $\theta = 0$ in the perfect-wetting case). These non-linear equations cannot be solved analytically in 3D, but one can easily see that the corresponding critical nucleus takes the form of a liquid bridge of finite lateral extent R^* , connecting the two solid surfaces (see figure 1(b)). This finite extent results physically from the balance between a 'surface' contribution

$$\Delta\Omega_1 \approx (\Delta\rho \Delta\mu H - 2(\gamma_{SV} - \gamma_{SL}))\pi R^2$$

which drives capillary condensation, and a linear contribution $\Delta\Omega_2 \approx 2\pi\gamma_{LV}RH$ specific to the 3D case which tends to close the bridge. Maximization of the free energy gives a finite extent R^* , yielding for the free-energy barrier

$$\Delta\Omega^\dagger \approx \frac{\pi\gamma_{LV}^2}{2(\gamma_{SV} - \gamma_{SL})} \frac{H^2 H_c}{H_c - H}. \tag{8}$$

Full details for the 3D case will be given in a forthcoming paper [16].

3. **The rough case**

Although a lot can be learned from the perfectly flat slab geometry, the latter is certainly too idealized to account for the kinetics of adsorption in 'real' experimental systems. Very slow logarithmic changes measured in various static properties of granular media in the presence of humidity (see figure 3 later and the remainder of the text) [9, 11] have been related to the kinetics of the capillary condensation. As we shall show here, these logarithmic time dependences may be understood by taking into account the influence of roughness on the dynamics of capillary condensation. Let us consider a simple model consisting of two surfaces facing each other and rough on the nanometric scale, as depicted in figure 2(a). As emphasized in the introduction, capillary condensation typically occurs in pores of nanometric size. We thus have to consider the roughness of the surfaces at the *nanometre level*. Here again we shall stay with

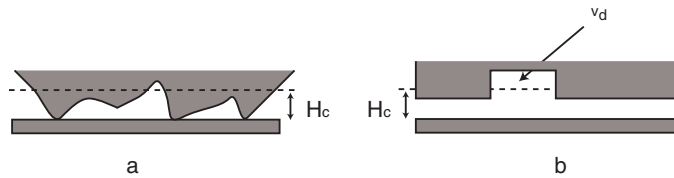


Figure 2. (a) A representation of two typical rough surfaces. Note that we consider the roughness at the nanometric scale. (b) A schematic representation of an asperity. v_d is the excess volume of the defect and a_d the area of the defect.

a macroscopic description, and focus on a qualitative picture of the influence of roughness on the transition mechanism. Without loss of generality, one may consider one of the walls to be perfectly flat. When roughness is present, there is a broad range of gaps between the surfaces. In particular, there are regions where the two surfaces are in close contact. In such regions, condensation should take place on a very short timescale. Thus at ‘early times’, one has to consider a set of wetted islands, which we shall consider as independent. Once these islands have formed, they should grow up to a point where the distance between the surfaces is equal to H_c , with the result that a meniscus of radius $R_c = H_c/2 \cos \theta$ forms at the liquid–vapour interface, allowing mechanical equilibrium.

When this happens however, the wetted area has to overcome unfavourable regions where the distance between the two surfaces is larger than H_c . Let us consider a specific jump over such a ‘defect’, as idealized in figure 2(b). We denote the ‘averaged’ gap inside the defect ($e_d > H_c$) as e_d and its area as a_d . The free-energy cost of the liquid bridge to overcoming this defect is given approximately by

$$\Delta\Omega^\ddagger \simeq a_d(\Delta\mu \Delta\rho e_d - 2(\gamma_{SV} - \gamma SL)) \equiv v_d \Delta\mu \Delta\rho \quad (9)$$

where v_d is the excess volume of the defect, $v_d = a_d (e_d - H_c)$. We can thus estimate the time taken to overcome the defect as

$$\tau = \tau_0 \exp \left\{ \frac{\Delta\Omega^\ddagger}{k_B T} \right\}. \quad (10)$$

One may expect the defects to exhibit a broad distribution of excess volume v_d , so the activation times τ are accordingly widely distributed. After a time t , only the defects with activation time τ smaller than t have been overcome. Using equations (9) and (10), these have an excess volume v_d which obeys

$$v_d < v_{dmax}(t) = k_B T (\Delta\mu \Delta\rho)^{-1} \ln(t/\tau_0).$$

The number of filled defects at a time t is then typically $N(t) = v_{dmax}(t)/v_0$ where v_0 is the typical width of the distribution of excess volume of the defects. Now, once a liquid bridge has bypassed a defect, it locally fills the volume surrounding the nucleating site and the wetted area increases by some typical (roughness-dependent) amount δA_0 . The time-dependent wetted area can thus be written as

$$A_w(t) \simeq N(t) \delta A_0 = \frac{\delta A_0}{[\Delta\mu/(k_B T)] \Delta\rho v_0} \ln \left(\frac{t}{\tau_0} \right). \quad (11)$$

Similar expressions, with logarithmic dependence on time, can be found for other quantities, like the time-dependent adsorbed amount, or the adhesion force between rough surfaces.

These logarithmic dependences have been observed in two kinds of experiment. In the first one (see figure 3(a)), we have measured the evolution of the mass of a sample of glass beads with a diameter smaller than $50 \mu\text{m}$ at fixed humidity ($RH = 68\%$) as a function of the resting time t [17]. The glass beads were first dried at high temperature and then kept at a fixed humidity controlled by the saturated-salt method described in [11]. The evolution of the mass fits well with a logarithmic behaviour, as described by equation (11). On the other hand, the cohesion force resulting from condensation of liquid bridges in a granular medium has been probed by measuring the maximum angle of stability as a function of resting time. As shown on figure 3(b), the latter exhibits a slow logarithmic dependence in agreement with equation (11) [9, 11].

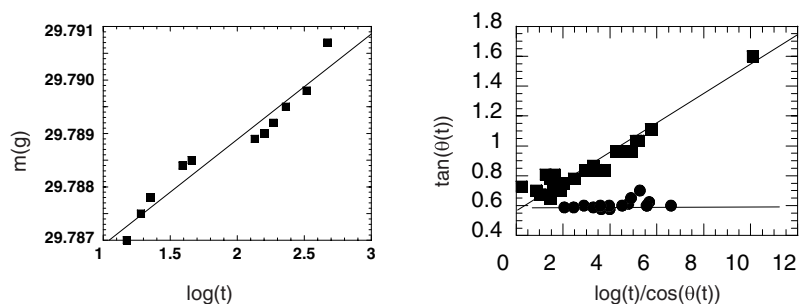


Figure 3. (a) The evolution of the mass m of a pile of glass beads of radius smaller than $50\ \mu\text{m}$ as a function of the logarithm of the resting time t in hours. Note that the time is between a few minutes and two weeks. The temperature is fixed at $31 \pm 0.1\ ^\circ\text{C}$. The relative humidity is fixed at 68% by the salt method described in reference [11]. The straight line is the best linear fit of the data. (b) The evolution of the tangent of the maximum stability angle θ_m of an assembly of glass beads as a function of the logarithm of the 'resting' time t in seconds (divided by the cosine of this angle, from geometrical arguments). This angle is measured in a cylinder. The full experimental set-up is described in [11]. \bullet : $RH = 3\%$; \blacksquare : $RH = 43\%$. The straight lines are the best linear fits of the data.

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