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Simulations of high T_c vapor–liquid phase transitions in nanoporous materials

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We have performed lattice grand canonical Monte Carlo simulations of benzene adsorption in Na-X zeolite, to determine whether strongly confined benzene molecules exhibit subcritical properties. We observe a phase transition from low to high density of adsorbed benzene, analogous to vapor–liquid equilibrium, at temperatures as high as 300 K and above. By performing thermodynamic integration to construct the coexistence curve, we obtain a critical point for benzene in Na-X at $T_c = 370 \pm 20$ K, $\theta_c = 0.45 \pm 0.05$ fractional coverage. © *1998 American Institute of Physics.* [S0021-9606(98)51644-3]

I. INTRODUCTION

The thermodynamic properties of confined fluids[1,2] play a central role in separations and reactions that take place within porous materials.[3] Of particular interest are hysteresis loops and precipitous jumps in adsorption isotherms, since these are often associated with vapor–liquid transitions of the confined fluid. Although there is a vast literature on such transitions in mesoporous materials,[1,2] there are very few reports of phase transitions in microporous solids such as zeolites. This is presumably because confinement into such small cavities ($<$ 20 Å) reduces the vapor–liquid critical temperature to extremely low values.

Nevertheless, there have been occasional reports of possible phase transitions in such systems. For example, hysteresis loops have been observed at 77 K for methane in $AlPO_4$-5,[4] a one-dimensional channel zeolite. Since phase transitions in one-dimensional systems are theoretically forbidden,[5] Radhakrishnan and Gubbins simulated this system to determine whether interactions among methanes in adjacent channels could account for the observed phase transition.[6] They found a critical temperature near 52 K, suggesting that interchannel interactions stronger than those assumed in their study may be present. For benzene in faujasite, a three-dimensional cage-type zeolite, a multiple-quantum proton NMR study detected a continuous network of coupled proton spins,[7] suggesting the importance of interactions among molecules in adjacent cages. In this communication, we use lattice simulation techniques and thermodynamic integration to demonstrate that these cooperative interactions can lead to vapor–liquid transitions for benzene in faujasite.

II. METHODOLOGY

We model benzene in faujasite by replacing the zeolite framework with a three dimensional lattice of binding sites. For example, benzene has two predominant binding sites in zeolite Na-X as shown in Fig. 1.[8,9] In the primary site, denoted as S_{II}, benzene is facially coordinated to a supercage 6-ring near Na(II). Locating the secondary site in Na-X, denoted as W, is more difficult because of the influence of additional Na cations in low-symmetry positions, denoted sites III and III′. Recent crystallographic studies[8] favor the prevalence of Na(III′) cations, which lie in the 12-ring window shown in Fig. 1. Benzene is likely to bind in the 12-ring window separating adjacent supercages near the Na(III′) cation. Thus the lattice of benzene binding sites in Na-X contains four tetrahedrally arranged S_{II} sites and four tetrahedrally arranged, doubly shared W sites per supercage. Saturation coverages of ca. 6 molecules per cage are found for benzene in Na-X, corresponding to occupation of all S_{II} and W sites. In what follows, the W and S_{II} sites are denoted sites 1 and 2, respectively.

We determined the adsorption isotherms with the Ising model, limiting the range of guest–guest interactions to nearest neighbors. The Ising interaction parameters are obtained from the second virial coefficient of the heat of adsorption,[10,11] yielding an interaction energy between -0.03 eV and -0.05 eV for nearest neighbor molecule pairs. The value of $J = -0.04$ eV is used in this work. The site binding energies of benzene at S_{II} and W sites are taken as $\varepsilon_2 = -0.78$ eV and $\varepsilon_1 = -0.63$ eV, respectively, consistent with values for benzene in Na-X.[12] In what follows, we describe the simulation methodology and mean field theory for calculating adsorption isotherms, in addition to the thermodynamic integration for constructing the coexistence curve.

We use the grand canonical Monte Carlo (GCMC) simulation method to study this system, where we fix the chemical potential, μ, volume, V, and temperature, T.[13] GCMC calculations are performed on a simulation cell that consists of eight Na-X unit cells, containing 128 W sites and 256 S_{II} sites. The number of adsorbed molecules is allowed to fluctuate, and the average fractional occupancy is calculated af-

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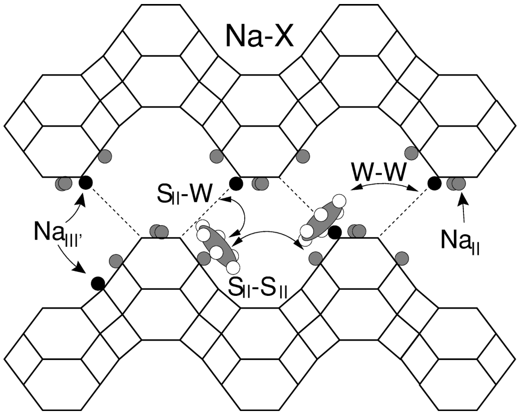

FIG. 1. Sorption sites and nearest neighbors for benzene in Na-X.

