Nucleation Theory for Capillary Condensation

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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. These results are compared to the numerical simulation of a Landau-Ginzburg model for the liquid-vapor interface combined with a Langevin dynamics.

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Humidity is known to strongly affect the mechanical properties of many substances, like granular media or porous materials (1). Water vapor may for example condense in the pores of the medium to form liquid bridges. This phenomenon is the well known capillary condensation (see e.g. (2)). The Laplace pressure inside such liquid bridges may reach a few atmospheres, and thus results in high adhesion forces inside the material. More fundamentally, capillary condensation is a confinement induced gas-liquid phase transition. While in the bulk the gas phase has a lower free energy, and is thus the phase equilibrium, in oversaturated situations (when \( \mu > \mu_{\text{sat}} \)), a nucleation barrier can be constructed in the bulk situation, and a critical nucleus identified. The latter takes the form of a spherical droplet, with a radius \( R_0 \sim \gamma_{LV}/\Delta \mu \Delta \rho \) maximizing the free energy of the droplet. Since capillary condensation is also a first order phase transition, it should be possible to identify a critical nucleus away from the spinodal line (3). However, the situation is more complicated in a confined geometry since the size of the critical nucleus \( R_0 \) competes with other length scales, like the separation \( H \) between the walls. In the following, we show how to construct the critical nucleus for capillary condensation. A simplified model keeping only the main ingredients for capillary condensation will be first considered. The latter has both advantages to allow tractable calculations and to capture the essential features of the involved physics. In our case, chemical potential, total volume and temperature are fixed. Our aim is thus to find out the saddle-point of the grand potential of the system corresponding to the critical nucleus.

A detailed theory for the dynamics of the capillary condensation providing an estimate of the condensation time is thus still lacking. The dynamics of the bulk gas-liquid transition have received on the contrary much more interest (4). Away from the spinodal line, in oversaturated situations (when \( \mu > \mu_{\text{sat}} \)), the spinodal line, in oversaturated situations (when \( \mu > \mu_{\text{sat}} \)), the nucleation barrier can be constructed in the bulk situation, and a critical nucleus identified. The latter takes the form of a spherical droplet, with a radius \( R_0 \sim \gamma_{LV}/\Delta \mu \Delta \rho \) maximizing the free energy of the droplet. Since capillary condensation is also a first order phase transition, it should be possible to identify a critical nucleus away from the spinodal line (3). However, the situation is more complicated in a confined geometry since the size of the critical nucleus \( R_0 \) competes with other length scales, like the separation \( H \) between the walls. In the following, we show how to construct the critical nucleus for capillary condensation. A simplified model keeping only the main ingredients for capillary condensation will be first considered. The latter has both advantages to allow tractable calculations and to capture the essential features of the involved physics. In our case, chemical potential, total volume and temperature are fixed. Our aim is thus to find out the saddle-point of the grand potential of the system corresponding to the critical nucleus.

To simplify further the discussion we first consider a two dimensional system and a perfect wetting situation: \( \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \). Both assumptions shall be relaxed at the end. In our simplified description, we shall assume that the phase equilibrium is determined by macroscopic considerations, so that the \( H \) dependences of the surface tensions are totally neglected. Finally, we assume that the system exhibits the mirror symmetry with respect to the \( H/2 \) plane. 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. (5),
the grand potential of the system may be written

\[ \Omega = -p_V V_V - p_L V_L + 2\gamma_{SL} A + 2\gamma_{LV} A \]  

(2)

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

\[ \Delta \omega(e) = \frac{1}{A} (\Omega - \Omega(e = 0)) = \Delta \rho \Delta \mu \ 2e \]  

(3)

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 at \( e = H/2 \) 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. Up to now, liquid-vapor interfaces were assumed to be planar. If we 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. Due to the mirror symmetry assumption, the two films are identical, so that one finds eventually

\[ \Delta \Omega_{tot} = \int dx \ \{ \gamma_{LV} |\nabla e|^2 + \Delta \omega(e) \} \]  

