

## Quasi-One-Dimensional Phase Transitions in Nanopores: Pore-Pore Correlation Effects

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For adsorbates confined within a single, sufficiently narrow cylindrical pore, no phase transitions occur because the system is too close to the one-dimensional limit. We study the influence of intermolecular correlations between adsorbed molecules in neighboring cylindrical pores, using molecular simulation. For a simple model of methane in the molecular sieve ALPO<sub>4-5</sub>, we find that a phase transition between two fluid states ("gas" and "liquid") occurs below a critical temperature that is depressed relative to the bulk value. [S0031-9007(97)04210-5]

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A generally accepted result of statistical mechanics [1] is that there can be no phase transitions in a one-dimensional system of molecules having intermolecular forces that are of short range (defined as decaying as  $r^{-1}$  or faster). An example of a nearly one-dimensional system consists of an adsorbate confined within a narrow cylindrical pore of sufficiently small diameter that the adsorbate molecules can move only along paths very close to the line of the pore axis. There are a number of classes of molecular sieve materials that are crystalline and have such narrow cylindrical pores, e.g., some aluminosilicates and aluminophosphates. Molecular simulation studies [2] have confirmed that in very narrow cylindrical pores, e.g., pores having  $D \approx 2\sigma$ , where  $D$  is the pore diameter (measured as the distance between the centers of wall atoms in the first layer on opposite sides of the pore) and  $\sigma$  is the diameter of an adsorbate molecule such as nitrogen or methane, no phase transitions are observed for temperatures  $T > 0$  K; in such pores the adsorption isotherms closely follow the behavior predicted for a one-dimensional system. As a result, it is commonly assumed that no phase transitions are possible in zeolites having pore diameters of around  $2\sigma$ , at least for adsorbates such as nitrogen, methane, etc.

Nevertheless, there have been occasional reports of possible phase transitions in such systems. For example, hysteresis loops have been observed in the adsorption isotherm for methane adsorbed in ALPO<sub>4-5</sub> at 77 K [3], suggesting a phase change [4]. ALPO<sub>4-5</sub> is an aluminophosphate having straight, parallel cylindrical pores of diameter 0.73 nm, as obtained from x-ray data; the pore cross sections are arranged in a hexagonal close-packed array. The methane molecule has a diameter of  $\sigma = 0.381$  nm, so that  $D = 1.92\sigma$ . This and similar examples suggest that phase transitions may be possible in these systems despite their proximity to the one-dimensional limit. A possible mechanism for such transitions is the interaction between adsorbate molecules in neighboring pores. In ALPO<sub>4-5</sub> and similar zeolites the pores are close together, so that such pore-pore correlation effects could lead to an increase in dimensionality for the confined fluid, and to phase transitions. As far as we

are aware this possibility has not been investigated previously, although Swift *et al.* [5] have studied the related problem of phase transitions in adsorbates in a connected pore system, using an Ising model.

In this Letter we report a molecular simulation study to investigate the possibility of phase transitions in such porous materials due to inter-pore correlation effects. We use the grand canonical ensemble Monte Carlo (GCMC) method as described elsewhere [6,7], since it is convenient to work with fixed chemical potential, temperature and volume, and study a simple model of the methane/ALPO<sub>4-5</sub> system. Periodic boundary conditions were applied in the axial dimension of the pores. Thermodynamic fluctuations were pronounced because of the reduced dimensionality, and so large systems were used for simulations near the critical point [8]. The pore structure consisted of a hexagonal array of straight parallel pores as shown in Fig. 1. The model of the pore walls is one used previously [7], and consists of a surface layer which is an amorphous array of oxygen atoms, each interacting with the adsorbate methane molecules via a Lennard-Jones (12,6) potential. The methane-methane interactions are also modeled using the Lennard-Jones (LJ) potential. Parameters for the intermolecular potentials and solid structure were taken from existing literature values [7,9], and were  $\epsilon_{ff}/k_B = 148.2$  K,  $\epsilon_{fw}/k_B = 137.8$  K,  $\sigma_{ff} = 0.381$  nm,  $\sigma_{fw} = 0.323$  nm,  $D = 0.73$  nm,  $\lambda_{o-o} = 0.325$  nm, where subscripts  $f$  and  $w$  refer to fluid (methane) and wall, respectively, and  $\lambda_{o-o}$  is the oxygen-oxygen distance in the solid lattice. LJ interactions were cut off at a distance of  $5\sigma$ . The fluid-wall interaction was averaged over the pore length [7], resulting in a two-dimensional potential  $u_{fw}(r, \theta)$ , where  $r$  is the radial position of the methane molecule in the pore and  $\theta$  is the polar angle in the plane normal to the pore axis. In our simulation, we use the residual chemical potential, defined as the chemical potential with reference to that of an ideal gas at a density of 1 molecule/Å<sup>3</sup> at the given temperature.

