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To cite this version:
Joël Puibasset. Cavitation in heterogeneous nanopores: The chemical ink-bottle. AIP Advances, 2021, 11 (9), pp.095311. 10.1063/5.0065166. hal-03405083

HAL Id: hal-03405083
https://hal.science/hal-03405083
Submitted on 27 Oct 2021

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Cavitation in Heterogeneous Nanopores: the Chemical Ink-Bottle

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KEYWORDS. Molecular simulation, cavitation, nanopores, inkbottle, chemical heterogeneity, classical nucleation theory.

ABSTRACT: The emptying of nanoporous media may either occur by meniscus recession from the outside or proceed via bubble formation in the core of the fluid (cavitation). In the latter case, the system has to overcome the high energy barrier associated to liquid rupture, and can be observed only if the porous network impedes meniscus recession. It is generally admitted that the ink-bottle geometry fulfills this condition: large cavities should be connected to the outside only through thin throats. We show that chemical heterogeneities can play a similar role (the so-called chemical ink-bottles) where cavities correspond to the pores with the lowest fluid-wall affinity, while throats are replaced by channels with the highest fluid-wall affinity. We consider a simple molecular model of nitrogen adsorption in a slit pore with different fluid-wall interactions to mimic the possible variations in the surface chemistry of realistic adsorbents. The highest-to-lowest affinity ratio is shown to be a key parameter that controls the metastability of the confined fluid. The direct measurement of the nucleation rate (lifetime method) compares well with the classical nucleation theory, with a better agreement if one takes into account the reduction of the surface tension of the small bubbles.
1. INTRODUCTION

Porous media emptying has attracted great attention, for practical as well as fundamental issues.\textsuperscript{1-11} When emptying occurs via reduction of the vapour pressure or chemical potential of the adsorbed fluid from the saturated state, two mechanisms are at play: recession of the liquid-vapour meniscus from outside or nucleation of vapour bubbles in the liquid confined in the porous media.\textsuperscript{9, 12-19}

The experimental determination of the desorption mechanism is difficult, since it is highly dependent on the elaboration of porous materials of controlled shape. Many systems have been proposed, with the common feature to contain ink-bottle pores, \textit{i.e.} large cavities connected to the outside through narrow windows (neck).\textsuperscript{9, 20-33} The principle is that cavitation is expected to occur in the cavities if the liquid is highly stretched and the meniscus cannot propagate from outside because of windows narrow enough to remain filled and stable. This scenario has been demonstrated in very recent experiments,\textsuperscript{33} opening new issues regarding the influence of geometric parameters (cavity and neck dimensions), or the influence of the surface chemistry of the pores.

To gain insight into desorption mechanism, molecular modelling offers the possibility to monitor the evolution of metastable confined fluids at the molecular scale. The most commonly used technique consists in studying the desorption isotherm of a nanopore in the grand canonical ensemble, either by Monte Carlo or by Molecular Dynamics (MD). However, these approaches are meant to describe the systems at \textit{equilibrium} with a gas reservoir, by creating or deleting molecules anywhere in the pore, and thus fail to describe the out-of-equilibrium mechanism of pore emptying which should take into account the mass transport in the pores.
It is thus proposed to consider a cavity filled with liquid and connected to an adjacent narrow pore (neck) which is half filled. The whole system is maintained in the canonical ensemble, but the chemical potential is imposed by the meniscus in the neck which plays the role of a finite reservoir. This configuration is thus more realistic than purely canonical systems of stretched fluid.\textsuperscript{34-40} It is also more realistic than the grand canonical ensemble since now the formation of a bubble in the cavity requires mass transport through the neck or window. This will improve the description of the spontaneous density fluctuations in the cavity which is an essential feature to spontaneous nucleation.

