I. INTRODUCTION

The properties of both pure fluids and fluid mixtures confined to nanoporous and microporous materials have found a lot of interest recently, both from the point of view of various applications, and because phase transitions in confined geometry are a problem of fundamental importance in statistical thermodynamics. Applications range from the technique to extract oil and gas from porous natural rocks, the use of artificial mesoporous materials such as various zeolites as catalysts, “molecular sieves” to separate fluids in fluid mixtures, and various microfluidic and nanofluidic devices. While in some cases (e.g., vycor glass) the random irregularity of the porous network structure is expected to lead to important physical effects, one can also study the idealized case of isolated long straight pores experimentally, both for pore widths on the scale of nanometers (e.g., filling fluids into carbon nanotubes) and for pore widths on the scale of up to 150 μm (producing arrays of such pores in silicon wafers, e.g., for the purpose of characterization of DNA put into such pores, etc.).

Since a long time it is known that the vapor to liquid transition in pores is typically shifted relative to the condition where it occurs in the bulk: for lyophilic pore walls the condensation already occurs at a chemical potential where the vapor in the bulk is still undersaturated (“capillary condensation”), but for lyophobic pore walls the opposite effect is also possible (“capillary evaporation”). To characterize these phenomena quantitatively, however, one needs to understand the extent to which wetting (or drying, respectively) phenomena exist in this restricted cylindrical geometry (obviously, infinitely thick wetting or drying layers do not exist in narrow cylinders). An experimentally important effect, that has also found a lot of theoretical attention, is the “adsorption hysteresis” that obscures the true equilibrium behavior of capillary condensation in pores, at least over some range of parameters. Another question concerns the understanding of critical phenomena when one reaches conditions where the density difference between the vapor-like and liquid-like “phases” in the pore vanishes. Here, one encounters a fundamental problem of statistical mechanics, since the correlation length of density fluctuations can show unlimited growth only along one direction (the pore axis), but one does not at all expect any phase transition for quasi-one-dimensional systems with short-range forces. Nevertheless, a lot of phase diagrams and critical points for various fluids confined in nanoscopic pores have been quoted in the experimental literature and in the theoretical work. This fluctuation-induced destruction of the phase transition is also not seen in theoretical work based on density-functional theory (related mean-field theories), and cannot be seen in computer simulations either, if one chooses pore lengths not much larger than the pore diameter, as is done in many cases, or if one constrains fluctuations by other methods.

In the present work, we wish to contribute to the theoretical understanding of these problems, presenting computer simulations of two models, the Ising/lattice gas model confined in cylindrical geometry (as well as its two-dimensional analog, Ising strips of finite width), and the Asakura-Oosawa (AO) model for colloid-polymer...
mixtures\cite{62,63,71,88}, confined in cylinders with hard (infinitely repulsive) walls. A distinctive feature of our work is that we pay detailed attention to the (physically relevant) case $L \gg D$ throughout.

Sec. 2 presents a selection of our numerical results for the Ising lattice, while Sec. 3 provides corresponding Monte Carlo data for the off-lattice AO model, and discusses the generic features of both models, interprets them in terms of phenomenological theoretical considerations, and draws some conclusions on pertinent experiments. Sec. 4 contains a brief summary of our work.

II. THE ORDER PARAMETER DISTRIBUTION FUNCTION $P_{L,D}(M)$ OF QUASI-ONE-DIMENSIONAL LATTICE GAS MODELS

A. Ising strips in the $L \times D$ geometry for $L \gg D$

Ising (lattice gas) models in quasi-one-dimensional geometry have already been considered extensively in the literature (e.g.\cite{62,63,71,88}) but here we focus attention to an aspect which (to our knowledge) has not been studied before, namely the relation between the correlation length $\xi$ in the long direction of the strip and the distribution $P_{L,D}(M)$ of the magnetization per spin $M$ in the system and the hysteresis behavior that one finds in Monte Carlo simulations applying the single spin flip algorithm\cite{39} (that realizes the kinetic Ising model with non-conserved magnetization\cite{39}). If one applies periodic boundary conditions in both $x, y$ directions, the Hamiltonian of the model simply is (we take the lattice spacing as our unit of length in this section)

$$\begin{align*}
\mathcal{H} &= -J \sum_{i=1}^{L} \sum_{j=1}^{D} S(i,j) [S(i+1,j) + S(i,j+1)] \\
&- H \sum_{i=1}^{L} \sum_{j=1}^{D} S(i,j),
\end{align*}$$

where we label the lattice sites by two indices $(i,j)$ in $x, y$ directions, $S(i,j) = \pm 1$, $J$ is the exchange energy, and $H$ the (normalized) magnetic field. Here, we are interested in the limit $L \to \infty$ for finite $D$. Note that lengths like $L, D, \xi$ etc. are dimensionless in the further analysis. First, we summarize some exactly known results which are useful for our analysis:

(i) The system does not develop a spontaneous magnetization. Rather the spin correlation function for large distances $x$ shows an exponential decay\cite{63,71,77}, for zero magnetic field,

$$g(x) = \langle S(i,j)S(i+x,j) \rangle_T \propto \exp(-x/\xi_D), \ x \to \infty .$$

with the correlation length of the strip $\xi_D$ being given by\cite{39}

$$\xi_D^{-1} = -\frac{1}{2} \gamma_0 - \frac{1}{2} \sum_{r=1}^{2D-1} (-1)^r \gamma_r$$

where $(\beta \equiv (k_BT)^{-1}),$

$$\gamma_0 = 2\beta J + \ln \tanh(\beta J)$$

and

$$\cosh \gamma_r = \cosh(2\beta J) \coth(2\beta J) - \cos(r \pi / D).$$

Note that in the limit $D \to \infty$ we simply get $\xi_D^{-1} = -\gamma_0$. At low temperatures ($\beta J$ large) Eq. (3) can be simply approximated by the result (neglecting logarithmic corrections of order $\ln D$)

$$\ln \xi_D \approx \beta D \sigma,$$

where $\sigma$ is the interfacial tension of the bulk two-dimensional Ising model\cite{21}.

$$\sigma = 2J - \beta^{-1} \ln[1 + \exp(-2\beta J) / (1 - \exp(-2\beta J))].$$

Eq. (6) may simply be understood in terms of a description of the Ising strip at low temperatures as a (dilute) gas of domain walls oriented in the $y$-direction and separating large domains of opposite magnetization\cite{21}. Such a description is plausible when one looks at snapshot pictures of the Ising strip (Fig. 1). Eq. (6) simply follows when one asks at which length $L$ of a quasi-one-dimensional system the free energy difference $\Delta F$ of a system with a domain wall (of free energy cost $F_{\text{int}}$) and
a system in a mono-domain configuration vanishes, taking the entropy gain \( \ln L \) of putting the interface somewhere, into account\(^{61,71}\).

\[
\Delta F = F_{\text{int}} - \beta^{-1} \ln L , \quad F_{\text{int}} = D\sigma .
\] (8)

However, Fig. 2 shows that in the temperature regime that is of interest for the present paper, \( 1.0 \leq k_B T / J \leq 2 / \ln(\sqrt{2} + 1) \approx 2.269 \), Eq. (6) holds only qualitatively, but not quantitatively. The exact results \{Eqs. (3)-(5)\} are also very useful to check that our Monte Carlo algorithm indeed provides a sufficiently accurate sampling: using the Wolff\(^{92}\) single cluster algorithm, systems of size \( L = 10^5 \) were simulated for \( D = 5, 10 \) and 20. The (second moment) correlation length \( \xi \) in \( x \)-direction was then obtained from a sampling of the wave-vector-dependent susceptibility \( \chi(\vec{k}) \),

\[
\chi(\vec{k}) = \beta LD(|M(\vec{k})|^2),
\]

\[
M(\vec{k}) = (LD)^{-1} \sum_{j,\ell} S(j, \ell) \exp(i\vec{k} \cdot \vec{r}_{j,\ell}) ,
\] (9)

orienting \( \vec{k} \) in \( x \)-direction and using the smallest possible value \( |\vec{k}_{\text{min}}| = k_{\text{min}} = 2\pi / L \), to obtain

\[
\xi = \frac{1}{2 \sin(k_{\text{min}}/2)} \left[ \chi(0)/\chi(\vec{k}_{\text{min}}) - 1 \right]^{1/2}. \] (10)

Eqs. (9), (10) are known as an efficient method to minimize finite size effects on the estimation of the correlation length \( \xi \) when \( L \) and \( \xi \) are of comparable size\(^{63}\), which is true for the case of the lowest temperatures studied, and then the direct estimation of \( \xi_D \) from the spin correlation function \{Eq. (2)\} becomes cumbersome. Fig. 2 shows that in this way it has been possible to “measure” the growth of the correlation length over 5 decades accurately.