(4)

with \( \Delta \Omega_{tot} = \Omega(e) - \Omega_V \) and a small slope hypothesis has been made. Extremalization of the grand potential in two dimensions leads to the following Euler-Lagrange equation for \( e(x) \), where \( x \) denote the lateral coordinate:

\[ 2\gamma_{LV} \frac{d^2 e}{dx^2} - \frac{d \Delta \omega(e)}{de} = 0 \]  

(5)

This last equation is formally equivalent to the mechanical motion of a particle of mass \( 2\gamma_{LV} \), with position \( e \) in the external potential \( -\Delta \omega(e) \); \( x \) plays the role of time. We look for solutions satisfying \( e = 0 \) and \( de/dx = 0 \) at infinity. Starting from \( e = 0 \), the “particle” is uniformly accelerated until it reaches \( e = H/2 \). We can choose this last point to fix the origin i.e. \( e(x = 0) = H/2 \). At this point, the discontinuity in the potential induces a specular reflexion, similar to a collision of the particle with a hard wall: \( de/dx \) is therefore discontinuous and antisymmetric at \( x = 0 \). After a straightforward calculation the complete solution, depicted in fig. [1], can now be obtained and is found to have a spatial extension \( x_c = \sqrt{\Pi R_c} \), with \( R_c = H_c/2 \). Explicitly one gets \( e(x) = (|x| - x_c)^2/2R_c \) for \( x \in [-x_c; x_c] \) and zero otherwise.

Let us note that the cusp in the solution at \( x = 0 \) stems from the discontinuity of \( \Delta \omega \) at \( e = H/2 \) resulting from the assumption of an infinitesimely narrow liquid-vapor interface. Condensation thus occurs through the exitation of short wavelength fluctuations, in agreement with the simulations results for the drying transition [8]. The corresponding energy of the nucleus (per unit length in the perpendicular direction) can be calculated by integrating eq. (4), to obtain

\[ \Delta \Omega^t = \frac{4}{3} (\Delta \mu \Delta \rho \gamma_{LV})^{1/2} H^{3/2} \]  

(6)

This energy can be identified with the energy barrier to overcome in order to condense the liquid phase from the metastable gas phase. When the energy barrier is not too small (compared to \( k_B T \)), the time needed to condense can be estimated to be \( \tau = \tau_0 \exp(\Delta \Omega^t/\kappa_B T) \), with \( \tau_0 \) a “microscopic” time. It is easy to check that \( \Delta \Omega^t \) corresponds to a saddle-point of the grand-potential. It is greater than both free energies of the gas and liquid phases. Moreover \( \Delta \Omega^t \) is smaller than the free energy of any other configuration maximizing the grand potential since it is the only solution of finite extension. We postpone the physical interpretation of the results to the end of the letter. We just point out that the parabolic solution obtained above is the small slope approximation to the circle with radius of curvature \( R_c \).

In order to verify the previous results, we have conducted numerical simulations of the capillary condensation in two dimensions. We start with a Landau-Ginzburg model for the grand potential of the system confined between two wall. In terms of the local density \( \rho(r) \), we write the “excess” part of the grand potential \( \Omega^{ex} = \Omega + P_{sat} V \), where \( P_{sat} \) is the pressure of the system at coexistence, as

\[ \Omega^{ex} = \int dr \left\{ \frac{m}{2} |\nabla \rho|^2 + W(\rho) + (\Delta \mu + V_{ext}(z)) \rho \right\} \]  