Another important issue is the chemical nature of pore walls. Theoretical models show that chemical heterogeneities in porous media are able to influence the position and shape of the adsorption/desorption isotherms, with drastic effects on hysteresis even for moderate fluid/wall potential variations.\textsuperscript{41-49} An important issue is to understand the role of these chemical variations on cavitation in porous materials. We thus propose a simple model of chemically heterogeneous pore able to produce metastable states and hysteresis. By analogy with the geometrical ink-bottle configuration, we consider a chemical ink-bottle: the large cavity is the same as for the geometric ink-bottle, but the narrow neck, which aims at stabilizing the liquid meniscus, is replaced by a region with the same geometrical dimensions as the cavity but enhanced fluid-wall interactions. We show that such a configuration is able to induce bubble nucleation in the cavity, and that cavitation is a relevant emptying mechanism in chemically heterogeneous porous media.

2. MODEL AND METHODS

2.1. Pore Models

Homogeneous slit pores: We use a simple molecular model of fluid adsorption in porous media.
We consider the example of nitrogen adsorption in silica pores, but the model is actually more generic and encompass many experimental situations. The pore geometry is chosen planar (slit pores) for several reasons: (i) it facilitates the observation of fluid density profiles and of bubbles formation; (ii) possible effects due to the curvature of the pore walls are avoided; (iii) this geometry minimizes the surface-to-volume ratio and thus maximizes the amount of bulklike fluid; (iv) the amount of fluid versus its distance to the walls follows a uniform distribution. The last two points are important regarding the localization of cavitation which is expected to occur in the core of the pore (the liquid wets the surfaces). The pore walls are chosen parallel to the x and y axis, with periodic boundary conditions in these two directions to mimic infinite pores. The dimensions are given in Fig 1a.

**Figure 1.** Schematic representation of the systems. (a) Infinite slit pore of width 3 nm, shown in perspective, with surfaces parallel to the x and y axis and periodic boundary conditions in these directions. The fluid-wall interaction V(z) is obtained by integration over the silica species with the parameters given in Table 1. To mimic a different surface chemistry, V(z) is simply multiplied by a factor h. (b) Heterogeneous slit pore of width 3 nm (side view), made of two regions: the left part (y < 0) is closed at the bottom at y = -8 nm, while the right part (y > 0) is left open with repulsive boundary conditions at y = 10 nm. The fluid-wall interaction is taken equal to V(z) in the left region, while an amplification factor h ≥ 1 is applied to the fluid-wall interaction for y > 0.
To describe the fluid-fluid and fluid-wall interactions we use simple van der Waals potentials, more specifically the Lennard-Jones (12-6) potential cut at 3 \( \sigma \), where \( \sigma \) is the molecular size. The interaction parameters are taken from Maddox et al.\(^5\) for nitrogen and Hiratsuka et al.\(^5\) for fluid-wall interactions (see Table 1). The silica walls are kept rigid and fluid-wall interactions are smoothed by integration over the atomic density of the silica species. The corresponding fluid-wall potential \( V(z) \) is given in Fig. 1a, right panel. Since the adsorption properties strongly depend on the intensity of the fluid-wall interaction, and we want to consider the impact of chemical heterogeneities, we will consider several pore models with their external potential \( V^h(z) \) amplified by a factor \( h \) : \( V^h(z) = hV(z) \) with \( h = 1, 1.2 \) and \( 1.4 \). Note that this external potential is exactly the one felt by a molecule with its fluid-wall interaction parameter multiplied by the same factor \( h \). This modulation of the fluid-wall interaction is used as a simple procedure to model more or less attractive adsorbents.

Table 1: 12-6 Lennard-Jones interaction parameters for nitrogen and silica species.\(^5\) The cross terms are obtained from the Lorentz-Berthelot mixing rules.