As is well known, the lack of better quantitative agreement between the exact result \{Eqs. (3)-(5)\} and the approximation based on Eqs. (6)-(8) can be attributed to the “capillary wave”\(^{12,16,39}\) excitations of the interfaces, which lead to an effective repulsive interaction between neighboring domain walls\(^{94}\), leading to a correction to Eq. (9), which for large \( D \) gets replaced by\(^{62}\)

\[
\xi_D \propto D^{1/2} \exp(\beta\sigma D) .
\] (11)

However, Eq. (11) still fails in the vicinity of \( T_c \) where one rather finds\(^{81}\)

\[
\xi_D(T_c) = 4D / \pi .
\] (12)

(ii) When for \( T < T_c \) the magnetic field is varied from positive to negative values the jump from positive

![FIG. 2. Correlation length \( \xi_D \) plotted vs. \( T \) for \( D = 5 \) (a), 10 (b) and 20 (c). Full curve shows Eq. (3) while broken curve shows the approximation Eq. (6). The error bars show Monte Carlo results that were extracted from systems with \( L = 10^5 \) (cf. text). The dot highlights the correlation length of the strip at bulk criticality\(^{63}\), \( \xi_D(T_c) = 4D / \pi \). Note the logarithmic scale of the ordinate.](image)
We then obtain periodic boundary conditions. Thus instead of Eq. (15) of the strip, we can replace \( M_L \) exactly into account, first, then \( H_0 \rightarrow 0 \) for \( T < T_c \). The second term describes the rounding of the transition: it extends over a region of fields where both terms in the square bracket of the denominator in Eq. (13) are of the same order needs to be considered. In order to quantify this behavior, we define the weight of the middle peak as

\[
\chi \propto \pm \frac{M^2}{k_BT} D \xi_D \propto D^{3/2} \exp(\beta \sigma D) .
\]  

As it should be, we find that the region of the rounding (Eq. (14)) times \( \chi \max \) covers just the range \( \pm M_0 \).

The simple result for \( \chi \max \) is easily interpreted in terms of the fluctuation relation (for \( L \rightarrow \infty \); note that in the \( \sum_{i,\ell} \) all relative distances occur twice)

\[
k_BT \chi \max = LD \langle M^2 \rangle_{H=0} = (LD)^{-1} \sum_{i,j,\ell,n} \langle S(i,j)S(l,n) \rangle \approx 2M_0^2 D \int_0^{\infty} dx \exp[-x/\xi_D] = 2M_0^2 D \xi_D .
\]  

Rather than taking correlations in the \( y \)-direction exactly into account, \( \sum_j S(i,j) \) is approximated by \( M_0 DS(i,j) \) in the first approximation step in Eq. (16). Of course, Eq. (16) is not to be used near \( T_c \) where \( M_0 \rightarrow 0 \).

Being interested in the effects due to the finite length \( L \) of the strip, we can replace \( g(x) = \exp(-x/\xi_D) \) by \( g(x) = \exp(-x/\xi_D) + \exp(-(L - x)/\xi_D) \), to account for periodic boundary conditions. Thus instead of Eq. (15) we then obtain

\[
\chi \max = \chi_\infty + 2D \frac{M^2}{k_BT} \xi_D \left[ 1 - \exp(-L/\xi_D) \right].
\]  

Eq. (17) is in fact a simple description of the crossover to the maximum susceptibility in the case of very short strips \( L \ll \xi_D \) where the system does not have any interfaces in \( y \)-direction at \( H = 0 \) in its typical configuration, and the jump between \( \pm M_0 \) is controlled by the total volume \( LD \) of the strip, rounding occurring over

\[
H = \pm k_BT/(2M_0 LD)
\]  

and the susceptibility maximum being

\[
\chi \max = \chi_\infty + 2M_0^2 D L/k_BT .
\]  

While some aspects of these results were tested for the equivalent problem of a quantum Ising chain in a transverse field, we are not aware of a full test of these predictions for the standard Ising model. Albano et al. studied the finite size scaling of Ising strips in a \( D \times L \) geometry near the bulk critical temperature, demonstrating scaling properties at constant aspect ratio \( D/L \). Another study considered capillary condensation in Ising strips with boundary fields, but considered the shift of the transition only, ignoring the rounding.

When one studies phase transitions by Monte Carlo methods, the standard method of analysis is based on finite size scaling studies of the order parameter distribution function \( P_{L,D}(M) \) and its moments. Working at \( H = 0 \), we can still use the same cluster algorithm as used for the Monte Carlo calculation of the correlation length (Fig. 2), but now we are also interested in studying the effect of varying both \( L \) and \( D \) (Fig. 3). We see that at low temperatures \( P_{L,D}(M) \) has the structure familiar from studies in the standard square \( (L \times L) \) or cube \( (L \times L \times L) \) geometry; there rather sharp peaks occur at \( \pm M_\max \) close to \( \pm M_0(T) \) (cf. Fig. 4). For comparison, the exact solution for the spontaneous magnetization of an infinite Ising lattice is included. One can see that in this case finite size effects lead to slightly but systematically larger values of the magnetization.

At low temperatures, the region of \( P_{L,D}(M) \) between the peaks has a perfectly horizontal part. As is well known, this flat part is due to the existence of just two, non-interacting, interfaces crossing the system in \( y \)-direction. The free energy cost of creating two interfaces \( (\beta F_{int} \gg \ln L) \) in \( L \) the entropic contribution where the interfaces at given \( M \) are placed, \( \approx (\beta F_{int} \approx 2D\sigma(T)) \), and actually the estimation of \( \ln [P_{L,D}(M_{\max})/P_{L,D}(0)] \sim 2\beta F_{int} \) is a useful method to numerically estimate \( \sigma(T) \).

However, all the above statements apply only when \( L \ll \xi_D(T) \), and since \( \xi_D(T) \) decreases rapidly when \( T \) increases (Fig. 2) the crossover when \( L \) and \( \xi_D(T) \) are of the same order needs to be considered. In \( P_{L,D}(M) \), this crossover shows up via a three-peak-structure: near \( M = 0 \) a third peak grows and gains in weight \( W \) as \( T \) is raised, and ultimately the peaks near \( \pm M_0(T) \) have lost all their weight and just disappear in the tails of the central peak. In order to quantify this behavior, we define the weight of the middle peak as
FIG. 3. Distribution function $P_{L,D}(M)$ plotted vs. $M$ for a) $D = 10, L = 80$; b) $D = 10, L = 480$; c) $D = 5, L = 80$; d) $D = 5, L = 480$. At $M = 0$ from top to bottom: curves for decreasing temperatures as indicated.

FIG. 4. Estimates for spontaneous magnetization extracted from the positions of the peaks of $P_{L,D}(M)$. The continuous curve shows the exact solution for an infinite system. Different choices of $L$ and $D$ are indicated.

$$W = \int_{-m}^{+m} P_{L,D}(M) dM / \int_{-1}^{+1} P_{L,D}(M) dM$$

where the minima of $P_{L,D}(M)$ are denoted as $\pm m$. Of course, at higher temperatures one always reaches a “spinodal temperature” $T_{sp}(L, D)$ where $M_{\text{max}}$ and $m$ merge, and then one no longer has a 3-peak structure, and Eq. (20) loses its meaning: however, before this occurs $W$ is practically indistinguishable from unity. We also emphasize that $T_{sp}(L, D)$ depends on both $L$ and $D$ significantly, and like other “spinodals” it does not have any physical significance, for systems with short-range interactions like considered here.