ter $(1.0-2.5)\times 10^7$ Monte Carlo (MC) steps, with an initial equilibration period of 10^6 MC steps. The GCMC calculation of 2.5×10^7 MC steps for one value of μ requires 80 CPU minutes on an IBM RS/6000 3CT. The GCMC isotherms are calculated over a grid of $\mu^* = (\mu-\varepsilon_2)/|J|$. In the deep subcritical regime we observe hysteresis between the GCMC calculations performed by adsorbing molecules onto an empty lattice, viz. the adsorption or gas branch; and desorbing molecules from a fully occupied lattice, viz. the desorption or liquid branch. For higher temperatures in the subcritical region, greater than 300 K ($T^* = k_B T/|J| = 0.65$), the hysteresis region becomes too narrow to be recovered from GCMC adsorption and desorption calculations. The liquid and gas branches for these temperatures are obtained by averaging separately the gas and liquid densities that arise from a single GCMC run. The liquid and gas branches are used for constructing the gas–liquid coexistence curve. In what follows we briefly describe the thermodynamic integration technique to detemine the coexistence envelope.

We define $-\phi = \Omega/V$ as the grand potential density, where Ω is the grand potential given by $\Omega = -k_B T \ln \Xi$, and Ξ is the grand canonical partition function. The negative grand potential density is the generalization of pressure for spatially inhomogenous systems.[14] We use the fact that the grand potential densities and chemical potentials must be equal for the coexisting phases in equilibrium. We apply thermodynamic integration techniques to determine the grand potential density as a function of chemical potential for the liquid and gas branch.[14,15] The grand potential density along the gas branch is evaluated by integrating the Gibbs isotherm at temperature T:

$$d\phi = \rho\, d\mu, \tag{1}$$

where ρ is the density of benzene molecules obtained by GCMC. For low density states in the gas branch, Henry's law is used for integration because the fluid behaves as an ideal gas.

The liquid branch is evaluated by integrating Eq. (1) after calculating the grand potential density, $\phi(\mu_0)$, at a reference state with a high chemical potential, (μ_0, V, T). Obtaining $\phi(\mu_0)$ requires two integrations. First, at a temperature T_0, well above the bulk fluid critical temperature, the grand potential density at μ_0 is evaluated by integrating the Gibbs isotherm, beginning in the low density region. Second, the Gibbs–Helmholtz relation,

$$\left[\frac{\partial(\phi/T)}{\partial T}\right]_{\mu_0} = \frac{\rho}{T^2}(\epsilon - \mu_0), \tag{2}$$

is used to determine $\phi(\mu_0)$ at the target temperature. Here $\epsilon = \langle E\rangle/\langle N\rangle$ is the average internal energy per molecule, where $\langle E\rangle$ is the average internal energy and $\langle N\rangle$ is the average loading. $\phi(\mu_0)$ is the reference grand potential density for integrating the Gibbs isotherm to obtain the liquid branch. The fractional coverage of the liquid and gas phase in equilibrium is determined from the slopes, $(\partial\phi/\partial\mu)_T$, of the gas and liquid branches, and are used to construct the coexistence curve.[6,14]

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 fitted the coexistence points to the Ising scaling law for the density difference between the liquid and gas phases for three-dimensional systems, i.e., $(T_c - T) = A(\rho_l - \rho_g)^3$, together with the law of rectilinear diameters.[6,16]

We apply mean field theory (MFT) in the grand canonical ensemble, averaging over the local fluctuations in the instantaneous field on each adsorption site, to determine how well MFT estimates the critical point. The fractional loadings, θ_1 and θ_2, at the two different sites W and S_{II}, respectively, are evaluated within the mean field approximation.[5] Two simultaneous, nonlinear equations for θ_1 and θ_2 are derived as a function of the guest–guest interaction energy, J, and the W and S_{II} site binding energies, ε_1 and ε_2.[12] The equations for θ_1 and θ_2 are solved self-consistently using the Newton–Raphson method. The fractional loading is then given by $\theta = \frac{1}{3}\theta_1 + \frac{2}{3}\theta_2$.

III. RESULTS AND DISCUSSION

We have performed GCMC adsorption and desorption calculations for benzene in Na-X over the temperature range 50–700 K. For $T > 400$ K ($T^* = 0.86$), the isotherms are continuous and reversible with respect to the adsorption and desorption branches. However, for lower temperatures, regions of hysteresis are observed because of metastabilty in the adsorbed state. In Fig. 2, we show the hysteresis region that arises at $T = 340$ K ($T^* = 0.73$). This hysteresis region is extremely narrow, with a width of only $0.02|J|$. This phase transition, analogous to the vapor–liquid transition of bulk benzene, occurs because of attractive interactions between benzene molecules in adjacent cages. These interactions are facilitated by benzene molecules in the W sites, which are shared between adjacent supercages, and hence are able to build a continuous network of coupled benzenes.

