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Adsorption hysteresis in nanopores

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Capillary condensation hysteresis in nanopores is studied by Monte Carlo simulations and the nonlocal density functional theory. Comparing the theoretical results with the experimental data on low temperature sorption of nitrogen and argon in cylindrical channels of mesoporous siliceous molecular sieves of MCM-41 type, we have revealed four qualitatively different sorption regimes depending on the temperature and pore size. As the pore size increases at a given temperature, or as the temperature decreases at a given pore size, the following regimes are consequently observed: volume filling without phase separation, reversible stepwise capillary condensation, irreversible capillary condensation with developing hysteresis, and capillary condensation with developed hysteresis. We show that, in the regime of developed hysteresis (pores wider than 5 nm in the case of nitrogen sorption at 77 K), condensation occurs spontaneously at the vaporlike spinodal while desorption takes place at the equilibrium. A quantitative agreement is found between the modeling results and the experimental hysteresis loops formed by the adsorption-desorption isotherms. The results obtained provide a better understanding of the general behavior of confined fluids and the specifics of sorption and phase transitions in nanomaterials.

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When a porous solid is exposed to a vapor, the latter condenses in the pores, forming a liquidlike dense state. This phenomenon, known as capillary condensation, occurs at gas pressures smaller than the pressure of the saturated vapor at the given temperature. As the temperature increases, the effect of capillary condensation disappears; however, the critical temperature of capillary condensation is lower than the bulk critical temperature. Capillary condensation indicates a shift of the bulk gas-liquid equilibrium caused by confinement. Experimentally, capillary condensation is characterized by a typical step in adsorption isotherms and, in the vast majority of systems, is associated with a pronounced hysteresis. Adsorption-desorption isotherms form a reproducible hysteresis loop, the shape of which depends on the peculiarities of the pore structure. In the physicochemical literature, there are numerous examples of adsorption hysteresis in various systems containing pores ranging from fractions to hundreds of nanometers; for comprehensive review, see Ref. [1]. Adsorption-desorption isotherms are of great practical interest for catalysis and separation technologies and are also widely used for pore structure characterization and calculations of porosity, specific surface area, pore size distribution, and fractal dimension [2]. Although the first theories of capillary condensation date back to Zigmondi's works at the beginning of the century [3], the problem of adsorption hysteresis still remains poorly understood. Recent experiments with MCM-41 mesoporous molecular sieves with controlled pore sizes [4] revealed that no theory exists which can provide a quantitatively accurate description of capillary condensation hysteresis and criticality in nanosized pores.

In this Rapid Communication, we present the results of comprehensive studies of capillary hysteresis in cylindrical pores using long-run Monte Carlo (MC) simulations and nonlocal density functional theory (NLDFT). The theoretical results are in quantitative agreement with the high resolution N_2 and Ar adsorption measurements on MCM-41 type materials. Although we do not attempt to present an all-encompassing description of capillary condensation, the combination of molecular level theoretical models and precise experiments has allowed us to make several well-founded conclusions, shedding light on specific features of this enigmatic phenomenon. We show that four regimes of sorption in cylindrical pores are distinguished as the pore diameter increases, starting from a molecular scale of 0.3–0.4 nm. These are volume filling without phase separation (supercritical sorption), reversible capillary condensation, capillary condensation with *developing* hysteresis, and capillary condensation with *developed* hysteresis. The boundaries of these regimes depend on a given temperature and fluid-substrate pair.