<table>
<thead>
<tr>
<th></th>
<th>( \varepsilon/k_B ) (K)</th>
<th>( \sigma ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>95.2</td>
<td>0.375</td>
</tr>
<tr>
<td>O</td>
<td>101.6</td>
<td>0.2708</td>
</tr>
<tr>
<td>Si</td>
<td>18.6</td>
<td>0.0677</td>
</tr>
</tbody>
</table>

Chemical ink-bottle model: The chemically heterogeneous pores are made of two regions (\( y < 0 \) and \( y > 0 \)) with different fluid-wall interactions (see Fig. 1b). The fluid-wall interaction is taken equal to the standard nitrogen-silica potential for \( y < 0 \), while it is amplified by the heterogeneity factor \( h > 1 \) for \( y > 0 \). In this case, for a molecule far enough from the central region of the pore \( y \)
= 0, the external potential equals \( V(z) \) for \( y < 0 \), and \( V^h(z) = hV(z) \) for \( y > 0 \). The situation is more complex in the central region, of the order of the interaction range (~1 nm), since the molecule interacts with the two parts of the pore with different interaction parameters. To keep the model simple, the external potential is smoothed linearly on the interval [-0.5nm; +0.5nm] between the two regions. Following the ink-bottle geometry, the pore is closed at one end (\( y = -8 \) nm) to form a cavity, with a piece of wall with the same fluid-wall interaction as in the rest of the cavity. This impacts the external potential in the bottom of the cavity over a distance equals to the interaction range, \( i.e. \) for \( y < 7 \)nm. The other end (\( z = +10 \) nm) is left open with repulsive boundary conditions so that the total number of molecules in the pore is constant. This pore construction corresponds to a chemical ink-bottle: the close ended region with \( h = 1 \) corresponds to the cavity, while the attractive region (\( h > 1 \)) corresponds to the narrow neck where the fluid-wall potential is lower.

2.2. Monte Carlo vs Molecular Dynamics

The standard adsorption/desorption isotherms are calculated in all systems (homogeneous slit pores and chemical ink-bottles). We use the Grand Canonical Monte Carlo (GCMC) technique, starting from the empty state and slowly increasing the vapour pressure (adsorption branch) until saturation is reached; the pressure is then decreased to acquire the desorption branch. It is well-known that a hysteresis develops: neither adsorption nor desorption occur at equilibrium (metastable states). Several methods exist to calculate the equilibrium pressure where both the adsorption and desorption branches have equal grand potential: this information will prove useful to interpret the results in the chemical ink-bottle.52-55

The molecular dynamics (MD) runs are meant to study the spontaneous cavitation in chemical ink-bottle, by the mean lifetime method.54,38,56 The initial configuration is prepared so that the closed region (cavity, \( y < 0 \)) is entirely filled with liquid nitrogen while the attractive region
(y > 0) is “half filled”. This system is run in the canonical ensemble (coupled to a thermostat, $T = 77.4$ K) with standard MD and an integration step of 5 fs. In the limiting case where the ink-bottle reduces to the homogeneous pore ($h = 1$), the fluid is at equilibrium and remains indefinitely stable (no bubble nucleation). This can be used to generate independent initial configurations at will (see below). An example of such a molecular configuration is given in Fig. 2, label A, where liquid nitrogen fills the cavity and a portion of the neck, while an adsorbed film is visible in the rightmost region of the neck. Since the neck region is half-filled, the liquid-vapour meniscus is free to move and therefore imposes its equilibrium chemical potential: the neck thus plays the role of the reservoir. When the pore is switched to its ink-bottle configuration (i.e. the parameter $h$ is set to a fixed value larger than 1), one observes a rapid thickening of the adsorbed film in the rightmost region of the pore and a slight decrease of the liquid density in the cavity: this is explained by the increase of the fluid-wall interaction in the neck which induces a larger fluid adsorption and a decrease of the chemical potential in the whole system including the cavity. This reorganisation of the fluid occurs within 1 ns, as shown in Fig. 2 (inset) which gives the evolution of the liquid density in the cavity as a function of time. This relaxation time is due to the mass transfer through the pore. From that time, chosen as the origin, the system has reached thermal and mechanical equilibrium. A typical molecular configuration is shown in Fig. 2, label B. For $h$ large enough, the system is shown to be metastable with a finite lifetime accessible to MD. Fig. 2 shows an example for $h = 1.4$, where the fluid density in the cavity fluctuates around a constant value during $\tau = 20.2$ ns (label C). At that time, the density exhibits a sharp decrease corresponding to the spontaneous nucleation of a vapour bubble in the cavity (see Fig. 2, label D): the averaged density in the cavity goes from its liquidlike value around $0.65 \text{ g/cm}^3$ down to $0.27 \text{ g/cm}^3$ within 0.1 ns ($\ll \tau$). After a short relaxation of 1 or 2 ns due to fluid reorganisation in the pore, the density in the cavity
fluctuates around a new value, which differs from the vapour density because the bubble growth is limited by the finite volume of the attractive region (see Fig. 2, label E).

