Understanding fluid transport on nanoscale is a key factor in the development of modern technologies such as nanofluidics, molecular sieving, heterogeneous catalysis, and deeper understanding of mass transfer in biological matter, porous media, and membranes. Different aspects of fluid phase equilibria under nanoscopic confinement have extensively been addressed by means of theory and experiment. In particular, size, geometry, and surface interaction effects are nowadays fairly well understood. Exploration of dynamical properties has been less studied although it has attracted renewed interest due to further developments in atomic force microscopy, surface force experiments, and the advent of nanotubes and nanofluidic devices providing an excellent basis for experimental studies. A particular phenomenon considered in this paper is capillary filling (CF) of nanochannels. This process has thoroughly been studied for open capillaries brought in contact with a liquid bath at one channel end. Under this condition, CF occurs under the competing action of the capillary force and viscous drag, giving rise to dynamics described by the Lucas–Washburn law. An alternative situation corresponds to CF in capped capillaries in contact with a vapor atmosphere. For wetting liquids, a thin adsorbed film is formed at low pressures $P$ at the channel inner surface, including the formation of a meniscus at the capped end. With further increase of $P$, the meniscus distance from the pore end scales proportional to $(P - P_0)^{-\alpha}$, where $P_0$ is the pressure of the saturated vapor and $\alpha = 1/4$ for dispersive fluid–solid interactions. At a certain pressure $P_{eq}$ (at subcritical temperatures), which one typically associates with the equilibrium capillary condensation pressure, the meniscus unbinds and the capillary fills by the liquid via the meniscus progression toward the pore opening. Thus, if the pressure is suddenly raised from low values to $P > P_{eq}$, transient uptake will occur in a few steps, including as the final one the meniscus detachment and its progression toward the pore opening. The filling velocity in this regime will be controlled by the mass transfer rates, determined by surface flow, diffusive transport, and the meniscus distance to the gas reservoir. The shorter the distance, the faster the uptake dynamics; i.e., the filling dynamics accelerates with increasing filling.

In this work, we study CF dynamics in capillaries with typical dimensions on the mesoscale (pore widths in the range of 2–50 nm). We show that, in striking contrast to the previous scenario, an interplay between thermodynamic and mass transfer properties of fluids confined to narrow capillaries may give rise to totally different mechanisms of CF. In particular, we find that stepwise increase of the external gas pressure from low values to values above $P_{eq}$ the capillary condensation transition pressure in open channels, combined with slow axial mass transfer rates may result in the occurrence of spontaneous capillary condensation events. For open channels $P_e$ exceeds $P_{eq}$ due to metastability on the adsorption branch in this case. The formation of capillary bridges occurs far from the capped end. Remarkably, in contrast to the previously described scenario, bridge formation causes the filling dynamics to slow down with increasing filling.

**MODEL**

For our study, we employ a simple cubic lattice gas model in an external field with nearest-neighbor interactions only. The configurational energy is given by

$$H(\{n_i\}) = -\frac{\epsilon}{2} \sum_{\langle ij \rangle} n_in_j + \sum_i n_i\phi_i$$

(1)

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where \(\{n_i\}\) is a set of occupation numbers on lattice coordinate vectors \(i\), \(\langle ij\rangle\) denotes the sum over all nearest-neighbor pairs, \(\varepsilon\) is an interaction constant, and \(\phi_i\) is the local external field, modeling the pore surface. The grand canonical potential in the mean field approximation (MFT) is

\[
\Omega = -\frac{\varepsilon}{2} \sum_{\langle ij\rangle} \rho_i \rho_j + \sum_i \rho_i \phi_i - \mu \sum_i \rho_i \\
+ \frac{1}{\beta} \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)]
\]

(2)

where \(\rho_i = \langle n_i \rangle\) is the ensemble average density at site \(i\), \(\mu\) is the chemical potential, and \(\beta = 1/kT\). By finding the global minimum in \(\Omega\) for fixed \(\mu\), \(V\), and \(T\), the equilibrium density distribution is found as

\[
\rho_i = (1 + e^{\beta \phi_i \sum_i \rho_i + \phi_i - \mu})^{-1}
\]