Fig. 3 shows the variation of $W$ with temperature for two choices of $D$ and a range of values for $L$. We recognize a gradual increase of $W$ from $W = 0$ (two-peak structure with perfectly flat variation of $P_{L,D}(M)$ near $M = 0$) to $W = 1$ (single Gaussian peak centered at $M = 0$) as $T$ increases. However, the larger $L$ becomes the more this gradual transition is depressed to lower temperature, and the sharper it becomes. It is interesting to correlate this transition with the fact that $\xi(D,T)$ decreases from values where $\xi(D,T)$ exceeds $L$ to values where $\xi(D,T)$ is much smaller than $L$. Thus, we have marked three temperatures for each curve where $\xi(D,T) = L$ ($W$ is close to 0.1 there) and where $\xi(D,T) = L/3$ ($W$ is close to 0.9 there, i.e. the transition is essentially completed). Thus, we can define a transition temperature $T_0(L,D)$ where at $H = 0$ the strip experiences a transition from a state where it is typically ordered ($\pm M_0$) to a state where it
Eq. (6) is accurate, we can use Eqs. (6), (7) to rewrite

\[
\langle M \rangle = \langle |M| \rangle \theta(T - T_0)
\]

is typically not uniformly ordered (\(\langle M \rangle \) close to \( M = 0 \)) although it is locally ordered (because the system is split into many domains of typical length \( \xi_D(T) \ll L \)). Hence we define \( T_0(L, D) \) implicitly via

\[
\xi_D(T_0(L, D)) = L/3 \quad ,
\]

and we define the temperature width \( \Delta T \) of this transition in terms of

\[
\xi_D(T_0(L, D) - \Delta T)/\xi_D(T_0(L, D) + \Delta T) = L/(L/9) = 9 \quad ,
\]

At large enough \( L \), where \( T_0(L, D) \) is so low that Eq. (6) is accurate, we can use Eqs. (6), (7) to rewrite \( \xi_D(T) \) as \( (X(T) = [\exp(2\beta) - 1]/[\exp(-2\beta) + 1]) \), choosing henceforth units where \( J/k_B = 1 \)

\[
\xi_D(T) = [X(T)]^D
\]

and hence Eqs. (21), (22) can be rearranged as, for \( L \rightarrow \infty \) \((k_B = 1, J = 1)\):

\[
X(T_0(L, D)) = \exp \left[ \frac{1}{D} \ln(L/3) \right],
T_0(L, D) \approx 2D/[\ln(L/3)] \quad .
\]

Similarly, in this limit the width \( \Delta T \) becomes

\[
\Delta T/T_0(L, D) \approx \ln 3/\ln(L/9) \quad .
\]

Thus for \( L \rightarrow \infty \) this transition temperature goes to zero, and the transition becomes gradually sharper and sharper, but the variations (Eqs. (24), (25)) both are of order \( 1/\ln L \) and hence very slow. The inset of Fig. 5 shows that for the temperatures accessible for our study, Eq. (24) is not yet accurate.

It is possible to monitor this transition also in a more conventional way, recording either the temperature variation of the second moment \( \langle M^2 \rangle \) or the “susceptibility”, cf. Fig. 6

\[
\chi' = \beta L D (\langle M^2 \rangle - \langle |M| \rangle^2) \quad .
\]

The use of Eq. (26) as an estimate for a “susceptibility” needs comment: of course, general statistical mechanics implies that \( \chi = \langle \partial \langle M \rangle/\partial H \rangle_T = \beta L D (\langle M^2 \rangle - \langle |M| \rangle^2) \), so there does not appear any term involving the absolute value of the magnetization, and since for \( H = 0 \) we also have \( \langle M \rangle = 0 \), \( \chi \) decreases monotonously with decreasing temperature, and no maximum occurs. As long as \( L \gg \xi_D(T) \), \( \langle |M| \rangle \) is small \((\langle |M| \rangle \rightarrow 0 \text{ for } L \rightarrow \infty)\), and then \( \chi \) as defined in Eq. (26) differs from the correct susceptibility by a constant factor (namely \( 1 - 2/\pi \)). However, when \( P_{L,D}(M) \) for \( L < \xi_D(T) \) just exhibits only two peaks at \( \pm M_{\text{max}} \), we have \( \langle |M| \rangle \approx M_{\text{max}} \) while still \( \langle M \rangle = 0 \) because of the symmetry of the distribution against a sign change of \( M \). Then \( \chi' \) as defined in Eq. (26) measures the width of the two peaks of the distribution at \( \pm M_{\text{max}} \), while \( \chi \approx \beta L D M_{\text{max}}^2 \). Thus the peak of \( \chi' \) is suitable to give information where the transition from the multiple domain states at \( H = 0 \) to single domain states in a finite strip occurs.

As expected, both the peak positions of \( \chi' \) and the inflection points of \( \langle M^2 \rangle \) correlate nicely with the criterion that \( W = 0.5 \). The strong depression of this transition with increasing \( L \) is clearly seen.

For \( T > T_0(L, D) \) the peaks of \( P_{L,D}(M) \) at \( \pm M_{\text{max}} \) have disappeared, and a broad peak near \( M = 0 \) remains. One can verify (Fig. 7) that this peak is simply a Gaussian.
FIG. 6. Plot of $\langle M^2 \rangle$ (a,b) and $\chi(c,d)$ vs. temperature, for a range of values of $L$, as indicated. Cases (a,c) refer to $D = 5$, cases (b,d) to $D = 10$. The asterisk in each curves marks the temperature at which $W = 0.5$.

FIG. 7. Distribution $P_{L,D}(M)$ in the region where $W \approx 1$ but $T$ is still distinctly smaller than $T_c$, so a well-identifiable multi-domain configuration is observed. Broken curves show fit to Eq. (27). Insert compares the fitted value to the prediction, Eq. (28).

$$P_{L,D}(M) \propto \exp[-M^2/2\langle M^2 \rangle] \quad . (27)$$

Noting that \{cf. Eq. (16)\} $\langle M^2 \rangle = k_B T \chi_{\max}/LD$ we find in this region that

$$\langle M^2 \rangle = k_B T \chi_{\infty}/LD + 2M_0^2(\xi_D/L) \quad . (28)$$

The simulations are roughly compatible with this prediction (inset of Fig. 7). Finally, we draw attention to the temperature variation of the free energy barrier between the maximum of $P_{L,D}(M)$ at $M_{\max}$ and the minimum at $m$,

$$\Delta F = k_B T \ln[P_{L,D}(M_{\max})/P_{L,D}(m)] \quad . (29)$$

Fig. 8 shows a plot of $\Delta F/T$ vs. $T$ for various choices of $L$ and $D$. The temperatures where these barriers extrapolate to zero would define the “spinodal temperatures” $T_{sp}(D,L)$ already mentioned above, but this is not the point we want to make now: rather we emphasize that barriers $\Delta F \approx 10k_B T$ are reached at temperatures far below $T_c$, where the local magnetization within a domain (Fig. 4) is still large. When $\Delta F$ becomes of the order of $10k_B T$ or less, nucleation of domain walls becomes easy, when $H$ is decreased and one wants to reverse the magnetization in the system. To test this consideration, we have performed computations of the magnetization reversal process of the Ising strips, using the single spin flip Monte Carlo algorithm\textsuperscript{89} to realize a (physically at least qualitatively realistic) dynamical evolution of the system (in terms of the Kinetic Ising model\textsuperscript{90}). Starting
nothing to do with $T_c$. (It also does not have anything to do with a finite size analog of $T_c$, where no longer distinct domains of opposite magnetization in the strip can be distinguished, but one has more or less isotropic clusters of correlated spins of size $\xi_D \approx D$). Instead, it correlates rather well with $T_0(L,D)$, the temperature where no longer uniformly ordered domains (over the full length $L$ of the strip) are stable.