Two pore geometries were studied, an isolated single pore [Fig. 1(a)] and a hexagonal array of seven interacting pores [Figs. 1(b) and 1(c)]. For the isolated

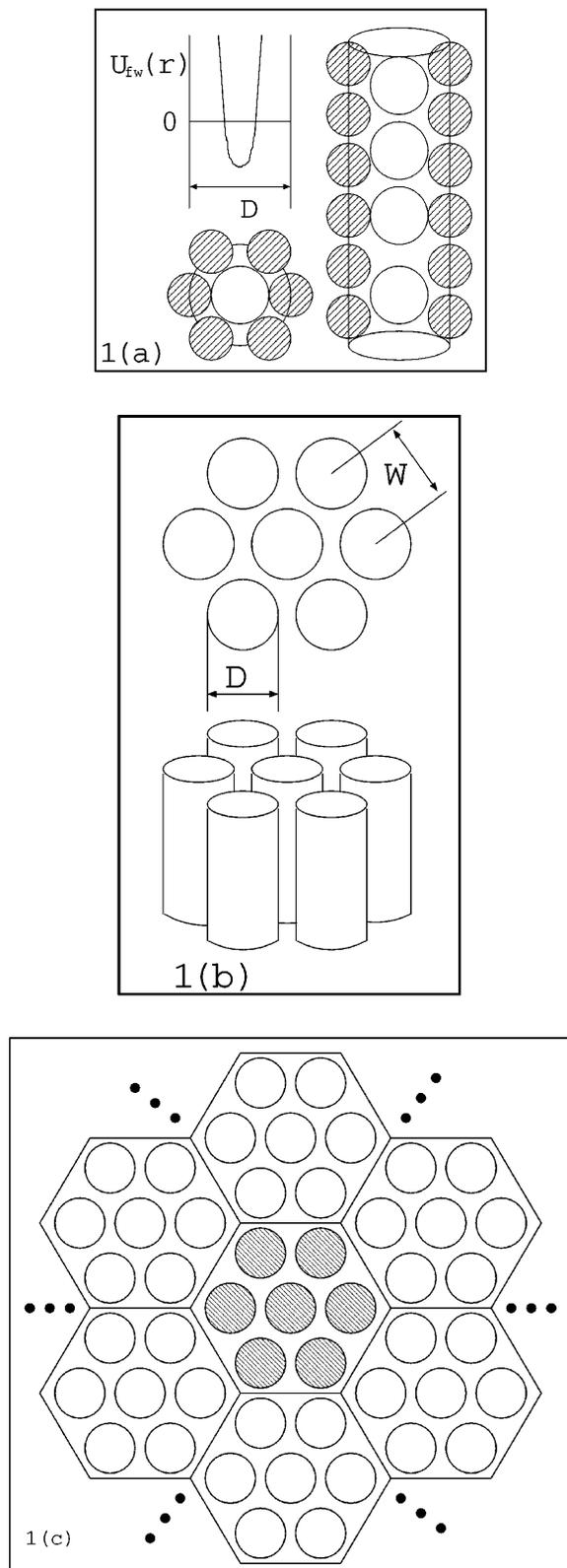


FIG. 1. Schematic view of pore model: (a) single pore showing end view, side view, and solid-fluid potential, with open spheres being adsorbed methane molecules, and shaded spheres oxygen atoms in the wall; (b) a hexagonal array of seven pores; (c) a cross section showing the central set of seven pores (hatched circles), with periodic images (open circles).