In the last few years, a number of attempts have been made to obtain a better understanding of capillary condensation hysteresis based on (i) the statistical mechanics of confined fluids, including various versions of the density functional theory [4,5], Monte Carlo [6] and molecular dynamics [7] simulations, and lattice gas models [8]; and (ii) model thermodynamic approaches [9], dating back to the seminal works of Derjaguin [10]. The model thermodynamic approaches, which are based on the utilization and modification of classical thermodynamics models of capillary condensation in cylindrical pores, assume that prior to capillary condensation the adsorbed fluid forms a uniform liquid film on the pore walls [10,11]. Although this assumption is reasonable for sufficiently wide pores (>10 nm), it is not adequate for narrow pores of less than ten molecular diameters in width (4 nm), in which a transition is observed from irreversible to reversible capillary condensation [4]. It is worth noting that before the discovery of the MCM-41 mesoporous molecular sieves in 1992 [12], there were no experimental systems with well defined pore channels, and the quantitative

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analysis of theoretical conclusions was hindered by the intrinsic geometrical heterogeneity of available samples. The MCM-41 type materials employed in our study contain uniform two-dimensional arrays of cylindrical pores of predetermined diameter, and serve as the best available references for adsorption studies [13,14]. The hexagonal symmetry and uniformity of the pore system in MCM-41 were confirmed by high resolution x-ray diffraction and transmission electron microscopy studies [12–14]. It is assumed that the pore blocking effects are negligible [4].

In MC simulations and NLDFT studies of the capillary condensation in pores of MCM-41 materials, the pores were modeled as infinitely long cylindrical channels. Solid-fluid interactions were represented by an integrated Lennard-Jones (LJ) potential induced by a structureless cylindrical layer of oxygen atoms [15]. Nitrogen and argon were modeled as LJ fluids. The MC simulations were carried out in the grand canonical ensemble. Periodic boundary conditions were applied in the direction parallel to the walls. The total length of the MC simulations was 4×10^4 steps per molecule. Each step included a sequence of attempts of molecule displacement, insertion, and removal. To determine the equilibrium, the thermodynamic integration method of Peterson and Gubbins [16] was applied. In the NLDFT calculations, we used Tarazona's smoothed density approximation [17]. Attractive fluid-fluid interactions were treated in a mean-field fashion using the Weeks-Chandler-Anderson scheme. The parameters of fluid-fluid and fluid-solid intermolecular potentials were chosen to fit with bulk properties of the adsorbates, including liquid-gas surface tension, and reference adsorption isotherms on nonporous substrates [4,18]. In the NLDFT calculations, the following LJ parameters and hard sphere diameter were used: $\epsilon_{\mathrm{ff}}/k_B=94.45$ K, and $\sigma_{\mathrm{ff}}=d_{\mathrm{HS}}=0.3575$ nm for nitrogen, and $\epsilon_{\mathrm{ff}}/k_B=118.05$ K, $\sigma_{\mathrm{ff}}=0.3305$ nm, and $d_{\mathrm{HS}}=0.339$ nm for argon. In the MC simulations, which were done for the LJ model of nitrogen at 77 K, the parameters were slightly different ($\epsilon_{\mathrm{ff}}/k_B=101.5$ K, and $\sigma_{\mathrm{ff}}=0.3615$ nm), which reflects intrinsic approximations of the NLDFT model. The LJ potential was truncated at $5\sigma_{\mathrm{ff}}$ in both models. Solid-fluid parameters $\rho_s\epsilon_{\mathrm{sf}}/k_B=2253$ K/nm^2, $\sigma_{\mathrm{sf}}=0.317$ nm and $\rho_s\epsilon_{\mathrm{sf}}/k_B=2620$ K/nm^2, $\sigma_{\mathrm{sf}}=0.30$ nm were used for nitrogen and argon, respectively.