### B. Ising cylinders without surface fields

Now we consider the analog of Eq. (1) on the simple cubic rather than the square lattice, but remove all lattice sites with $x$ and $y$ coordinates (when we define the $z$-axis as the axis of the cylinder) that satisfy

$$x^2 + y^2 > R^2.$$  \hfill (30)

As a boundary condition, we first choose the simple free boundary condition, i.e., interactions to “missing spins” do not occur. Of course, due to the lattice structure (which does not fit to a cylindrical surface) we have necessarily inequivalent sites at the surface: i.e., for $R = 4$ any cross section of the “cylinder” is not a sphere bounded by a circle, but rather we have 4 spins with three missing neighbors each (in a positive and negative $x$, $y$ directions), on next nearest neighbor sites to those sites we have 8 spins with one missing neighbor, and then 8 spins with 2 missing neighbors follow. The consequence of this non-uniformity of the boundary condition have not been studied, however, since we do not consider it to be of real physical interest.

If one does not apply any “surface magnetic fields” $H_{\perp}^{100,101}$ at these boundaries the single cluster algorithm can be straightforwardly implemented for this problem as well, and the probability distribution $P_{L,D}(M)$ (where $D = 2R$ is the diameter of the cylinder) and its moments can be recorded, as described in Sec. II A. Fig. 10-12 show that the findings indeed are qualitatively similar. Of course, $\chi'$ in $d = 3$ dimensions is defined as (for $H = 0$)

$$\chi' = \beta N (\langle M^2 \rangle - \langle |M| \rangle^2).$$ \hfill (31)

where $N$ is the total number of spins belonging to the “cylinder”. Unlike the two-dimensional strips (with periodic boundary conditions also in the $y$-direction across the strip) now the ordering tendency is strongly suppressed already for the smallest value of $L$ and due to the missing spins at the boundary the order in the “cylinder” is destabilized as expected. The same effect is seen when one studies $L \times L$ squares or $L \times L \times L$ cubes or $L \times L \times D$ films with free boundaries, as is well known.

We also expect in this case a simple exponential decay of the spin correlation function in the axial direction of

---

**Fig. 8.** Barrier $\Delta F$ against nucleation of interfaces in Ising strips plotted vs. temperature. Several choices of $L$ and $D$ are shown as indicated. The three rightmost curves correspond to $D = 10$, the three leftmost curves to $D = 5$. In each case, from left to right: $L = 480$, 240, 80.

**Fig. 9.** Magnetization of Ising strips for $L = 480$, $D = 10$ plotted vs. field $H$ at $T = 1.6, 1.7, 1.8$ and 2.0. Runs with decreasing $H$ are shown as full curves, runs with increasing $H$ as broken curves. While for $T = 1.6$ a strong hysteresis can still be observed, a detailed analysis shows that hysteresis disappears at $T = 1.9$. At $H = 0.05$ we decrease the magnetic field in steps of $\Delta H = 0.001$, equilibrating at each state for $\Delta t = 2$ million Monte Carlo steps per spin. Fig. 9 shows some examples of the hysteresis loops that were recorded in this way. As expected, hysteresis loops become quickly narrow as the temperature is increased and when $\Delta F \approx 10k_B T$ hysteresis essentially disappears completely. As a consequence, we see that the “hysteresis critical temperature” $T_{ch}$, where hysteresis loops of our strips disappear, has
the cylinder, analogous to Eq. (2), but the corresponding correlation length $\xi_D$ is not known independently. In analogy to Eq. (9), we expect that $\xi_D$ at low temperatures (and $L \to \infty$) simply varies exponentially with the cross-sectional area $A$ of the cylinder,

$$\xi_D \propto \exp(\beta A \sigma), \quad A = D^2 \pi / 4,$$

where the simple relation between $A$ and $D$ applies for off-lattice models with strictly circular cross section of the cylinder (in the present Ising model case, $A = N_c(R)$, the number of spins in a cross sectional plane for the considered choice of $R$, i.e. $N_c(3) = 29$, $N_c(4) = 49$ and $N_c(5) = 69$). Now $\sigma$ is the interfacial free energy per spin for the three-dimensional Ising model. However, using the same reasoning as in Eqs. (8), (21) we now obtain that the effective transition temperature $T_0(L, D)$ of a long cylinder from a multi-domain configuration to the single-domain configuration is given by

$$k_B T_0(L, D)/\sigma(T_0) = A / \ln(L/3), \quad L \text{ large}.$$  

While for $T \to 0$ again $\sigma(T) \to 2J$ for planar interfaces, for the temperatures of interest for the present study Eq. (33) is not expected to be quantitatively accurate (at not so low temperatures due to boundary effects we expect that the actual interfacial energy $F_{\text{int}}$ is smaller than the asymptotic estimate $A \sigma$, for the small radii $R$ studied here). Nevertheless, Fig. (12) shows that $T_0(L, D)$ exhibits a distinct decrease with increasing $L$, as expected.
C. Ising cylinders with surface fields

When the Ising model is re-interpreted as a lattice gas, it is natural to assume that a “free surface” boundary condition is physically caused by a confining external wall, which then is expected to provide an external potential to the particles adjacent to the wall. In “magnetic language”, such a wall potential translates to a “surface magnetic field” $H_{1}$.

While in the absence of $H_{1}$ the spin reversal symmetry of the Ising model ensures that phase coexistence between domains of opposite spontaneous magnetization occurs for bulk field $H = 0$, for $H_{1} \neq 0$ this symmetry is broken. Thus, the lattice gas model in thin film geometry with $H_{1} \neq 0$ has been thoroughly discussed as a model for capillary condensation.

Choosing a surface field $H_{1} = 0.75, J = 1$ that acts on all spins in the surface layer (i.e., spins that have “missing neighbors”) we have to carry out scans where $H$ is varied to locate $H_{\text{coex}}(T)$, i.e. the field where in short pores phase coexistence occurs. At low temperatures, where for the considered choices of pore length $L$ at phase coexistence only two peaks occur in the distribution function $P_{L,D}(M)$ (cf. Fig. 13) an accurate sampling of $P_{L,D}(M)$ is possible combining the standard Metropolis algorithm with successive umbrella sampling methods. Note that the single cluster algorithm or the related Swendsen-Wang algorithm can be extended to include bulk and surface fields but become very inefficient (apart from the case where both surface and bulk fields become extremely small) and then would not present any advantage.

The location of the coexistence field $H_{\text{coex}}(T)$ in the regime where $P_{L,D}(M)$ shows only two peaks can be based on the “equal area rule” as for phase transitions in the bulk. Of course, in the present case, i.e. for finite pore diameter $D$, we still expect that this transition never becomes sharp, irrespectively how large $L$ becomes. Thus, in the limit $L \rightarrow \infty$ the susceptibility $\chi$, which now needs to be defined by

$$\chi = \beta N (\langle M^2 \rangle - \langle M \rangle^2)$$

becomes a delta function (the limiting behavior for first order transitions) only for $T \rightarrow 0$. In the case of $L$ finite where at low $T$ only two peaks in $P_{L,D}(M)$ occur, we expect that $\langle M^2 \rangle - \langle M \rangle^2$ reaches at $H = H_{\text{coex}}(T)$
a maximum of order unity which we denote as $c_{\text{max}}(T)$ (since the spin reversal symmetry is broken due to the surface field, we can no longer conclude that $\langle M \rangle = 0$ at $H = H_{\text{coex}}(T)$). Thus we conclude that $\chi$ reaches a maximum value

$$\chi_{\text{max}}(T) = \beta N c_{\text{max}}(T), \quad H = H_{\text{coex}}(T) \quad (35)$$

while in the region of fields where $P_{L,D}(M)$ has a single maximum only (at the considered low temperature where $\xi_{\text{D}}(T) \gg L$) the susceptibility $\chi$ will be of order unity. Following the reasoning of $^{113}$ we can conclude that in this region the rounding of the transitions is simply given by the condition that

$$\chi_{\text{max}} \Delta H \lesssim 1, \quad \beta \Delta H \propto 1/N, \quad \Delta H \equiv H - H_{\text{coex}}(T) \quad . \quad (36)$$

Since $N$ is very large throughout our study, $\Delta H$ is very small, and $H_{\text{coex}}(T)$ in this regime of low temperatures is rather well defined.