single pore, the calculated adsorption isotherms were continuous and reversible, and showed no indication of a phase transition for all temperatures down to 0 K. These isotherms were found to conform very closely to those predicted for a one-dimensional system with only nearest neighbor interactions [10]. For the array of pores, simulations were carried out for two cases differing in boundary conditions. The first involved just the interaction among the seven pores. The second included the central set of seven pores plus periodic images of these seven pores in the plane perpendicular to the pore axes. Very close to the critical point, the results for this second case will show a crossover from the real, infinite system behavior to mean field behavior, as shown by Mon and Binder [11], but at lower temperatures should accurately describe the infinite crystal. Both systems yielded the same results (within statistical uncertainties) for the temperatures well removed from the critical value. Under these conditions, the fluctuations are small so that the lack of periodic boundaries results in only a weak perturbation. In what follows we report results for the second case, including periodic images. For reduced temperatures above about  $T^* = k_B T / \epsilon_{ff} = 0.37$  (55 K), the isotherms were continuous and reversible, but for significantly lower temperatures a clear phase transition was observed. An example is shown in Fig. 2 for a temperature of 40 K. For the array of pores there is a sharp, discontinuous jump in adsorption to an adsorbed state of liquidlike density; on desorption the reverse jump occurs at a lower chemical potential (bulk pressure), showing the usual hysteresis attached to such phase transitions. The hysteresis results from metastability in the adsorbate. The chemical potential for the true thermodynamic transition can be determined by using thermodynamic integration to calculate the grand free energy,  $\Omega$ , for the two adsorption branches using the method of Peterson and Gubbins [12]. An example, the result for 40 K, is shown in Fig. 3. By determining the transition points at various temperatures we were able to construct the coexistence curve, which is shown in Fig. 4. Because of large fluctuations, it is not possible to approach the critical point very closely. In order to obtain an estimate of the critical point, we therefore fitted the coexistence points at the higher temperatures to the Ising scaling law for the density difference between the two phases for three-dimensional systems,  $\rho_l - \rho_g = A(T_c - T)^\beta$ , where  $\beta = 0.33$ , together with the law of rectilinear diameters [13]. This is the curve in Fig. 4, and shows a critical temperature of about  $T_c \approx 51.7$  K. The critical pressure was estimated to be  $1.16 \times 10^{-5}$  N/m<sup>2</sup> from the corresponding chemical potential, using the virial equation of state. This rather low critical pressure is due to the high attractive potential ( $\approx -30k_B T$ ) of the pore walls of ALPO<sub>4</sub>-5. Calculations of the one-dimensional pair correlation function and the structure factor for the adsorbed molecules showed that the two coexisting

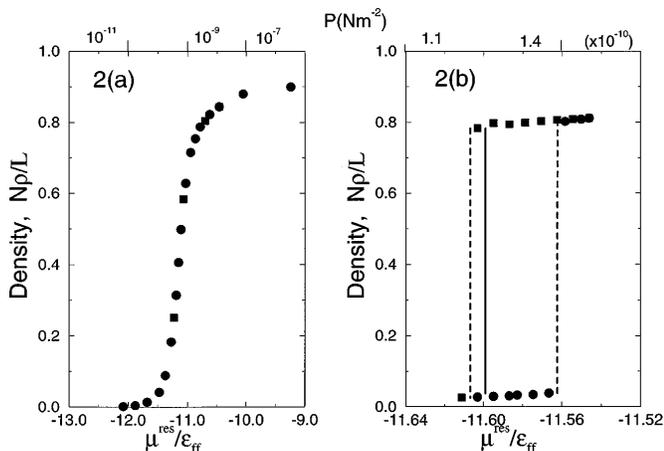


FIG. 2. Adsorption isotherms for methane in a model  $\text{ALPO}_4\text{-5}$  pore at  $T^* = 0.27$  ( $T = 40$  K), showing adsorption (circles) and desorption (squares), for (a) an isolated pore, and (b) an array of pores with intermolecular interaction between pores. The vertical dashed lines show the phase changes on adsorption and desorption. The true thermodynamic phase transition is given by the solid vertical line. The horizontal axis shows the reduced residual chemical potential and the pressure, and the vertical one the density as the number of molecules per pore per unit length.

phases in the pore are fluidlike, one corresponding to a low density (“gas”) and one to a considerably higher density (“liquid”) phase.