**Figure 2.** Upper panel: reduced density of the fluid inside the cavity as a function of time \( t \).

For \( t < -1 \text{ ns} \), the molecular dynamics is performed for the homogeneous pore \( (h = 1, \text{ fluid at equilibrium}) \). At \( t = -1 \text{ ns} \), the \( h \) parameter is switched to a fixed value larger than 1 (1.4 in this case). After a short equilibration (1 ns, greyed region, see inset) the fluid in the cavity remains metastable for \( t > 0 \). After a while (denoted \( \tau \)) a rapid variation in density is observed corresponding to bubble nucleation (within 0.1 ns, greyed region) followed by a short relaxation (see inset). The labels A to E refer to particular times for which the molecular configurations are given in the lower panels.
It is observed that the nucleation delay $\tau$ strongly depends on the initial configuration, as expected for a stochastic event. We have thus prepared ten different initial configurations extracted from a long run performed with $h = 1$ for which the fluid is at equilibrium (see above). The ten lifetime values are then averaged, as expected in a stochastic model of spontaneous decay.

3. RESULTS AND DISCUSSIONS

3.1. Adsorption/desorption isotherms

The adsorption/desorption isotherms acquired by GCMC at $T = 77.4$ K in the different slit pores and the chemical ink-bottle are shown in Fig 3. For comparisons, all data are normalized to the surface area of the pores. The isotherms for the slit pores are given in the same panel, while the ink-bottle isotherms are shown separately with identical scales.

![Graph of adsorption/desorption isotherms](image)

**Figure 3.** GCMC adsorption (up triangles) and desorption (down triangles) isotherms ($T = 77.4$ K) in the pore models described in fig.1. Upper panel: homogeneous slit pores with periodic boundary conditions and three level of fluid-wall interaction: $h = 1$ (blue) corresponds to the nitrogen-silica interaction parameters given in Table 1. $h = 1.2$ and 1.4 correspond to enhanced
interaction by a factor 1.2 and 1.4 respectively (see text). Lower panel: chemical ink-bottle with $h = 1.4$ (see Fig. 1b). The vertical dotted lines are guides to the eye materializing the irreversible transitions. The vertical dashed lines correspond to equilibrium in the homogeneous slit pores. The insets give typical molecular configurations. Stars and horizontal arrow: path followed by the MD run during the spontaneous cavitation (see text).

The isotherms in the homogeneous slit pores show two distinct adsorption and desorption branches, the former being characterized by an adsorbed film and the latter by a liquidlike fluid filling the pores. The transitions between branches are sharp and irreversible: once initiated, the transition is complete and intermediate densities are out of equilibrium. The film-to-liquid transition corresponds to the capillary condensation by destabilisation of the film and formation of a liquid meniscus. The liquid-to-film transition corresponds to cavitation, i.e. formation of a gas bubble in the liquid, because of the periodic boundary conditions. Three values of the fluid-wall interaction are considered corresponding to $h = 1.0$, 1.2 and 1.4. As can be seen, the amount of fluid adsorbed along the dense liquidlike branch is moderately sensitive to the fluid-wall interaction (less than 10% variations between $h = 1.0$ and 1.4), whereas the amount of fluid adsorbed along the gaslike branch is highly sensitive (up to a factor 5 between $h = 1.0$ and 1.4). The spontaneous film-to-liquid transition (capillary condensation) occurs for a lower pressure when $h$ increases. This is explained by a larger film thickness which favours the nucleation of a liquid bridge in the pore. On the other hand, the liquid-to-film transition (cavitation) is not expected to depend on $h$ because we are in wetting conditions and thus cavitation is expected to occur in the core of the liquid. However a small dependence is observed: the half-width of the cavity being comparable to the range of the fluid-wall interaction, the liquid in the central region of the cavity is slightly stabilized
by its interaction with the walls. As expected, the equilibrium is also affected, the corresponding pressure being lower for higher fluid-wall interaction.