Of course, the situation becomes more subtle at higher temperatures, where the third peak in the distribution $P_{L,D}(M)$ appears (Fig. 13). As long as the weight of this central peak is not yet much larger than the weight of the two other, sharper, peaks, we simply can ignore this peak and still apply the equal weight rule with respect to the two outer peaks. However, the equal weight rule method for estimating $H_{\text{coex}}(T)$ becomes obsolete when the weights of the two outer peaks become relatively small (and ultimately the two outer peaks completely disappear!)

Thus, we resort to a general alternative method to estimate $H_{\text{coex}}(T)$, which requires to scan $\chi(H)$, as defined in Eq. $^{33}$, as a function of the field $H$. This method would have been very inconvenient at low temperatures - the increments $\delta H$ of the field $H$ necessary to perform such a scan would need to satisfy the condition $\delta H \ll \Delta H$ and since $\Delta H$ is so small [$\{\text{Eq. (36)}\}$ and $H_{\text{coex}}(T)$ is not known beforehand, an enormous (and not reasonable) effort of computer resources would be implied (and furthermore the transition would easily be missed due to hysteresis). However, for $T \geq T_{0}(L,D)$ hysteresis is no longer a severe problem, and the rounding of the transition is much smaller, since now $(N_{c} = \text{the number of spins in a cross sectional plane, } N = N_{c} L)$

$$\chi_{\text{max}}(T) \approx 2 \beta \xi_{\text{D}}(T) N_{c} c_{\text{max}}(T) \quad (37)$$

and thus $\chi_{\text{max}}(T)$ is much smaller than in the region where Eq. $^{33}$ holds. So $\Delta H$ is no longer so small; furthermore, one can get a first estimate for $H_{\text{coex}}(T)$ by an extrapolation from the region where $P_{L,D}(M)$ has only two peaks, and the analysis as described above works.

Thus, we have scanned the region of interest choosing steps $\Delta H = 0.0002$, carrying out runs with 2 million MC steps per spin at each state point $(H, T)$. Histogram reweighting methods were used to improve the accuracy of the results, as is standard. Fig. 14a presents typical data for the case $R = 4, L = 300$. Since we have found that also $\chi'$ as defined in Eq. $^{33}$ has a sharp peak at $H \approx H_{\text{coex}}$ we used the location $\chi_{\text{max}}$ as well. Note that in the region where $P_{L,D}(M)$ has a single peak, the width of this peak is rather narrow if $H$ differs appreciably from $H_{\text{coex}}(T)$, since there then the state of the pore is uniform, no nucleation of two-phase fluctuations takes place. Then $\langle M^{2} \rangle \approx \langle |M| \rangle^{2}$ irrespective of the value of the peak, and $\chi'$ is of order unity. Only for $H$ near $H_{\text{coex}}$ will the distribution $P_{L,D}(M)$ show some anomalous broadening, resulting from the fluctuations associated with the coexistence of multiple domains. Therefore, recording the maxima of $\chi'$, which at temperatures near $T_{0}(L, D)$ are much easier to sample (Fig. 14b), is a useful method to
estimate $H_{\text{coex}}(T)$ for $T \geq T_0(L, D)$, see Fig. 14.

It is interesting to note that the coexisting phases of the cylinder (in the region $T \leq T_0(L, D)$) are inhomogeneous. This is evidenced both by snapshot pictures (Fig. 15) and radial order parameter profiles (Fig. 16) taken for our systems. One can see that on the outside surface of the cylinder (seen in the projection snapshots of Fig. 15) there is always more disorder. The reduction of the local magnetization at the surface, when the bulk of the cylinder has positive magnetization, can be interpreted as a precursor of wetting phenomena. Of course, true wetting layers cannot form in nanopore cylinders, and hence we also do not find a transition as proposed by Liu et al.\textsuperscript{67}. Crossing the wetting transition temperature $T_w(H_1)$\textsuperscript{16,37--40} it was predicted that a transition from "plugs" to "capsules" should occur,\textsuperscript{67} and an attempt was made\textsuperscript{114} to locate this transition by Monte Carlo simulations in $L_1 \times L_1 \times L$ systems with $L_1 = 14, 20$ and 28, varying $L$ from $L = 40$ to $L = 320$, and various choices of $H_1$. However, for such rather wide and short pores the problem of multiple domains did not yet arise, and the issues about intrinsic rounding of transitions in the quasi-one-dimensional pore geometry were not studied in these investigations.\textsuperscript{67,114}

As a final point of this section, we present in Fig. 17 the "phase diagram" of our model, both in the $T - M$ plane and the $H - T$ plane. Note that this "phase diagram" is only meant to describe the phase coexistence that persists if $\xi_D(T) \gg D$ on a local scale in long cylinders (or in short cylinders, if $\xi_D(T)$ still exceeds $L$). On the scale of the axes chosen in Fig. 17, the "phase boundaries" still look sharp, although the transition line in Fig. 17 is intrinsically rounded over some width $\Delta H$, but for the temperature region shown, the rounding is still small. However, this phase diagram cannot uniquely be continued up to a "capillary critical point": when $\xi_D(T)$ has decreased to a value comparable to $D$, the rounding gets very strong, and different criteria to locate a "transition" will no longer coincide (e.g., the position of a maximum...
for \( \chi(H) \) and \( \chi'(H) \) will no longer agree, etc.) Thus, our “phase diagram” ends in an “open way” at \( T = 4.0 \): for pores as narrow as \( R = 4 \), the difference between the order parameter of the two coexisting phases then has already decreased significantly, and at slightly higher temperatures it is no longer possible to distinguish the regions of the “pure coexisting phases” inside the pore from the interfaces separating them. However, it is always of interest to study in very long pores the transition at \( \xi_D(T) \approx L/3 \) from the multiple domain phase coexistence at \( H_{\text{coex}}(T) \) to the “pure” coexisting phases inside the pore. Fig. 18a compares this transition for three choices of \( H_1 \): we see that increasing the surface field shifts the transition to lower temperatures, but the qualitative characteristics stay the same.

As in the case of the Ising strip, we can verify that in the same region of temperatures where the change of \( P_{L,D}(M) \) from the double-peak distribution to the triple-peak distribution occurs (cf. Fig. 13a) the hysteresis in the magnetization process vanishes (Fig. 18b), namely near \( T \approx 3.6 \). The figure shows that at this temperature one still can identify clearly the difference in order parameter of the vapor-like and liquid-like branch of the lattice gas model. The data in Fig. 18b) are for a rather short pore, namely \( L = 200 \): It is clear (cf. also Fig. 13a) that for a longer \( L \) this change of \( P_{L,D}(M) \) occurs for lower
temperatures, and also the onset of hysteresis occurs at the lower temperature the larger the pore length $L$ is considered.

III. COLLOID-POLYMER MIXTURES CONFINED IN CYLINDERS: A MONTE CARLO STUDY OF THE ASAKURA-OOSAWA MODEL

Colloidal dispersions have become model systems for the study of phase behavior of condensed matter, since the large size of the colloidal particles allows the use of experimental observation techniques that cannot be used for small molecular systems. Furthermore, interactions among colloidal particles are tunable to a large extent. Colloid-polymer mixtures have been particularly suitable to study liquid-vapor-like phase separation into colloid-rich and colloid-poor phases, including their interfacial behavior. There also exists a very simple theoretical model, due to Asakura and Oosawa (henceforth referred to as “AO model”), well suited for Monte Carlo simulation studies. In this model, colloids are simply described as hard spheres of radius $R_c$ while polymers are soft spheres of radius $R_p$. While overlap among colloids and between polymers and colloids is strictly forbidden, i.e. the potential energy is given by

$$U_{cc}(r < 2R_c) = \infty, \quad U_{cc}(r \geq 2R_c) = 0 \quad (38)$$

$$U_{pc}(r < R_p + R_c) = \infty, \quad U_{pc}(r \geq R_p + R_c) = 0 \quad (39)$$

two polymer coils can interpenetrate and hence overlap with no energy cost, $U_{pp}(r) = 0$ irrespective of distance $r$. Vink et al. have already performed an extensive study of capillary condensation for colloid-polymer mixtures confined between two parallel hard walls a distance $D$ apart, and have shown that for distance $D$ of the order of a few colloid diameters a crossover from three-dimensional to two-dimensional Ising critical behavior occurs. Due to the large sizes of colloid particles, it should be experimentally feasible to also study capillaries which are only a few colloids’ diameters wide, and since for particles in the size range of a $\mu m$ the atomistic corrugation of real walls clearly is negligible, fairly ideal conditions should be realizable.