(7)
In this equation, $m$ is a phenomenological parameter; $V_{ext}(z)$ is the confining external potential, which we took for each wall as $V_{ext}(z) = -\epsilon(\sigma/(\Delta z + \sigma))^2$, with $\Delta z$ the distance to the corresponding wall; $\epsilon$ and $\sigma$ have the dimensions of an energy and a distance. $W(\rho)$ can be interpreted as the negative of the “excess” pressure $\mu_{sat} \rho - f(\rho) - P_{sat}$, with $f(\rho)$ the free-energy density \cite{14}. As usually done, we assume a phenomenological double-well form for $W(\rho)$: $W(\rho) = a(\rho - \rho_V)^2(\rho - \rho_L)^2$, where $a$ is a phenomenological parameter \cite{12}. The system is then driven by a non-conserved Langevin equation for $\rho$:

$$\frac{\partial \rho}{\partial t} = -\Gamma \frac{\partial \Omega_{xx}}{\partial \rho} + \eta(\mathbf{r}, t)$$

where $\Gamma$ is a phenomenological friction coefficient and $\eta$ is a Gaussian noise field related to $\Gamma$ through the fluctuation-dissipation relationship \cite{13}. An equivalent model has been successfully used for the (bulk) classic nucleation problem \cite{14}. Physically, the non-conserved dynamics assume an infinitely fast transport of matter in the system, which is justified in view of the time-scale involved for condensation. We solved (8) by numerical integration using standard methods, identical to those of ref. \cite{14}. The units of energy, length are such that $\sigma = \epsilon = 1$. Time is in unit of $t_0 = (\Gamma \epsilon \sigma^2)^{-1}$ with $\Gamma = \frac{1}{3}$. In these units, we took $m = 1.66$, $a = 3.33$, $\rho_L = 1$, $\rho_V = 0.1$. Typical values of the chemical potential and temperature are $\Delta \mu \sim 0.016$, $T \sim 0.06$ (which is roughly half the energy barrier between vapor and liquid with the form for $W(\rho)$ used in our model). Periodic boundary condition with periodicity $L_x$ were applied in the lateral direction.

Typically $L_x \sim 2H$ was used, but we have checked that increasing $L_x$ up to $20H$ does not affect the results for the activation dynamics. We emphasize that this lack of sensitivity is not an obvious result since it is known that the amplitude of capillary waves increases with the lateral dimension of the system for free interfaces \cite{3}. In our case however, the long-range effects of the fluctuations of the liquid film are expected to be screened due to the presence of the external potential. Moreover, as predicted by the model, nucleation should occur via the excitation of localized fluctuations. The observed insensitivity of the results with respect to finite size effects is then an encouraging feature for the model presented in this letter.

The simulated system is initially a gas state filling the whole pore, and its evolution is described by eq. (8). A typical evolution of the mean density in the slit $\bar{\rho}(t)$ is plotted on fig 3. An average over different realizations (from 10 to 30) is next performed to get an averaged time-dependent density $\bar{\rho}(t)$. As expected \cite{3}, due to the long range nature of the external potential a thick liquid film of thickness $\ell$ rapidly forms on both walls on a short time scale $\tau_1 (\ell \approx 3.8 \sigma$ and $\tau_1 \approx 5t_0$ in our case). The first step of the dynamics is thus the wetting of the solid substrates. This process is not thermally activated. In a second stage, fluctuations of the interfaces around their mean value $\ell$ induce after a while a sudden coalescence of the films (see fig. 3). This second process has a characteristic time $\tau$. It is numerically convenient to define the total coalescence time, $\tau_1 + \tau$, as the time for the average density in the slab between the two wetting films to reach $(\rho_V + \rho_L)/2$ \cite{14}, which corresponds in our case to the condition $\bar{\rho}(\tau + \tau_1) \approx 0.8$. The physical results do not depend anyway on the precise definition of $\tau$. In fig. 3, we plot the variation of $\ln(\tau)$ as a function of the inverse temperature $1/T$.