(3)

The evolution of the density distribution of confined lattice gases during relaxation processes arising from any changes in the chemical potential of the surrounding bulk phase can be evolved via \(^{24,25,30}\)

\[
\frac{\partial \rho_i(t)}{\partial t} = - \sum_j [\omega_{i\rightarrow j}(1 - \rho_j) - \omega_{j\rightarrow i}(1 - \rho_i)]
\]

(4)

where \(\omega_{i\rightarrow j}\) is the probability of a transition from site \(i\) to site \(j\). \(\omega_{i\rightarrow j}\) is chosen to follow the Metropolis transition rules. \(^{24,30}\) We refer to the theory emerging from the solution of eq 4 as dynamic mean field theory (DMFT).

Notably, DMFT takes into account the dependence of the mobility on the local density but neglects the effects of fluctuations. It may thus be inaccurate for the medium density states, especially in the critical region. \(^{29}\)

To assess the results obtained from the MFT and DMFT calculations, we compare them with those obtained from grand canonical Monte Carlo (GCMC) and Kawasaki dynamics MC (KDMC) simulations. These calculations followed the methods used and described in detail in the recent paper by Edison and Monson. \(^{31}\) KDMC is a dynamic Monte Carlo simulation where successive states are obtained by attempting moves of particles to nearest-neighbor sites using the Metropolis transition probabilities. \(^{32}\) DMFT is an approximation to the average dynamics computed from an ensemble of KDMC trajectories.

We consider a lattice gas confined in a duct-shaped capillary open at one end in the \(x\)-direction and closed at the other end. The choice of the capillary shape has only quantitative rather than qualitative effect on the results. All calculations were made by including only nearest-neighbor interactions and at the temperature \(T^* = (2/3)T_{c,b}\) where the critical temperature \(T_{c,b}\) in MFT is \(T_{c,b,MFT} = 3/2\), whereas \(T_{c,b,MC} \approx 1.128^{33}\). We compare DMFT and MC results at the same value of \(T/T_{c,b}\) in order to reduce the effects of the errors in the mean field bulk thermodynamics upon the comparison. For the surface field we use \(\phi = 3\varepsilon\), which leads to complete wetting of a free surface by the dense lattice fluid (liquid) phase.

**RESULTS**

Figure 1 shows the adsorption/desorption isotherm of normalized density as a function of relative pressure, \(P/P_0\), obtained using MFT and GCMC, where \(P_0\) is the bulk saturated vapor pressure. Both isotherms exhibit qualitatively identical behavior, showing the 2D surface transition at low gas pressures and capillary condensation transition with essentially no hysteresis at higher pressures. For the simulations there is no hysteresis within the margin of error of the simulations. There is very slight hysteresis in the MFT calculations, but this could simply be due to the limitations of the numerical work in the MFT solutions. Recently, Do and co-workers \(^{34}\) have presented evidence for hysteresis in closed channels from GCMC simulations that is more substantial than the only slight hysteresis seen here. \(^{35}\)

Our results appear to be consistent with theoretical analyses indicating no hysteresis. \(^{7}\) The differences between the GCMC and MFT results reflect the neglect of fluctuations in MFT as well as the scaling of the temperatures based on bulk critical conditions rather than a state of the confined systems. In what follows, we address the kinetics of the filling processes upon a stepwise increase of the external pressure from zero to high density states as indicated in Figure 1.