The liquid and gas branches in Fig. 2 are used to calculate the grand potential density using thermodynamic integration. For $T = 340$ K ($T^* = 0.73$), the result is shown in Fig. 3, where we plot $\phi^* = \phi\Delta V/|J|$ vs μ^*, where $\Delta V = (6.9\text{Å})^3$ is the volume per adsorption site. The $(\partial\phi/\partial\mu)_T$

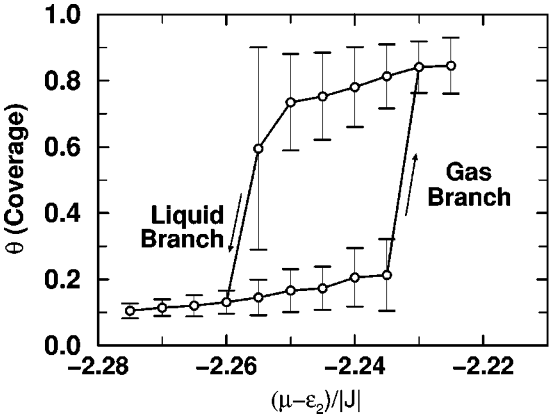

FIG. 2. GCMC calculation showing hysteresis at $T=340$ K ($T^*=0.73$).

slopes at the coexistence point in Fig. 3 ($\mu^*=-2.248$, $\phi^*=0.0403$), provide the densities of the coexisting gas and liquid phases at $T=340$ K.

The coexistence envelope for benzene in Na-X obtained from thermodynamic integration is shown in Fig. 4. We estimated the critical point by fitting the data to the three-dimensional Ising scaling law and law of rectilinear diameters, as discussed in the previous section. The asymmetry in the coexistence curve arises from the presence of two different types of sites in our model. The critical point we estimate for benzene in Na-X is $T_c=370\pm20$ K ($T_c^*=0.79\pm0.04$) and $\theta_c=0.45\pm0.05$. Applying the same analysis to adsorption isotherms obtained with MFT, we obtain a mean field critical temperature of 691 K [$T_c^*(\text{MFT})=1.48$]. We thus find that MFT greatly over estimates the critical temperature for this lattice model, hence requiring the GCMC simulation technique.

In conclusion, we have reported grand canonical Monte Carlo simulations demonstrating that high T_c vapor–liquid phase transitions can occur for molecules adsorbed in nanoporous solids such as zeolites. We attribute this to the adsorption of molecules in sites that are doubly shared between adjacent zeolite cages. These sites facilitate the formation of large clusters of coupled benzene molecules resulting in the phase transition. We have used thermodynamic integration techniques to determine the coexistence region and the critical point, obtaining $T_c=370\pm20$ K ($T_c^*=0.79\pm0.04$) and $\theta_c=0.45\pm0.05$ for a particular value of the guest–guest interaction parameter. We have also calculated the mean field theory critical temperature and find that mean field theory greatly over estimates the critical temperature for this system. An analysis of the dependence of T_c on the interaction parameters for this and related systems will be reported in a forthcoming publication.

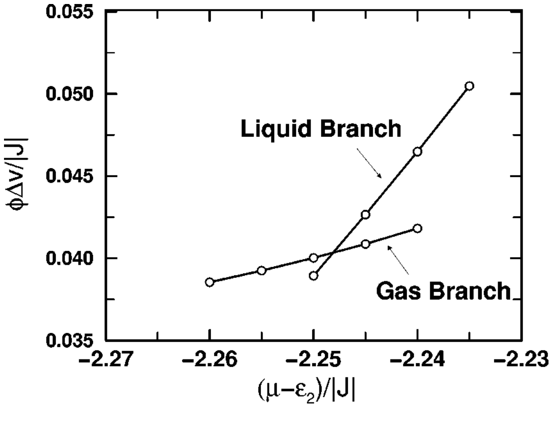

FIG. 3. Grand potential density ($\phi^*=\phi\Delta V/|J|$) for gas and liquid branches calculated by thermodynamic integration at $T=340$ K ($T^*=0.73$).

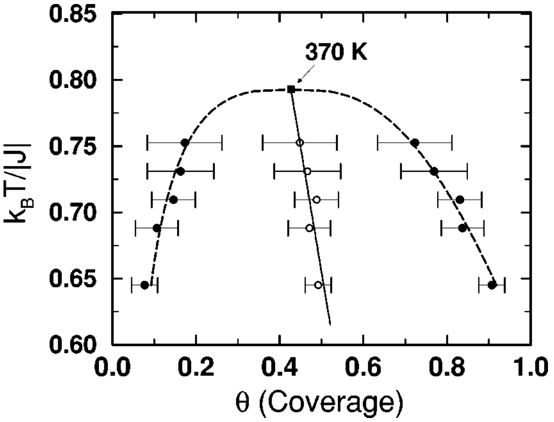

FIG. 4. Simulated coexistence envelope for benzene in Na-X, giving $T_c=370\pm20$ K ($T_c^*=0.79\pm0.04$).

We have thus described the thermodynamics of a special class of host–guest zeolite systems, involving both strong confinement and formation of large clusters. We expect that careful adsorption experiments will reveal this vapor–liquid transition for benzene in faujasite, and possibly for a wide array of other systems.

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