Thermally Activated Dynamics of the Capillary Condensation

Frdric Restagno § †, Lydric Bocquet † Thierry Biben † and Élisabeth Charlaix ‡

† Laboratoire de Physique (UMR CNRS 5672, École Normale Supérieure de Lyon, 46 allée d’Italie, 69364 Lyon Cedex 07, France,
‡ Département de Physique des Matériaux (UMR CNRS 5586), Université Lyon I, 69622 Villeurbanne cedex, France

Abstract. This paper is devoted to the thermally activated dynamics of the 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 informations 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 in the case of rough surfaces which is closer to the experimental case and allows comparison with experimental datas.

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§ To whom correspondence should be addressed. E-mail address: frestagn@ens-lyon.fr
1. Introduction

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

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

where $\Delta \rho = \rho_l - \rho_g$ is 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 $\mu_{sat}$ the chemical potential at bulk coexistence [1]. If the vapor is assumed to be a perfect gas, then $\Delta \mu \approx k_B T \ln(P_{sat}/P_{vap}) = k_B T \ln(1/RH)$, where $RH$ is the relative humidity. At standard ambient conditions for water ($\gamma_{LV} = 72$ mJ.m$^{-2}$, $\rho_L \approx 3.10^{28}$ m$^{-3}$, $H = 40\%$), we obtain $H_c \approx 2$ nm. Capillary condensation is usually invoked to interpret adsorption isotherms of gases in mesoporous media [2]. This transition is now well understood and documented, both from the experimental [3, 4, 5] and theoretical point of view [6, 7].

On the other hand, the problem of the dynamics of the transition has received very little attention. Experimentally, only indirect informations on the dynamics are available in the literature. Experimental studies of capillary condensation using the Surface Force Apparatus (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 points out the strong metastability of the gas phase when $H < H_c$, which persists over macroscopic times. Recent experiments with SFA have studied the growth of the liquid meniscus after the nucleation [8] but no attention has been given to the nucleation time which is much larger than this growing time. Experiments measuring the cohesion inside divided materials may provide indirect information on the dynamics of the transition too [9, 10, 11]. Theoretically, lattice-gas simulations showed that the (topologically equivalent) drying transition occurs via the creation of “tubes” connecting the two wetting films [12].

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

In the following, we show how to construct the critical nucleus for capillary condensation. First, a simplified model in the slab geometry keeping only the main ingredients for capillary condensation will be considered. The latter has both advantages to allow tractable calculations and to capture the essential features of the involved physics. In a second part, we show how the natural roughness of the surfaces on a nanometric scale can be taken into account on the dynamics of the transition. Applications to the adsorption kinetics in a granular medium shall 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 $\mu$.

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. [13, 6], the grand
potential of the system may be written
\[ \Omega = -p_V V - p_L V_L + 2\gamma_{SL} A + 2\gamma_{LV} A \]  
where \( V \) (resp. \( V_L \)) is the volume of the gas (resp. liquid) phase and \( A \) is the surface area. Using \( V_L = 2A e \), \( V = A(H - 2e) \) and \( p_V - p_L \approx \Delta \rho \Delta \mu \), one gets
\[ \Delta \omega(e) \equiv 1/A (\Omega - \Omega(e = 0)) = \Delta \rho \Delta \mu 2e \]  
Note that in the complete wetting situation \( \Omega(e = 0) \) can be identified with \( \Omega_V \), the grand-potential of the system filled with the gas phase only. The situation \( e = H/2 \) corresponds to the opposite case where the two liquid films merge to fill the pore. The grand potential thus exhibits a discontinuity in \( e = H/2 \) corresponding to the disappearance of the two liquid-vapor interfaces, and its value is reduced by \( 2\gamma_{LV} A \). 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 eq. (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, i.e. the thickness \( e \) is now a function of the lateral coordinates, the corresponding cost has to be added to the grand potential. We assume also a mirror symmetry of the interfaces, so that one finds in this case:
\[ \Delta \Omega_{tot} = \gamma_{LV} \Delta A_{LV} + \int dS \Delta \omega(e) \]  
with \( \Delta \Omega_{tot} = \Omega(\{e\}) - \Omega_V \) and \( \Delta A_{LV} = A_{LV} - A \) 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, \( \Delta A_{LV} \approx \int dx \gamma_{LV} |\nabla e|^2 \), extremalization of the grand potential leads to the following Euler-Lagrange equation for \( e(x) \), where \( x \) denotes the lateral coordinate:
\[ 2\gamma_{LV} \frac{d^2 e}{dx^2} - \frac{d\Delta \omega(e)}{de} = 0 \]  
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 fig 1.a, can be obtained in the form of parabolic branches with a spatial extension \( x_c = \sqrt{HR_c} \), where \( R_c = H_c/2 \). Let us note that the cusp in the solution in \( x = 0 \) stems from the discontinuity of \( \Delta \omega \) in \( e = H/2 \) resulting from the assumption of an infinitesimally narrow liquid-vapor interface. Condensation thus occurs through the exitation of short wavelength fluctuations, in agreement with the simulations results for the drying transition [12]. The corresponding energy of the nucleus (per unit length in the perpendicular direction) can be calculated by integration of eq. (4):
\[ \Delta \Omega^f = \frac{4}{3} (\Delta \mu \Delta \rho \gamma_{LV})^{1/2} H^{3/2} \]  
It is easy to check that \( \Delta \Omega^f \) corresponds to a saddle-point of the grand-potential. It is greater than both free energies of the gas and liquid phases. Moreover \( \Delta \Omega^f \) is smaller than the free energy of any other configuration maximizing the grand potential since it is the only solution of finite extension. 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 mention that the prediction for $\Delta \Omega^\dagger$ in eq. 6 is in agreement with numerical simulations results, 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 \[14\].