The chemical ink-bottle exhibits a more complex behaviour, with two-steps adsorption and desorption branches. Upon adsorption, for $P/P_{\text{sat}} < 0.6$, the amount adsorbed essentially equals to the addition of the most attractive region ($h = 1.4$) and the cavity ($h = 1$) in proportion to their size. The discrepancy is less than 10% and can be attributed to the bottom of the cavity and the intermediate zone between the two regions. At $P/P_{\text{sat}} = 0.61$ a first vertical jump is associated to the nucleation of a meniscus in the neck (where $h = 1.4$) and the subsequent filling of that region (see Fig. 3, insets). This occurs at the same pressure as for the homogeneous slit pore with $h = 1.4$, which confirms this scenario. At $P/P_{\text{sat}} = 0.67$ a second transition occurs, corresponding to the filling of the cavity (where $h = 1.0$) by meniscus advancing towards the bottom of the pore. Note that this pressure also corresponds to the equilibrium between the liquid and gas in the slit pore with $h = 1.0$, showing that the filling of the cavity occurs at equilibrium.

Upon desorption, the ink-bottle exhibits hysteresis: the system remains filled down to $P/P_{\text{sat}} = 0.50$. A sharp transition occurs just below that value, corresponding to the emptying of the cavity region where $h = 1.0$, the neck remaining filled (see Fig. 3, insets). The emptying occurs via formation of a bubble (cavitation mechanism), as for the slit pore with $h = 1.0$, and at the same relative pressure (within 2%). The complete emptying occurs at $P/P_{\text{sat}} = 0.485$ by meniscus recession in the neck (where $h = 1.4$), at a relative pressure very close to the equilibrium pressure in the slit pore with $h = 1.4$ ($P/P_{\text{sat}} = 0.49$).

The important point is that GCMC results show that the initiation of desorption can occur via cavitation mechanism (instead of meniscus propagation) in the chemically heterogeneous pore despite the fact that a liquid-gas meniscus is always present at the mouth of the bottle. Comparison
with the GCMC data in homogeneous pores enlighten the importance of the $h$ parameter, which has to be high enough so that the liquid-gas meniscus remains at the pore mouth even for pressures reaching the cavitation pressure in the cavity. This is possible if the liquidlike branch remains stable in the most attractive region (neck), i.e. if the corresponding equilibrium pressure falls below the cavitation pressure in the cavity.

It is however emphasized that the GCMC algorithm is meant to describe the system at equilibrium with a gas reservoir, and is not expected to describe the true path followed by the system during cavitation (pore emptying). In particular, the algorithm uses random displacements and addition or removal of molecules to generate new configurations, while the true nucleation mechanism follows Newton laws implying mass transfer through the pore. The next section is devoted to this mechanism by means of MD.

### 3.2. Spontaneous Cavitation

The spontaneous cavitation is examined by MD in the chemical ink-bottle. The initial configuration is prepared so that the cavity region is entirely filled, while the attractive region with $h = 1.4$ is only partially filled: the resulting total coverage equals 22.6 micromol/m$^2$. After thermal equilibration, the chemical potential in the system is uniform, and corresponds to that imposed by the liquid-gas meniscus in the partially filled neck region where $h = 1.4$, i.e. $P/P_{\text{sat}} = 0.49$. The corresponding point for this initial configuration is shown in Fig. 3 (solid star). The Monte Carlo data show that at this relative pressure, the liquid into the cavity is highly superheated (metastable) because it is out of the hysteresis of the $h = 1.0$ pore (cavity): as a consequence, a bubble is expected to nucleate in the cavity. This is indeed what is observed after a while (denoted $\tau$) which depends on the particular initial configuration. Once nucleated, the bubble grows irreversibly until the neck is filled. At that point the system is at equilibrium, the chemical potential being imposed by the
meniscus which is now in the cavity, \( i.e. \ P/P^{\text{sat}} = 0.67 \). The corresponding point is shown in Fig. 3 (empty star). The horizontal arrow materializes the path followed by the system (constant total number of molecules), which crosses the hysteresis.

