Simulation of Phase Behavior of Fluids in Gels

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Abstract. It is found experimentally that the coexistence region of a vapor–liquid system is substantially narrowed when the fluid is confined in a silica aerogel with a high degree of porosity (e.g. of the order of 95%). A Hamiltonian model for this system has been recently introduced. This is the usual Ginzburg–Landau model for a scalar concentration field $m(\mathbf{r})$ used in binary phase–transitions plus the inclusion of an additional term representing the superficial stress in the neighborhood of the gel: $\mathcal{H} = \int_V dV \left[-\frac{\theta}{2}m^2(\mathbf{r}) + \frac{\chi}{4}m^4(\mathbf{r}) - Hm(\mathbf{r}) + \frac{1}{2}|\nabla m(\mathbf{r})|^2\right] + \oint_S ds \left[-H_1 m(\mathbf{r}) - \frac{g}{2}m^2(\mathbf{r})\right]$. Volume V is the available volume for the fluid and the surface S is the set of fluid points in contact with the gel. We perform Monte–Carlo simulations of the above Hamiltonian in order to find the phase diagram. We consider a three-dimensional lattice with periodic boundary conditions. The gel sites in this lattice form a periodic fractal structure generated by a DLCA (diffusion–limited–cluster–aggregation) process. To find the phase diagram for a defined value of the surface field H_1, the surface enhancement parameter g and the width of the coexistence curve χ, we use the following scheme: for each reduced temperature θ, we compute the hysteresis loop and the Gibbs free–energy (evaluated by integration of the ensemble average order parameter $\bar{M}(H)$ from $H = \pm\infty$) for several values of total field H. The two minima of the free–energy identify the two coexisting phases and indicate the actual location of the transition causing the hysteresis loop, i.e. the actual value H_0 of the total field H such that the two phases have the same value for the free–energy. We find in this way the function $H_0 = H_0(\theta)$ which allows us to compute the phase diagram. This is qualitatively similar to that observed experimentally: the coexistence region in the presence of gel is narrowed and shifted with respect to the non–gel situation. However, it is difficult to perform simulations near the critical point and, hence, we have not been able yet to obtain an accurate value for the critical exponents of the model.

References

Donley, J., Liu, A. (1996): *in preprint*, "Phase Behavior of Near–Critical Fluids Confined in Periodic Gels"
Wong, A., Chan, M. (1990): *Phys. Rev. Lett.* **65**, 2567–2570
Falicov, A., Berker, A. (1995): *Phys. Rev. Lett.* **74**, 426–429
Nakanishi, H., Fisher, M. (1983): *J. Chem. Phys.* **78**, 3279–3293

Proceedings of the 4th Granada Seminar on Computational Physics,
P. Garrido, J. Marro, eds. Springer (1996)