These results can be generalized to the partial wetting case. The only difference is that the contact angle $\theta$ on the surfaces is now non vanishing and obeys Young’s law, $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$. To leading order on $H/H_c$, one gets \[14\]:

$$\Delta \Omega^\dagger \approx 2\gamma_{LV} \sin \theta H$$

(7)

2.2. The 3D case

The previous approach can now be directly generalized to the 3D case. The physical understanding of the results can be however greatly simplified if one realizes that maximization of the grand potential, eq. (4), leads to two mechanical equilibrium conditions: the usual Laplace equation, relating the local curvature $\kappa$ to the pressure drop $\gamma_{LV} \kappa = \Delta p \approx \Delta \mu \Delta \rho$; and the 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 understand that the corresponding critical nucleus takes the form of a liquid bridge of finite lateral extension $R^*$, connecting the two solid surfaces (see fig 1b). This finite extension results physically from the balance between a “surface” contribution $\Delta \Omega_1 \approx (\Delta \rho \Delta \mu \Delta \rho H - 2(\gamma_{SV} - \gamma_{SL}))\pi R^2$ 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 extension $R^*$, yielding for the free energy barrier:

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

(8)

Full details in the 3D case shall be given in a forthcoming paper \[15\].

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. In particular, very slow logarithmic depedence have been measured on
Various static properties of granular media in the presence of humidity (see fig 3 and text hereafter) [9, 10]. As we shall show hereafter, these logarithmic time dependence 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 at the nanometric scale, as depicted on fig. (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 nanometer level. Without loss of generality, one may consider that one of the walls is 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 time-scale. 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 $H_c$, so that a meniscus of radius $R_c = H_c / 2 \cos \theta$ forms at the liquid-vapor interface, allowing for mechanical equilibrium.

In doing so however, the wetted area has to overcome unfavorable regions where the distance between the two surfaces is larger then $H_c$. Let us consider a specific jump over such a “defect”, as idealized in fig. (2.b). We denote by $e_d$ the “averaged” gap inside the defect ($e_d > H_c$), and by $a_d$ its area. The free energy cost for the liquid bridge to overcome this defect is approximatively given by

$$\Delta \Omega^i \approx a_d (\Delta \mu \Delta \rho e_d - 2 \Delta \gamma)$$

$$\equiv \Delta \Omega^i$$

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

$$\tau = \tau_0 exp \left\{ \frac{\Delta \Omega^i}{k_B T} \right\}$$

One may expect the defects to exhibit a broad distribution of excess volume $v_d$, so that the activation times $\tau$ are accordingly widely distributed. After a time $t$, only the defects with an activation time $\tau$ smaller than $t$ have been overcome. Using eq. 9 and 10 these have an excess volume $v_d$ which verifies $v_d < v_{d_{\text{max}}}(t) = k_B T (\Delta \mu \Delta \rho)^{-1} \ln(t/\tau_0)$. At a time $t$, the number of overcome defects is then typically $N(t) = v_{d_{\text{max}}}(t)/v_0$ where $v_0$ is the typical width of the distribution of excess volume

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\text{Figure 2.} \ a: \text{Typical representation of two rough surfaces. Note that we consider the roughness at the nanometric scale.}
\b: \text{Schematic representation of an asperity. } v_d \text{ is the excess volume of the defect, } a_d \text{ the area of the defect.}
\]
Figure 3. a : Evolution of the mass $m$ of a pile of glass beads of radius smaller than 50 $\mu$m as a function of the logarithm of the resting time $t$ in hours. Note that the time is comprised between a few minutes and 2 weeks. The temperature is fixed at $31 \pm 0.1$ °C. The relative humidity is fixed at 68% by the salt method described in reference [10]. The straight line is the best linear fit of the data. b : Evolution of the tangent of the maximum stability angle $\theta_m$ of a assembly of glass beads as a function of the logarithm of the "resting" time $t$ in seconds (divided by the cosine of this angle which comes from geometrical arguments). This angle is measured in a cylinder. The full experimental setup is described in [10]. (•) : $RH = 3\%$, (■) : $RH = 43\%$. The straight lines are the best linear fits of the data.

of the defects. Now, once a liquid bridge has bypassed a defect, it fills locally the volume surrounding the nucleating site and the wetted area increases by some typical (roughness dependent) amount $\delta A_0$. The time dependent wetted area can thus be written:

$$A_w(t) \simeq N(t) \delta A_0 = \frac{\delta A_0}{\Delta \mu/(k_B T) \Delta \rho v_0} \ln \left( \frac{t}{t_0} \right)$$

(11)

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

These logarithmic dependence have been observed in two kinds of experiments. In the first one (see fig. 3.a), we have measured the evolution of the mass of a sample of glass beads with a diameter smaller than 50 micrometers at fixed humidity ($RH = 68\%$) as a function of the resting time $t$ [16]. The glass beads where first dried at high temperature and put at the fixed humidity controlled by the saturated-salt method described in [10]. The evolution of the mass fits well with a logarithmic behavior, as described on eq. 11. On the other hand, the cohesion force resulting from condensation of liquid bridges has been probed in a granular medium 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 eq. 11 [9, 10].

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