![Figure 4](image)

\textbf{Figure 4.} (a) Schematic representation of the localisation (crosses) of the nucleation centres in the chemical ink-bottle (Fig.1 b). The greyed region corresponds to the average localisation of the liquid before nucleation \( (0 < t < \tau) \), \( i.e. \) when the system is metastable. The arrow gives the scale corresponding to 2 molecular diameters. (b) Solid line: cumulative distribution function of the position of the nucleation centres along the \( y \) axis; dashed line: first diagonal, corresponding to a uniform distribution. (c) Histogram of the position of the nucleation centres along \( y \).

We have measured the position of the centre of the nucleating bubbles for all simulations and gathered the results in a schematic representation of the ink-bottle (see Fig 4a). The region of the pore filled with liquid nitrogen when the nucleation occurs has been represented by the greyed
region. As can be seen, the nucleations do not occur everywhere in this greyed region: more specifically, all nucleations occur in the cavity region (y < 0), except of course in the bottom of the pore (y < -7 nm) due to the fluid-wall interaction. No unexpected events are observed in the region around y = 0 where h varies linearly: the transition is smooth enough without destabilisation of the fluid structure. Visual inspection shows that nucleation preferentially occurs in the core of the fluid, far from the walls (2 molecular diameters), supporting the homogeneous nucleation scenario. Fig 4b shows the cumulative distribution of the position of the nucleation centre along the main cavity axis (y). As can be seen, it departs significantly from the uniform distribution (first diagonal, dashed line). The deviation (below the diagonal) indicates that the nucleation occurs preferentially in the region of the cavity opened to the neck and the fluid reservoir. Conversely, the region close to the bottom appears less favourable for bubble nucleation. The distribution, shown in Fig. 4c, suggests that the nucleation rate decreases when going deeper into the cavity from its mouth, with a steeper decrease when approaching the bottom. We interpret this as a consequence of the mass transport required to form the bubble (the compressibility of the liquid nitrogen in the cavity is not enough to assume the volume of the nucleus).

3.3. Nucleation rate: influence of chemical heterogeneity and temperature

The bubble nucleation rate is obtained from the averaged lifetime \( \tau \) and normalised to the size of the cavity (3×3×8 nm³) without considering the fact that the nucleations actually never occur close to the walls. For \( h = 1.4 \) and \( T = 77.4 \text{ K} \), the average lifetime is \( \tau = 82 \text{ ns} \), which gives a nucleation rate of \( 1.7 \times 10^{32} \text{ m}^{-3} \text{s}^{-1} \). As expected, this is a huge value compared to experiments: the MD runs are performed at a high degree of superheat to be able to observe spontaneous nucleation within typical MD runs.
Figure 5 shows the effect of the heterogeneity factor $h$ on the nucleation rate. For $T = 77.4$ K, $h$ is between 1.35 and 1.55. Above $h = 1.55$, the lifetime $\tau$ (associated to metastability) is hardly measurable because it is shorter than the mechanical relaxation time at the beginning of the run (1 ns). Below $h = 1.35$, $\tau$ is larger than 1 ms, and exceeds the typical length of our MD calculations. As can be seen, the nucleation rate increases by nearly 3 orders of magnitude when changing $h$ from 1.35 to 1.55. This result shows that the chemical heterogeneity is able to induce cavitation, as would do a geometric constriction, and the heterogeneity factor $h$ plays an important role regarding the metastability of the confined liquid.