Figure 2 shows two different scenarios for the density equilibration as revealed by the DMFT calculations. It was found that, for the sufficiently short ducts, the CF process is first accompanied by a fast density increase due to the accommodation of molecules on the inner pore surface, followed by the meniscus unbinding. In the second stage, the meniscus accelerates toward the pore opening (Figure 2a). For the long ducts, the first stage is identical to the previous case, but the late-stage CF is very different. As shown in Figure 2b, after the detachment of the meniscus at the capped end, the formation of a liquid bridge occurs close to the open pore end. Once the bridge is formed, the motion of the meniscus at the capped end is arrested and CF results as the growth of the bridge. In this case, the meniscus opposite to that at the capped end recedes toward the closed pore end. Notably, we recover totally different dynamics for this scenario; i.e., it slows down with increasing time. Our calculations show that for a given set of thermodynamic (the final pressure \(P\) and structural (the duct width \(H\) and length \(L\)) parameters there is a sharp transition between the two CF mechanisms in DMFT. The corresponding dynamic phase diagrams for ducts of the width \(H = 6\) and \(H = 8\) lattice sites are shown in Figure 3. At a given final value of \(P/P_0\) or of the pore width we see that there is a transition to bridge formation as the pore length increases. This
transition moves to shorter pores as the final value of $P/P_0$ increases and to longer pores as the pore width increases.

Figure 4 contains more details about the two CF processes for the two representative model systems of Figure 2. Figure 4a presents the menisci positions $\xi$ during transient uptake, while Figures 4b and 4c show the evolutions of the mean densities (averaged over $y$–$z$ cross-sectional area) with progressing time. These data illuminate several interesting features about the mechanism of CF. Prior to the bridge formation, the menisci at the capped end behave identically. Second, regions with higher (over the rest part of the channel) fluid density close to the pore openings are observed. For the situation shown in Figure 4c, this density enhancement acts as a precursor for the bridge formation. Finally, the occurrence of a gradient in the average density in the low-density region of the capillary is noted. The formation of the liquid bridge eliminates the gradient; i.e., the average local density in the region surrounded by the domains of capillary condensed liquid is nearly constant and is relatively low.

As it has been mentioned earlier, the DMFT calculations do not take account of the existence of thermal fluctuations in the confined fluids. Under certain conditions, these fluctuations may facilitate the removal of metastable system states. In particular, they can promote the transition from metastable low-density to equilibrium high-density states at lower chemical potentials. This may have effects also during transient density equilibration and would challenge the findings of the DMFT calculations. In order to get deeper insight into the effects of the density fluctuations, we have therefore performed the KDMC study of the same system.

As shown in Figure 5, the KDMC simulations confirm the occurrence of two different transient equilibration pathways. In contrast to DMFT, however, the transition between the two CF mechanisms is found to be less well-defined. As exemplified in the figure insets, for one and the same set of the geometric ($L$, $H$) and thermodynamic ($P$) parameters, different KDMC trajectories can evolve by different CF mechanisms. Some trajectories revealed purely the meniscus–progression mechanism of CF, while the rest involved the formation of the capillary bridges. The overall, statistically averaged behavior is thus determined by the occurrence frequencies of either type of the trajectories. It turned out that, for short capillaries, the probability of the bridge formation was low. This probability increased with increasing capillary length. In full accordance with the DMFT predictions, the probability of a bridge formation closer to the pore openings was found to be higher. Altogether, these results conform qualitatively the transient behaviors for the average densities revealed by the DMFT calculations. In particular, the data of Figure 5a show that the late-stage CF dynamics for relatively short ducts speeds up with increasing time. For longer capillaries, however, there is a transition to a regime where the CF dynamics slows down with increasing time.

■ DISCUSSION

The occurrence of two different pathways for the equilibration dynamics in capped nanocapillaries should necessarily involve a
mechanism responsible for the symmetry breaking in the filling dynamics. We anticipate that this phenomenon emerges as a combined effect of mass transfer and thermodynamics of confined fluids. A stepwise increase of the gas pressure from a low value, corresponding to an empty or low-density state capillary, to \( P > P_n \) results in a high flux of the gas across the pore opening. The rapid increase of the overall density in the channel on the first stage (prior to the meniscus detachment from the capped end) is associated with the mass accommodation on the channel walls. This process slows down with increasing thickness of the adsorbed layers since it is accompanied by a decrease of the gradient in the chemical potential between the external gas reservoir and the fluid in the channel. Further dynamics is determined by the competition between the bridge nucleation rate, which is a function of the local, transient fluid density, and the channel width, \( \xi \) and the rate of advancement of the meniscus detached from the closed end.

