

## **Computational Studies of Capillary Phenomena: The Effects of Aerogel Compliance on Adsorptive Behavior**

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We present results from simulations of gas adsorption in aerogels in which the flexibility of the gel matrix is treated explicitly. This is accomplished by coupling a coarse-grained model for the aerogel with a mean-field on-lattice density functional model for the adsorbing gas.

Adsorption in aerogel materials has been studied for a number of years both by simulation and experiment. The extremely low density of these materials has made them particularly attractive for studies of the effects of weak confinement on fluid critical properties, but adsorption under conditions nearer to the fluid triple point has also been of considerable interest. Unlike porous materials such as vycor glasses and xerogels, low density aerogels have very low bulk moduli (generally in the range 1-100 bar). As a result they therefore display nontrivial mechanical deformations during adsorption and desorption processes, especially near to the capillary rise and desorption shoulder [1].

Due to the large length scales in aerogels, computational studies of adsorption have generally used lattice-based density functional theory approaches (a la Kierlik, et al. [2,3]) rather than molecular simulation. All such studies to date have kept the gel structure itself (generally obtained by DLCA or similar simulation [4]) frozen, which is a poor approximation for these materials; the purpose of this study is to address this approximation.

We introduce a simple coarse-grained model for silica sol-gels [5]. This model is fully flexible and can account for bond breaking and creation upon deformation of the gel structure. This model is structurally reasonable, and for appropriate choice of bond-formation control parameters, quantitative results for bulk modulus and the behavior under mechanical loading can be obtained.

In this work, the commonly used lattice-based fluid adsorption model is coupled to our coarse-grained off-lattice aerogel model using thermodynamic perturbation theory. This provides a complete free energy surface describing the behavior of the gel/fluid system at varying compression and fluid chemical potential. The resulting isotherms and dependence of gel compression on gas pressure are in excellent qualitative agreement with experimental findings, which are intuitively explained as motion on the underlying free energy surface. Perhaps most interestingly, in rigid aerogel models the adsorption isotherms are continuous in the capillary rise region, but when the gel is allowed to relax a sharp jump, corresponding to a first-order transition, is observed.

Finally, we discuss recent work on a new form of fluid density functional theory that uses a finely discretized lattice hard-sphere fluid as a reference state instead of the more usual off-lattice model. This leads to dramatic reductions in computational cost, permitting application of this approach in three-dimensionally inhomogeneous sorbent models [6].

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