In the present work, we have extended this work to confinement in cylindrical pores of diameters $D = 12R_c$ and lengths $L$ up to $L = 540R_c$, for $R_p/R_c = 0.8$. In the following, $R_c = 1$ shall be used as unit of length in this section. The Monte Carlo simulations were carried out in the grand-canonical ensemble, choosing the chemical potential $\mu_p$ of the colloids and the polymer reservoir packing fraction $\eta_p^*$

$$\eta_p^* = \left(4 \pi R_p^3 / 3\right) \exp(\mu_p / k_B T) \quad (40)$$

FIG. 19. Radial density of colloids ($\rho_c(r)$) and polymers ($\rho_p(r)$) plotted vs. distance from the cylinder axis for $\eta_p^* = 1.30$, $L = 60$, $D = 12$. Case a) shows these profiles in the vapor-like phase, case (b) for the liquid-like phase.

FIG. 20. Parallelization scheme of the “Wang-Landau” algorithm. The first row of numbers is the CPU index. $M_i$ is the number of Monte Carlo steps, which is performed. $W_i$ is the weight function of CPU $i$. The brackets denote an average weighted by the number of MC steps. The average replaces the weight function $W_i$ of every process $i$. 

\[ a \]

\[ b \]
where \( \mu_p \) is the chemical potential of the polymers, as independent control variables. Observables of interest then are both global average densities \( \rho_p = N_p/V \), \( \rho_c = N_c/V \) of colloids and polymers \( (N_p, N_c) \) are the total number of polymers and colloids in the volume \( V = (\pi D^2/4)L \) as well as the corresponding radial density profiles \( \rho_p(r) \), \( \rho_c(r) \), see Fig. 19. One can see that in the vapor-like phase the polymer density is reduced near the pore wall, while colloids are attracted to the pore wall both in the vapor-like and liquid-like phase. Note that phase coexistence in the pore was located as for the thin film case by scanning the chemical potential \( \mu_c \) until one finds a double-peak distribution, where then the equal weight rule \(^{112, 113}\) is applied to estimate the value of the chemical potential at coexistence \( \mu_{c, \text{coex}} \). As for the case of the AO model in the bulk \(^{127–129}\) and in thin film geometry \(^{130–132}\), cluster moves \(^{127}\) and successive umbrella sampling methods \(^{110}\) are applied throughout. For large systems a parallel version of the “Wang-Landau” algorithm \(^{133}\) was implemented. The idea, schematically shown in Fig. 20, is to correlate a priori independent simulations by taking averages over the weight functions iteratively generated by the “Wang-Landau” algorithm on each CPU. The average between the weight functions of the single simulations is weighted with the MC steps done so far and is used as a new weight function for all CPUs. This procedure uses only a very small amount of communication and scales therefore almost linearly up to 1440 CPUs. In comparison to the same number of non-communicating independent simulations, a reduction of the systematic error of the biasing algorithm was observed, which leads to a faster convergence of the weight function to the true free energy landscape.

While for the case shown in Fig. 19 the state of the cylinder at phase coexistence is axially homogeneous, and this fact also shows up in the probability distribution \( P_{L,D}(\eta_c) \). \( \eta_c = (4\pi R^2_c / 3)\rho_c \) being the colloid packing fraction, Fig. 21 since \( P_{L,D}(\eta_c) \) just has two peaks and is flat in between, at lower values of \( \eta_c \), one again finds a distribution with three peaks. As in the Ising case, the interpretation of the distribution exhibiting a “central” peak is the formation of multiple domain walls across the pore (Fig. 22).

Fig. 23a shows the average colloid density \( \langle \rho_c \rangle \) as a function of \( \mu_c \). The maximum value of the fluctuation \( \langle (\rho_c - \langle \rho_c \rangle)^2 \rangle \) studied as a function of \( \eta_p \) for several choices of \( L \) is shown in Fig. 23a. Also the corresponding phase diagram is shown (Fig. 23b). While in the bulk well-defined vapor-liquid like phase coexistence occurs, ending in a critical point at \( \eta_{p,cr} = 0.765 \), \( \eta_{c,cr} = 0.13 \), the phase coexistence in the cylindrical pore exists over a finite correlation length \( \xi_D \) only. The value of \( \langle \eta_c \rangle \) in the coexisting vapor-like and liquid-like phases depend on \( L \) only very weakly: however, the larger \( L \) the larger \( \eta_c \) has to be chosen to ensure that one still has phase coexistence between single-domain states in the pore, rather than a multiple domain structure.

Again it is of central importance to verify the connection between the change of the distribution \( P(\eta_c) \) with decreasing \( \eta_p \) from the double peak behavior at large \( \eta_p \) to the three-peak behavior at somewhat smaller \( \eta_p \) (cf. Fig. 21) and the disappearance of hysteresis at a value of \( \eta_c \) which is still distinctly larger than the pore critical temperature (where in Fig. 22: the vapor-like and liquid-like branches of the coexistence curve of the fluid confined in the pore have merged). This connection is verified by Fig. 23 which shows that for \( D = 12 \) and \( L = 180 \) hysteresis indeed disappears in between \( \eta_p = 1.2 \) and
and $\eta^r_p = 1.1$, while the coexistence curve branches exist up to about $\eta^c_p = 1.0$ (Fig. 23c). Again we predict that this difference between the pore critical temperature and the hysteresis critical temperature should increase with $L$. As an analogue to Fig. 8 the free energy barriers are shown in Fig. 23d for various choices of $L$.

An alternative way to explore this transition from axially symmetric phase coexistence in the cylindrical pore to a multiple domain structure uses a very long pore ($L = 1800$) which is cut into a one-dimensional array of $N_s$ subsystems, and recording the distribution $P_{D_s N_c}(N_c)$ of the number of colloids in the subsystems (Fig. 25). One can nicely see that for short enough subsystems (i.e., for $N_s \geq 60$) the subsystem is typically homogeneous, since

---

**FIG. 23.** a) Average density $\langle \rho_c \rangle$ of the colloids in a pore of linear dimensions $L = 60$, $D = 12$ plotted vs. $\mu_c$ at various values of $\eta^r_p$ as indicated. b) Plot of the maximum value of the density fluctuation for $D = 12$ and various $L$ as indicated, plotted vs. $\eta^r_p$. c) Phase diagram of the AO model in the plane of variables $(\eta^r_p, \eta_c)$ shown for cylinders of diameter $D = 12$ and three choices of $L$. Full curve shows the coexistence curve for the corresponding bulk AO model. The symbols at $\eta_c \approx 0.16$ to 0.17 show the transition from the single-domain to the multiple domain state in the pore. d) Barrier $\Delta F/T$ against nucleation of interfaces in the AO model confined to a cylindrical pore of diameter $D = 12$ plotted versus inverse polymer reservoir packing fraction.

**FIG. 24.** Two hysteresis plots for the AO model. The chemical potential was varied in steps of 0.001$k_BT$. Several simulation runs (up to 38) were averaged. For high polymer reservoir packing fractions large sample to sample fluctuations occur. The open symbols show data for which the chemical potential was increased step-wise while the full symbols show data for which the value of the chemical potential was decreased step by step. (a) shows the disappearance of the hysteresis for a system with $D = 12$ and $L = 180$. (b) shows the disappearance of the hysteresis for a system with $D = 6$ and $L = 100$. 