The phase transformation occurs at the meniscus position, \( \xi(t) \); i.e., the meniscus advancement is driven by the conversion of an excess vapor density to the capillary condensed phase. The gradient in the chemical potential for the mass transfer along the channel is determined by the state of the system at the open end and at \( \xi(t) \). If \( \xi(t) \) is sufficiently close to the pore opening, the resulting flux will be high and will prevent the chemical potential anywhere in the channel attaining values sufficient to overcome the nucleation barrier. \( \xi \) Thus, the formation of the liquid bridges will be prohibited. In the opposite case, the bridge may be formed. In this case, the density in the low-density region surrounded by the capillary condensed domains drops to a value found for \( \mu_{eq} \). Because the mass can be supplied only from the open channel end, the phase transformation occurs predominantly at the meniscus opposite to that at the capped end. This situation is reminiscent of the classical Stefan problem, \( \xi \), which predicts that the position of the moving interface between two phases scale as

\[
\xi(t) = \xi_0 + \alpha \sqrt{t - t_0}
\]

where \( \xi_0 \) is the initial position of the interface, \( t_0 \) is the initial time, and the coefficient \( \alpha \) is determined by the mass transfer rates in the low- and high-density regions and the phase transformation rate at the meniscus. As shown in Figure 4, eq 5 nicely reproduce the result obtained in the DMFT calculations. It is worth noting that eq 5 has the same time dependence as \( t \) the Lucas–Washburn equation but has a totally different physical origin. Under certain experimental conditions, eq 5 might provide an alternative and more plausible explanation for the observation of \( \sqrt{t} \) dependence in CF experiments. \( \xi \)

The observed phenomena have a relationship with what is observed in the CF for pores open at both ends. \( \xi \) In DMFT calculations it has been seen that for shorter pores the CF dynamics occurs via the nucleation of a single liquid bridge in the pore. \( \xi \) For longer pores the CF dynamics can occur by the nucleation of two bridges, one near each end of the pore, and this has been confirmed by the KDMC simulations. \( \xi \) The formation of two bridges occurs when the nucleation rate for the bridge formation is faster than the time taken to build up sufficient mass in the pore interior to allow for bridge nucleation there. In the present case we have the competition between the rate of meniscus advance from the closed end of the pore and the rate of bridge nucleation near the pore end. For longer pores the bridge nucleation is sufficiently fast that it occurs before the meniscus formed at the closed end has advanced even halfway to the open pore end. Once the bridge
is formed near the pore end, it controls mass transfer into the pore. The remaining pore filling occurs by growth of the bridge and motion of the interior bridge meniscus back into the pore with the meniscus formed at the closed end remaining close to stationary.

**CONCLUSIONS**

In summary, by means of dynamic mean field theory of a confined lattice gas, we have shown that capillary filling of capped nanochannels from the vapor phase can occur via two different mechanisms, which are accompanied by totally different dynamics. The first well-known one refers to the filling by the meniscus detachment from the capped end and its progressive advancement toward the channel opening. In striking contrast, for other sets of thermodynamic and structural parameters, the filling can instead be accompanied by the formation of a liquid bridge in the proximity of the open end, followed by capillary filling via recession of the meniscus on the internal side of the liquid bridge toward the capped end. In this case the dynamics is found to slow down dramatically. These predictions are further confirmed using Kawasaki dynamics simulations, which include thermal density fluctuations.

These results show that the dynamics of pore filling for closed end pores can be very different from the traditionally understood mechanism. This result has potential impact in our understanding of pore filling kinetics in several contexts including recent experiments on porous silicon as well as materials with side stream pores. In ongoing work we are extending these studies to a wider range of conditions, including studies of the sensitivity to the initial and final states of the system, as well as to other pore geometries such as closed end pores as side streams in pore networks.

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Notes

The authors declare no competing financial interest.

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