We have also investigated the effect of changes in the system variables on the resulting phase transitions and coexistence curve. The relevant variables are (a) the fluid-fluid energy parameter,  $\epsilon_{ff}$ ; (b) the reduced fluid-wall energy parameter,  $\alpha = \epsilon_{fw}/\epsilon_{ff}$ ; (c) the interpore distance,  $W$ ; and (d) the parameters  $\sigma_{ff}$  and  $\sigma_{fw}/\sigma_{ff}$ . The first three of these variables are the most important. For given values of  $\alpha$  and  $W$  it is easy to show that the critical temperature scales as  $\epsilon_{ff}$ ; for  $\epsilon_{ff}/k_B =$

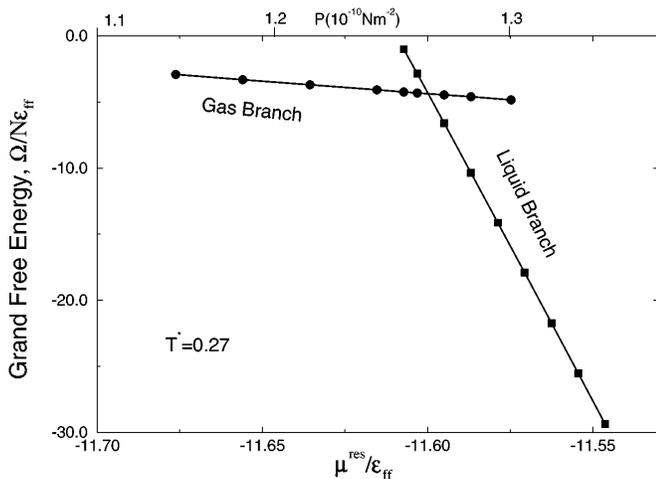


FIG. 3. The grand free energy for the adsorption and desorption branches at  $T^* = 0.27$ , showing the transition as the intersection of these.

335 K, for example, we find from simulation  $T_c \approx 117$  K with other parameters ( $\alpha$ ,  $W$ , etc.) the same as for the  $\text{CH}_4/\text{ALPO}_4\text{-5}$  model, in agreement with this simple scaling. Decreasing the strength of interaction of the fluid with the wall causes the critical temperature to go up, but this effect is small; for example, decreasing  $\alpha$  from 0.93 (its value for  $\text{CH}_4/\text{ALPO}_4\text{-5}$ ) to 0.6 only increases  $T_c$  from 51.7 to 53 K. This insensitivity to the  $\alpha$  value is expected, since the adsorbate molecules are already so closely confined to the pore axes that changes in  $\epsilon_{fw}$  should have little effect. However, this change in  $\alpha$  causes the critical pressure to change by nearly 5 orders of magnitude, from  $1.16 \times 10^{-5}$  to  $0.59$   $\text{N/m}^2$ . The value of the chemical potential of an adsorbed molecule is largely governed by the potential energy due to the pore walls, which depends linearly on  $\epsilon_{fw}$ . The drastic increase of the critical pressure is due to the exponential dependence of the pressure on the chemical potential. The interpore spacing  $W$  is expected to have a large effect on the critical temperature. The critical point for the porous array can be thought of as occurring when the temperature is reduced to a point where the correlation length for the 1D system,  $\xi_{1d}$ , grows to be of the order of the interpore separation  $W$ . Although this is not a rigorous argument, it has been found successful in treating model networks [5]. For the 1D Ising model, which has a critical point at 0 K [14],

$$\frac{1}{\xi_{1d}} = -\ln[\tanh(J/k_B T)], \quad (1)$$

where  $J$  is the nearest neighbor interaction parameter. This leads to the scaling

$$e^{-\frac{1}{W}} = \tanh(J/k_B T_c). \quad (2)$$

We have determined the approximate critical points for various values of  $W$ , for a system in which the other parameters are those of  $\text{CH}_4/\text{ALPO}_4\text{-5}$ , and show the results