An alternative way to explore this transition from axially symmetric phase coexistence in the cylindrical pore to a multiple domain structure uses a very long pore ($L = 1800$) which is cut into a one-dimensional array of $N_s$ subsystems, and recording the distribution $P_{D_s N_c}(N_c)$ of the number of colloids in the subsystems (Fig. 25). One can nicely see that for short enough subsystems (i.e., for $N_s \geq 60$) the subsystem is typically homogeneous, since
FIG. 25. Three-dimensional plot (left part) and contour plot (right part) of $P_{D,N_s}(N_c)$ vs. number of subsystems $N_s$, for $y_p = 1.1$ (first two graphs) and $y_p = 1.5$ (last two graphs). Note that the number of colloids $N_c$ is normalized by the length $L/N_s$.

there occur just two peaks with a minimum in between. However, for very large $L/N_s$ one still finds the middle peak, as a signature of the multiple domain structure, and the transition between both types of behaviors (as a function of $L/N_s$ or $y_p$, respectively) is completely gradual. Thus, the fact that the coexisting phases in the phase diagram of Fig. 23 show practically no $L$-dependence, and the fact that the equilibrium isotherms (Fig. 24) at large $y_p$ have an almost perpendicular part should not be taken as evidence that in the cylindrical pore a sharp, well-defined phase transition exists: as in the Ising model, the transition is rounded, but for large $\mu_p$ the extent of rounding is very small.

IV. CONCLUSIONS

In this paper, the characteristic features of phase transitions of Ising-like systems in a quasi-one dimensional geometry have been explored by Monte Carlo simulations for four generic models: (i) Ising $L \times D$ strips with $L \gg D$ and periodic boundary conditions throughout; (ii) Ising “cylinders” of length $L$ and cross section containing $N_{cr}$ sites enclosed by a circle of radius $R$, with a “missing neighbor” boundary condition that does not destroy the symmetry between the coexisting phases in the ground state; (iii) the same model as in (ii), but with a surface field $H_1$ acting on the spins which have “missing neighbors”, so that the spin reversal symmetry is broken, and the model (interpreted as a lattice gas) exhibits capillary condensation; and (iv) the AO model confined to cylindrical pores of diameter $D$ and length $L$, confined by hard repulsive walls, as an off-lattice model that lacks any particular symmetries already in the bulk.

We have shown that all models exhibit qualitatively similar behavior, namely two strongly rounded transitions occur when at phase coexistence conditions the temperature (or temperature-like variable, such as $(\mu_p)^{-1}$ in the case of the colloid-polymer mixture, respectively) is lowered: at a temperature rather close to the critical temperature of the bulk, a rounded transition occurs from the disordered phase (which may have nontrivial order parameter profiles in the phase perpendicular to the cylinder axis, induced by the boundaries, if there is no complete symmetry between the coexisting phases) to a locally ordered phase, where the size of the domains $\xi_D(T)$ in axial direction exceeds distinctly the pore diameter, so that a long cylinder ($L \gg \xi_D(T) \gg D$) is characterized by a sequence of interfaces across the cylinder axis. The order parameter distribution at coexistence is then a very broad Gaussian characterized by a very large response function (if the transition is studied as a function of the field conjugate to the order parameter, the rounding is exponentially small in the cross-sectional areas of the cylinder). At $L/3 \approx \xi_D(T)$, i.e. at $T = T_0(L,D)$, a second, again rounded, transition occurs, where the state of the system is again axially uniform and either
the vapor-like or liquid-like phase dominates. When one studies the kinetics of the transition between vapor-like and fluid-like phases, varying the field conjugate to the order parameter, one finds pronounced hysteresis in this low temperature region, $T < T_0(L, D)$ where $\xi_D(T) > L$, but these hysteresis loops get narrow when $T \approx T_0(L, D)$ and vanish completely for $T > T_0(L, D)$. Thus, we suggest that the “hysteresis critical point” can be associated with the lower temperature $T_0(L, D)$ rather than the upper pseudo-critical temperature of the capillary (where $\xi_D(T) \approx D$ and the difference in order parameter between the coexisting phases disappears).

A prediction that could be tested experimentally is our result that the difference between this “hysteresis critical temperature” and the “pore critical temperature” should increase logarithmically with the length $L$ of the cylindrical pore. We hope that our study stimulates additional experimental work using pores of both well-controlled diameter and length to check our predictions and thus confirm that a long-standing puzzle about the phase behavior of fluids adsorbed in pores is now better understood.

Acknowledgments: We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for partial support (grant N° TR6/A5 and C4) and thank the NIC Jülich for a generous grant of computer time.