![FIG. 2. Averaged density as a function of time $t$ (in units of $t_0$) for a few realizations of the noise ($H = 13$, $\Delta \mu = 0.016$ and $T = 0.07$). The dashed line is the average over all the realizations, $\bar{\rho}(t)$.](image)

![FIG. 3. Logarithm of condensation time as a function of the inverse temperature ($\Delta \mu = 0.016$, $H = 13$). The dashed line is least-square fit of the datas.](image)

As expected, far from the spinodal (i.e., for large enough $H$, $H \geq 3\ell$), $\tau$ is found to obey an Arrhenius law $\tau = \tau_0 \exp(\Delta \Omega^f/k_B T)$, where $\Delta \Omega^f$ is identified as the energy barrier for nucleation. We now focus on the variations of $\ln(\tau)$ as a function of $L_x$ and $H$, which one
assumes to be mainly controlled by the variation of $\Delta \Omega$. First, as already noticed above, we found no variation of $\ln(\tau)$ as a function of $L_x$, in agreement with our prediction of a localized critical nucleus. The dependence on $H$ ($\Delta \mu$ being fixed) is plotted on fig. 4. The previous model predicts a $H^{3/2}$ dependence. However the long range of the external potential (of the van der Waals type), produces thick wetting films whose thickness has to be subtracted from $H$. A more careful analysis of the critical nucleus shows in fact that the total effective thickness of the films has to be replaced by $3\ell$ (instead of $2\ell$), in order to take correctly into account the long range character of the external potential. This result is in agreement with other theoretical and experimental findings for capillary condensation in the presence of van der Waals forces \[15\]. As seen on fig. 4, a good agreement with the theoretical prediction is found. Dependence on the other parameters ($\Delta \mu$, ..., $\epsilon$) shall be discussed in a longer version of this paper.

\[\Delta \Omega = \gamma_{LV} H_c \left( \alpha - \sin \alpha \cos(\alpha + \theta) \right) \quad (9)\]

with $\alpha$ defined through $\cos(\alpha + \theta) = \cos(\theta) - H/H_c$.

The previous result, eq. (3), is recovered in the limiting case $\theta = 0$, $H \ll H_c$. In three dimensions, the nucleus takes the form of a liquid bridge of finite lateral extension connecting the two solid surfaces, due in particular to the supplementary (negative) axisymmetric curvature. When $H$ is small compared to $H_c$, this predicts $\Delta \Omega \propto \gamma_{LV} H^2 + O(\Delta \mu)$, but the full dependence on $\Delta \mu$ for any $H$ needs a numerical resolution. This will be done in a forthcoming paper together with the corresponding simulations.

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\frac{\Delta \Omega}{\gamma} & = \frac{\gamma_{LV} H_c}{\gamma} \left( \alpha - \sin \alpha \cos(\alpha + \theta) \right) \\
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\[\text{FIG. 4. Logarithm of condensation time as a function of the “effective” width of the slab $H - 3\ell$ for fixed $\Delta \mu = 0.016$. The dashed line is the theoretical prediction $\ln(\tau) = \ln(\tau_0) + \alpha(H - 3\ell)^{3/2}$. The two parameters $\ln(\tau_0)$ and $\alpha$ have been obtained from a least-square fit of the datas in a $\ln(\tau)$ versus $(H - 3\ell)^{3/2}$ plot.}
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The simulation results in the 2D perfect wetting case are thus in agreement with the theoretical predictions. Now it is possible to relax the assumptions done in the presentation above, i.e. perfect wetting, two-dimensional system, small slopes. More generally, one may realize that the extremalization of the grand potential leads in one hand to the usual Laplace equation, relating the local curvature $\kappa$ to the pressure drop $\gamma_{LV} \kappa = \Delta \rho \approx \Delta \mu \Delta \rho$; and in the other hand, it fixes the contact angle of the meniscus on the solid substrate according to Young’s law $\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$. In our case however, the corresponding nucleus corresponds to a maximum of the grand potential. In two dimension the general solution is of the same geometrical form as the one obtained above and pictured in fig. 4, with a corresponding nucleation energy

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