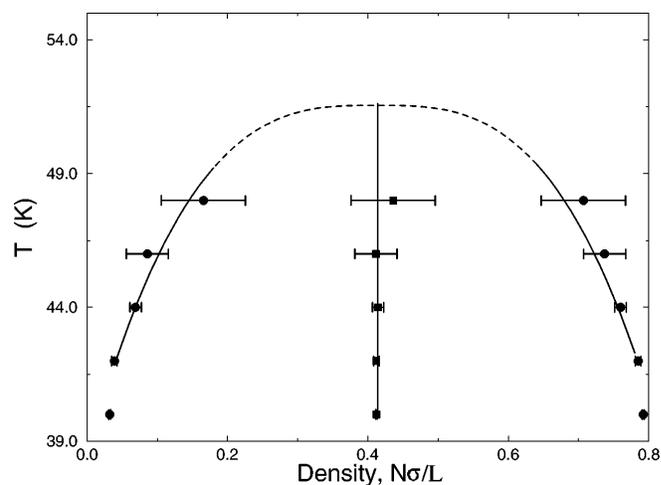


FIG. 4. Coexistence curve for the array of pores. The curve is a fit to the Ising scaling law for a three-dimensional system. Solid squares represent  $(\rho_l + \rho_g)/2$  and the line through them is a fit to the law of rectilinear diameters,  $(\rho_l + \rho_g)/2 = \rho_c + a(T - T_c)$ .

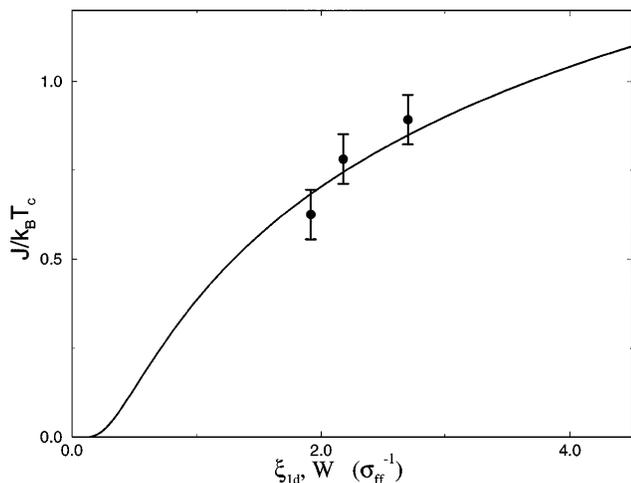


FIG. 5. Effect of interpore distance  $W$  on critical temperature; the points are simulation results for  $T_c$  at different values of  $W$ ; the solid curve is from Eq. (1).

in Fig. 5. The plot shows good agreement with Eq. (2); in applying Eq. (2),  $J$  was calculated from the nearest neighbor interaction energy at complete pore filling.

Our results show that interpore correlations will lead to phase separation below the temperature at which the correlation length grows to about the interpore separation distance  $W$ ; this phase transition is analogous to the well-known capillary condensation. However, the critical temperature for such a transition will fall well below the bulk fluid value. For the model of  $\text{CH}_4/\text{ALPO}_4\text{-5}$  studied here, the critical temperature occurs at 51.7 K (about 27% of the bulk critical temperature for LJ methane), and the estimated critical pressure is  $1.16 \times 10^{-5} \text{ N/m}^2$ . These values are too low to explain the results of Martin *et al.* [3], which seem to result from a structural rearrangement of the adsorbed methane [15]. We note that such pore-pore correlation effects should be considerably larger for strongly dipolar fluids such as water, ammonia, and methyl fluoride. For such cases the critical temperature should be substantially higher than for methane.

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