Figure 5. Cavitation rates $J$ at 77.4 and 82.4 K for the metastable liquid nitrogen confined in the chemical ink-bottle, as a function of the heterogeneity factor $h$ (main panel) or as a function of the negative liquid pressure $P_L$ at 77.4 K (inset). Symbols: MD results; dashed lines: CNT prediction with $J_0 = 1.9 \times 10^{40}$ m$^{-3}$s$^{-1}$; solid lines: CNT prediction with a constant correction factor of 0.95 for the surface tension and $J_0 = 1.8 \times 10^{39}$ m$^{-3}$s$^{-1}$.
The origin of cavitation is the tensile stress in the liquid imposed by the most attractive region (neck) which plays the role of a reservoir due to the presence of a liquid/vapour meniscus. The negative pressure $P^h_L$ in the liquid in equilibrium with the vapour at $P^h_V$ is given by $P^h_L = \rho_L k_B T \ln(P^h_V/P^{\text{sat}})$ with the assumption of an ideal vapour and an incompressible liquid; $\rho_L$ is the molecular density of the liquid, $k_B$ is Boltzmann’s constant, $T$ the temperature, and $P^h_V/P^{\text{sat}}$ is the vapour pressure in the neck relative to saturation. This pressure is that given by the liquid/vapour coexistence in a slit pore with fluid-wall interactions $V^h(z)$. The inset in Fig. 5 gives the nucleation rate versus the (negative) pressure in the liquid for $T = 77.4$ K. The cavitation occurs for negative pressures between -12 and -10 MPa. A 20% variation in pressure implies 3 orders of magnitude variation in the nucleation rate. This rapid variation suggests an activated process for evaporation. The corresponding barrier can in principle be estimated by acquiring the nucleation rate for a slightly different temperature. Figure 5 shows the results for $T = 82.4$ K, i.e. 5 K above the nitrogen boiling point. As can be seen, the nucleation rate is two orders of magnitude higher (for $h = 1.35$ or 1.40) showing the strong influence of temperature. Note that the corresponding barrier cannot be deduced from an Arrhenius plot in this temperature range due to the rapid variation of the work of nucleation (between 12.6 and 17.5 $k_B T$ as given by the classical nucleation theory, see below).

3.4. Comparison with the Classical Nucleation Theory

The classical nucleation theory (CNT)\textsuperscript{57} relates the nucleation rate $J$ to fundamental thermodynamic properties of the fluid, like surface tension and fluid pressure, that are well established for the model used:\textsuperscript{58, 59} $J = J_0 \exp(-W/k_B T)$, where $J_0$ is an attempt rate, $W = (16\pi/3) \gamma^3/(P - P_L)^2$ is the energy barrier, $k_B$ is the Boltzmann constant, $T$ the temperature and
\( \gamma \) the surface tension. Different expressions for \( J_0 \) have been proposed (equations 12 and 23 in Ref [57]) leading to a range of values between \( 6 \times 10^{39} \) and \( 3 \times 10^{41} \, \text{m}^{-3} \text{s}^{-1} \) for liquid nitrogen at 77 K. Using these formulas, the expected nucleation rate \( J \) for our fluid model in the chemical ink-bottle with \( h = 1.4 \) is between \( 5 \times 10^{31} \) and \( 2.5 \times 10^{33} \, \text{m}^{-3} \text{s}^{-1} \), in good agreement with our MD results (\( 1.7 \times 10^{32} \, \text{m}^{-3} \text{s}^{-1} \)). However, such an agreement is only poorly conclusive considering the large uncertainties in the theoretical determination of \( J_0 \). More interesting is the comparison of the variation of the nucleation rate with \( h \). As can be seen in Fig. 5, an overall agreement can be obtained within error by adjusting the attempt rate to \( J_0 = 1.9 \times 10^{40} \, \text{m}^{-3} \text{s}^{-1} \) (dashed lines), a value compatible with the CNT prediction for liquid nitrogen at 77 K given above. This agreement between CNT and MD suggests that the main hypotheses of CNT are valid.