Both methods, NLDFT and MC simulations, allow one to determine three characteristic points on adsorption-desorption isotherms: the point of equilibrium capillary condensation transition, P_{eq}/P_0; the point of spontaneous capillary condensation (vaporlike spinodal), P_{sc}/P_0; and the point of spontaneous desorption (liquidlike spinodal), P_{sd}/P_0 (Fig. 1). Note that the results of NLDFT and MC simulations are fairly consistent. A series of detailed van der Waals type, *S*-shaped isotherms was constructed in pores of different diameters by the recently proposed canonical ensemble density functional theory model [20]. As the pore diameter decreases, the hysteresis loop narrows, and, in the pore of the critical width, it disappears. This behavior is similar to that of the bulk phase equilibrium; the hysteresis loop vanishes at critical conditions of the capillary condensation transition. Thus, in virtual experiments, assuming that the density fluctuations are sufficiently suppressed and the boundary effects are insignificant, hysteresis is an inherent property of capillary condensation. A similar disappearance of the hysteresis loop above a certain critical temperature is observed in a series of adsorption isotherms in a given pore structure calculated at different temperatures. Capillary condensation criticality is a well-established concept supported by many experiments [19] and theories [21]. However, this concept leads to only two regimes of sorption: the regime of reversible supercritical adsorption, known in the adsorption literature as the volume filling of micropores; and the capillary condensation regime inevitably accompanied by hysteresis.

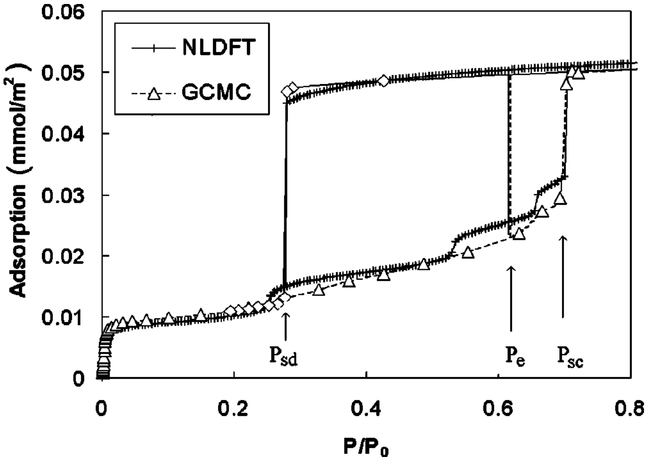

FIG. 1. MC and NLDFT isotherms of nitrogen adsorption in a 6.97 nm cylindrical silica pore at 77.4 K. The arrows indicate the positions of the liquidlike spinodal (left), equilibrium transition (middle), and vaporlike spinodal (right).

A series of MC simulations of capillary condensation in the pore cells of different length (10, 30, and 60 molecular diameters) is presented in Fig. 2. As the cell length increases, the point of spontaneous desorption shifts toward the point of equilibrium transition, while the point of spontaneous condensation remains unchanged. This complies with the expected conclusion that in sufficiently long cylindrical capillaries of supercritical diameter, desorption should occur at

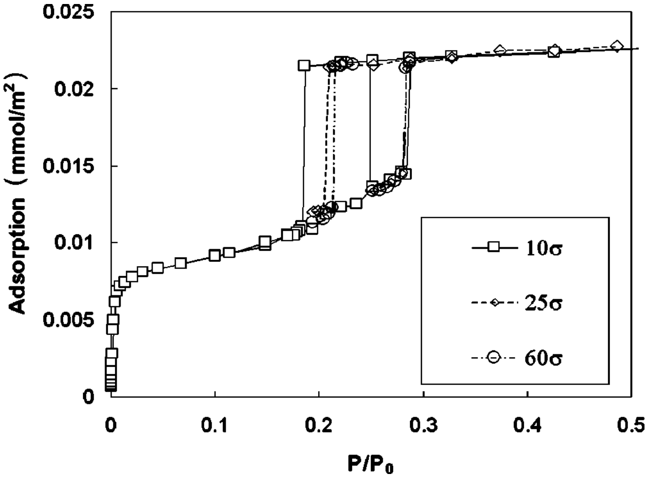

FIG. 2. MC isotherms of nitrogen adsorption in a 3.35 nm cylindrical silica pore at 77.4 K, calculated with different sizes of the simulation cell. Thin vertical lines show the locations of the spontaneous capillary condensation transition (right), spontaneous evaporation transition (left), and vapor-liquid equilibrium in the pore (middle).