1L.D. Gelb, K.E. Gubbins, R. Radhakrishnan, and M. Sliwinska-Bartkowiak, Rep. Progr. Phys. 62, 1573 (1999)
2M. Schön and S. Klapp, Reviews in Computational Chemistry, Vo. 2f (Wiley-VCH, Hoboken, 2007)
3I. Brovchenko and A. Oleinikova, Interfacial and Conflned Wa-
ter (Elsevier, Amsterdam, 2008)
4S.J. Gregg and K.S.W. Sing, Adsorption, Surface Area, and Porosity (Academic Press, New York, 2nd ed., 1982)
5A.J. Liapis (ed.) Fundamentals of Adsorption (Engineering Foundation, New York, 1987)
6J. Fraissard (ed.) Physical Adsorption, Theory, and Applications (Kluwer Acad. Publ., Dordrecht, 1997)
7F. Rouquerol, J. Rouquerol, and K.S.W. Sing, Adsorption by Powders and Porous Solids: Principles, Methodology, and Ap-
lications (Academic Press, San Diego, 1999)
8T. Thorsen, S.J. Maerkli, and S.R. Quake, Science 298, 580 (2002)
9A. Meller, J. Phys.: Condens. Matter 15, 581 (2003)
10E.I. Wolf, Nanophysics and Nanotechnology (Wiley-VCH, Wein-
gen, Germany, 2004)
11J.M. Squires and S.R. Quake, Rev. Mod. Phys. 77, 977 (2005)
12J.S. Rowlinson and B. Widom, Molecular Theory of Capillarity (Oxford Univ. Press, Oxford, 1982)
13C.A. Croxton (ed.) Fluid Interfacial Phenomena (Wiley, New York, 1985)
14I. Charvolin, J.-F. Joanny, and J. Zinn-Justin (eds.) Liquids at Interfaces (North-Holland, Amsterdam, 1990)
15D. Henderson (ed.) Fundamentals of Inhomogeneous Fluids (M. Dekker, New York, 1992)
16K. Binder, D.P. Landau, and M. Müller, J. Stat. Phys. 110, 1411 (2003)
17P. Wiltzius, S.B. Dierker, and B.S. Dennis, Phys. Rev. Lett. 62, 804 (1989)
18M.Y. Lin, S.K. Sinha, J.M. Drake, X.-I. Wu, P. Thiagagarajan, and H.B. Stanley, Phys. Rev. Lett. 72, 2207 (1994)
19E. Kierlik, P.A. Monson, M.I. Rosinberg, and G. Tarjus, J. Phys.: Condens. Matter 14, 9295 (2002)
20S. Inoue, N. Ichikuni, T. Suzuki, T. Uematsu, and K. Kaneko, J. Phys. Chem. B 102, 4689 (1998)
21M. Meyyappan (ed.) Carbon Nanotubes: Science and Applications (CRC Press, Boca Raton, 2004)
22Z.N. Yu, H. Gao, W. Wu, H.X. Ge, and S.Y. Chou, J. Vac. Sci. Technol. B 21, 2874 (2003)
23W. Reineker, K.J. Morton, R. Rühn, Y.M. Wang, Z. Yu, M. Rosen, J.C. Sturm, S.Y. Chou, E. Frey, and R.H. Austin, Phys. Rev. Lett. 94, 196101 (2005)
24W.T. Thomson (Lord Kelvin), Philos. Mag. 42, 448 (1871)
25M.E. Fisher and H. Nakanishi, J. Chem. Phys. 75, 5857 (1981)
26H. Nakanishi and M.E. Fisher, J. Chem. Phys. 78, 3279 (1983)
27R. Evans and P. Tarazona, Phys. Rev. Lett. 52, 557 (1984)
28R. Evans, U. Marini Bettolo Marconi, and P. Tarazona, J. Chem. Soc. Faraday Trans. 2, 1763 (1986)
29G. Heffelfinger, F. Swol, and K. Gubbins, Mol. Phys. 60, 1381 (1987)
30R. Evans, J. Phys.: Condens. Matter 46, 9899 (1990)
31H. Domínguez, M.P. Allen, and R. Evans, Mol. Phys. 96, 209 (1999)
32S. Varga, D. Boda, D. Henderson, and S. Sokolowski, J. Colloid Interface Sci. 227, 223 (2000)
33I. Brovchenko, A. Geiger, and D. Paschek, Fluid Phase Equil. 183, 331 (2001)
34M. Schmidt, A. Fortini, and M. Dijkstra, J. Phys.: Condens. Matter 16, 4159 (2004)
35B. Lefevre, A. Saugé, J.L. Barrat, L. Bocquet, E. Charlaix, P.F. Gobin and G. Vigier, J. Chem. Phys. 120, 4927 (2004)
36N. Desbiens, I. Demachy, A. Fuchs, H. Kirsch-Rodeschini, M. Soufard and J. Patarin, Angew. Chem. 117, 5444 (2005)
37P.G. de Gennes, Rev. Mod. Phys. 57, 825 (1985)
38D.E. Sullivan and M.M. Telo da Gama, in Fluid Interfacial Phenomena (C.A. Croxton, ed.) p. 45 (Wiley, New York, 1986)
39S. Dietrich, in Phase Transitions and Critical Phenomena, Vol. XII (C. Domb and J.L. Lebowitz, eds.) p. 1 (Academic, New York, 1988)
40M. Schick, in Liquids at Interfaces (J. Charvolin, J.F. Joanny and J. Zinn-Justin, eds.) p. 415 (North-Holland, Amsterdam, 1990)
41D. Chatain, Ann. Rev. Mat. Res. 38, 45 (2008)
42D. Quéro, Ann. Rev. Mat. Res. 38, 71 (2008)
43S. Herminghaus, M. Brinkmann, and R. Seemann, Ann. Rev. Mat. Res. 38, 101 (2008)
44K. Binder, Ann. Rev. Mat. Res. 38, 123 (2008)
45D.H. Everett and J.M. Haynes, J. Colloid Interface Sci. 38, 125 (1972)
46W.F. Saam and M.W. Cole, Phys. Rev. B 11, 1086 (1975)
47B.V. Derjaguin and N.V. Churaev, J. Colloid Interface Sci. 54, 157 (1976)
48G. Mason, Proc. R. Soc. London, Ser. A 390, 47 (1983)
49G.S. Heffelfinger, F. van Swol, and K.E. Gubbins, J. Chem. Phys. 89, 5202 (1988)
50P.C. Ball and R. Evans, Langmuir 5, 714 (1989)
51C.G.V. Burgess, D.H. Everett and S. Nutall, Pure Appl. Chem. 61, 1845 (1989)
52W.D. Machin, Langmuir 10, 1235 (1994)
53M. Thommes and G.H. Findenegg, Langmuir 10, 4270 (1994); T. Michalski, A. Benini, and G.H. Findenegg, Langmuir 7, 185 (1991)
54M. Thommes, G.H. Findenegg, and M. Schoen, Langmuir 11, 2137 (1995)
55K. Morishige, H. Fujii, M. Uga, and D. Kinukawa, Langmuir 13, 3494 (1997)
56K. Morishige and M. Shikimi, J. Chem. Phys. 108, 7821 (1998)
57A.V. Neimark, P.I. Ravikovich, and A. Vishnyakov, Phys. Rev. E 62, R1493 (2000)
58A. Vishnyakov and A.V. Neimark, J. Phys. Chem. B 105, 7009 (2001)
59K.G. Kornev, I.K. Shingareva, and A.V. Neimark, Ad. Coll. Interface Sci. 96, 143 (2002)
K. Morishige and M. Ito, J. Chem. Phys. 117, 8036 (2002)
L.D. Landau and E.M. Lifshitz, Statistical Physics, 3rd ed. (Pergamon Press, Oxford, 1959)
V. Privman and M.E. Fisher, J. Stat. Phys. 33, 385 (1983)
M.N. Barber, in Phase Transitions and Critical Phenomena, edited by C. Domb and J.L. Lebowitz (Academic, London, 1983) Vol. 8, Ch. 2
D.L. Gelb and K.E. Gubbins, Phys. Rev. E 56, 3185 (1997)
W.D. Machin, Langmuir 15, 169 (1999)
G.S. Heffelfinger, Z. Tan, K.E. Gubbins, U. Marini Bettolo Marconi, and F. van Swol, Mol. Simul. 2, 393 (1989)
A.J. Liu, D.J. Durian, E. Herbolzheimer, and S.A. Safran, Phys. Rev. Lett. 65, 1897 (1990)
I. Brovchenko, A. Geiger, and A. Oleinikova, Phys. Chem. Chem. Phys. 3, 1567 (2001)
I. Brovchenko, A. Geiger, and A. Oleinikova, J. Phys.: Condens. Matter 16, S5345 (2004)
S. Asakura and Oosawa, J. Chem. Phys. 22, 1255 (1954)
M.E. Fisher, J. Phys. Soc. Jpn. Suppl. 26, 87 (1969)
A.E. Ferdinand and M.E. Fisher, Phys. Rev. 185, 832 (1969)
B.M. McCoy and T.T. Wu, The two-dimensional Ising model (Harvard University Press, Cambridge, Mass., 1973)
H. Au-Yang, and M.E. Fisher, Phys. Rev. B 11, 3469 (1975)
H. Au-Yang and M.E. Fisher, Phys. Rev. B 21, 3956 (1980)
M.E. Fisher and H. Au-Yang, Physica A 101, 255 (1980)
G.C. Cabrera, R. Jullien, E. Brézin and J. Zinn-Justin, J. Physique 47, 1305 (1986)
E.V. Albano, K. Binder, D.W. Heermann, and W. Paul, Z. Phys. B 77, 445 (1989)
E.V. Albano, K. Binder, D.W. Heermann, K. Binder, J. Chem. Phys. 91, 3700 (1989)
E.V. Albano, K. Binder, D.W. Heermann, and W. Paul, Surface Sci. 223, 151 (1989)
V. Privman, in Finite Size Scaling and Numerical Simulation of Statistical Systems (ed. by V. Privman) p.1 (World Scientific, Singapore, 1990)
A.O. Parry and R. Evans, Physica A 181, 250 (1992)
J. Stecki, A. Maciokle and K. Olaussen, Phys. Rev. B 49, 1092 (1993)
R. Evans and J. Stecki, Phys. Rev. B 49, 8842 (1994)
T.W. Burkhardt and E. Eisenriegler, Phys. Rev. Lett. 74, 3189 (1995)
A. Maciokle and J. Stecki, Phys. Rev. B 49, 8842 (1996)
E. Carlon, A. Drzewinski and J. Rogiers, Phys. Rev. B 58, 5070 (1998)
P. Nowakowski and M. Napiorkowski, J. Phys. A: Math. Theor. 42, 475005 (2009)
D.P. Landau and K. Binder, A Guide to Monte Carlo Simulation in Statistical Physics, 3rd ed. (Cambridge Univ. Press, Cambridge, 2009)
K. Kawasaki, in Phase Transitions and Critical Phenomena, Vol. 2, edited by C. Domb and M.S. Green (Academic, London, 1972), Chap. 11.
L. Onsager, Phys. Rev. 65, 117 (1944)
U. Wolff, Phys. Rev. Lett. 62, 361 (1989)
W.C. Poon, J. Phys.: Condens. Matter 14, S245 (2003)
D.G.A.L. Aarts, M. Schmidt, and H.N.W. Lekkerkerker, Science 304, 847 (2004)
A. J. Liu and G.S. Grest, Phys. Rev. B 60, 1567 (2001)
D.G.A.L. Aarts, J.H. van der Wiel, and H.N.W. Lekkerkerker, Phys. Rev. A 44, 7894 (1991)
D.G.A.L. Aarts, M. Schmidt, and H.N.W. Lekkerkerker, Science 304, 847 (2004)