It can however be noticed that the slope of the CNT curve at 82.4 K departs significantly from the MD data. A similar behaviour was observed when comparing CNT with experimental data on hexane or heptane.\(^{33, 60} \) A better agreement was obtained at the expense of reducing the surface tension of the nucleus due to the nanometric curvature radius.\(^{61-64} \) The same observation holds when comparing the CNT with molecular simulation calculations in bulk stretched fluids.\(^{39, 40, 65-68} \) We have followed this hypothesis and obtained a better agreement with a correction factor 0.95 applied to the surface tension and \( J_0 = 1.8 \times 10^{39} \, \text{m}^{-3} \text{s}^{-1} \) (Fig. 5, solid lines), confirming the influence of the bubble size on the surface tension in the nanometre range.

Comparison to experiments is difficult since we are in a nucleation regime (around \( 10^{32} \, \text{m}^{-3} \text{s}^{-1} \)) far beyond the experimentally accessible domain (around \( 10^{16} \, \text{m}^{-3} \text{s}^{-1} \)). Furthermore, important thermodynamic properties of the fluid model like surface tension are highly dependent on the Lennard-Jones parameters and the cutoff used to accelerate the MD calculations. One can however attempt a comparison by extrapolating the CNT predictions down to nucleation rates close to
experimental values. As shown by Fig. 5, the nucleation rate varies rapidly with the chemical heterogeneity factor $h$, and can be extrapolated down to $h = 1$ (absence of heterogeneity) using the CNT curves. For $T = 77.4$ K, the rate decreases to $10^{20}$ m$^3$s$^{-1}$, closer to experimental values. This suggests that on experimental time scales (1 to $10^3$ seconds), cavitation should be observed for $h$ values much lower than 1.4, *i.e.* for weak heterogeneities. Note that the limiting $J$ value for $h = 1$ ($10^{20}$ m$^3$s$^{-1}$) remains quite large, meaning that cavitation would occur very rapidly on experimental time scale. This is due to the fact that the pore is quite small (3 nm), and imposes to the fluid a high stretch which makes it highly metastable. This is supported by the experimental observation that hysteresis and cavitation cannot be observed in small pores. We plan to perform MD calculations in larger pores to study the pore size effects on the nucleation rate. Using a more realistic potential for N$_2$ is also considered to allow more reliable comparisons with experiments.

3. CONCLUSION

We have performed MD simulations of a simple Lennard-Jones fluid confined in a chemically heterogeneous pore. The chemical heterogeneity is such that the system is similar to a geometric ink-bottle from a thermodynamic point of view, *i.e.* the fluid in the cavity is metastable while the fluid in the neck open to the gas reservoir is stabilized by the higher fluid-wall affinity. The main conclusion of this work is that *chemical* ink-bottles (heterogeneities) are able to induce spontaneous cavitation in porous media. The calculated nucleation rate (lifetime method) compares well with the classical nucleation theory (CNT), the agreement improving if the bubble size dependence of the surface tension is taken into account. Furthermore, CNT extrapolation to low heterogeneity value (few percent in amplitude) show drastic reduction of the nucleation rates, approaching experimentally accessible values. These chemical ink-bottles are thus able to induce metastable states with lifetime observable in experimental systems, and are therefore expected to
play an important role in porous media. They can be produced by changing the surface chemistry of materials during elaboration,\textsuperscript{69} offering the possibility to elaborate controlled chemical ink-bottles. Such systems open new routes to study deeply metastable liquids in thermodynamic conditions inaccessible to geometrical ink-bottles. In particular, chemical treatment could be used to build system where non-wetting defects are absent, since these are known to impede to reach the limit of stability of stretched liquids.\textsuperscript{70-73}

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Funding Sources

We acknowledge financial support of the French National Agency through the contract CAVCONF ANR-17-CE30-0002-04.

Notes

The author declare no competing financial interest.

ACKNOWLEDGMENT
My colleagues E. Rolley and P.-E. Wolf are gratefully acknowledged for stimulating discussions and critical reading of the manuscript. We acknowledge financial support of the French National Agency through the contract CAVCONF ANR-17-CE30-0002.

ABBREVIATIONS

MD, molecular dynamics; GCMC, Grand canonical Monte Carlo; CNT, classical nucleation theory.

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