Vapor-Liquid Coexistence in Microporous Systems

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The immense importance of vapor/liquid equilibrium in industrial processes has been extensively studied for several decades. The description of how molecules distribute themselves in an equilibrium system is important for chemists, physicists, and chemical engineers on a daily basis. In this work, we describe the equilibrium between a liquid-like and vapor-like phase of benzene in a microporous material, a system with three-dimensional cages on a molecular scale (MOF-5). The two-phase equilibrium has been studied using computer simulations as well as NMR relaxation measurements. Both of these techniques confirm the two phases are on a length scale significantly longer then the characteristic size of the pores. Previously, two-phase equilibrium has been thought impossible in such a nanoporous material. However, with a sufficiently open structure, the interactions between neighboring cages allow for interactions between guest-molecules, thereby lowering the critical point. At sufficiently high temperatures, the two phases transition into a single critical phase. Using computer simulations, we have described a phase-diagram for benzene in MOF-5. This phase-diagram is comparable to the phase-diagram seen for bulk-systems, but with a significant lowering of the critical point. By systematically changing the pore size, the critical point can be lowered from the bulk-phase critical point, and for very small cage sizes, the critical point disappears completely. This transition from two-phases to a super-critical phase has been verified experimentally, and is in good agreement with the simulation data for this system.