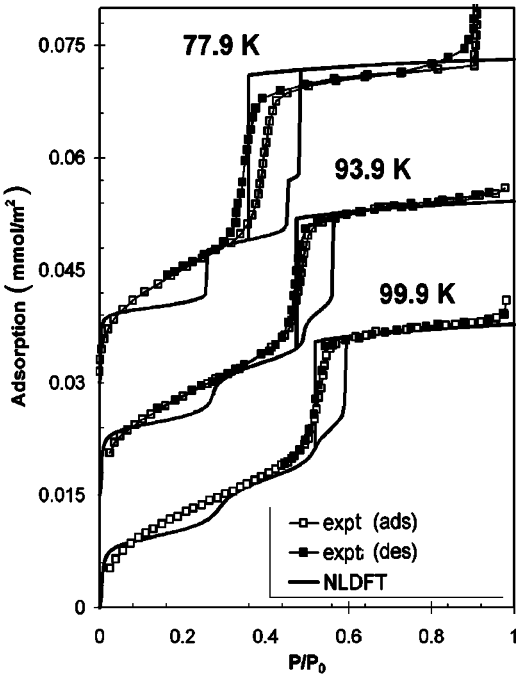

FIG. 3. Isotherms of argon adsorption on reference MCM-41 sample. Lines: NLDFT calculations for a 4.4-nm pore; points: experimental data [19]. At 77.9 K pressures are related to the saturation pressure of supercooled liquid Ar.

the point of equilibrium transition and condensation, at the vaporlike spinodal, which represents the true limit of stability of metastable adsorbed films. This conclusion correlates with the classical scenario of capillary condensation hysteresis in open-ended cylindrical pores [1,21]. We will refer to this regime as capillary condensation with developed hysteresis. In real experiments, intrinsic fluctuations, boundary effects, and irregularities of any kind may lead to a shift of the points of spontaneous condensation and desorption transitions from the spinodals toward the point of equilibrium transition. One expects that the experimental isotherm should be bounded by theoretical spinodals. That is, the theoretical hysteresis loop is broader than the experimental hysteresis loop. In the case of MCM-41 materials with presumably long open-ended cylindrical channels, the prediction may be more precise: condensation should take place between the spinodal and equilibrium, whereas desorption occurs near the point of equilibrium. The regime in which the observed adsorption branch is significantly rounded and shifted compared with the spinodal is referred to as capillary condensation with developing hysteresis. A comparison of theoretical predictions with experimental data allows us to estimate the boundaries of different sorption regimes.

Typical examples of the correlation between theoretical and experimental isotherms are presented in Figs. 3 and 4. In Fig. 3, three Ar adsorption-desorption isotherms measured on a MCM-41 sample with a mean pore size of ~4.4 nm at 99.9, 93.3, and 77.9 K [19] are compared with theoretical isotherms calculated by the NLDFT model with the desorption branch limited by the point of equilibrium transition. The capillary condensation/desorption step on the experimental isotherms is slightly rounded, as expected for a phase transition in a system composed of a large number of finite size pores with inevitable variations in pore diameter (± 0.2 nm for the sample in Fig. 3). However, the inflection point agrees satisfactorily with the position of the theoretical equilibrium transition in a pore of the mean size. From this example, we see that capillary condensation as a first order phase transition, which is indicated by a prominent step on the isotherm, occurs either irreversibly at sufficiently low temperatures or reversibly at higher temperatures. The existence of hysteresis is not an obligatory condition of capillary condensation, as assumed in earlier theories [1,21]. The disappearance of hysteresis with a decrease of the pore size or with an increase of temperature cannot be explained by the established concept of the critical temperature of capillary condensation [21]. For the first time, to our knowledge, this conclusion was made in our studies of nitrogen sorption in the reference MCM-41 samples [4] and then confirmed in Ref. [19]. We note that the theoretical equilibrium desorption step quantitatively reflects the temperature dependence of the experimental desorption branch in both reversible and hysteretic situations. The deviations between theoretical and experimental isotherms in the region of polymolecular adsorption is likely caused by neglect of the intrinsic energetic and geometrical heterogeneities of the pore walls.

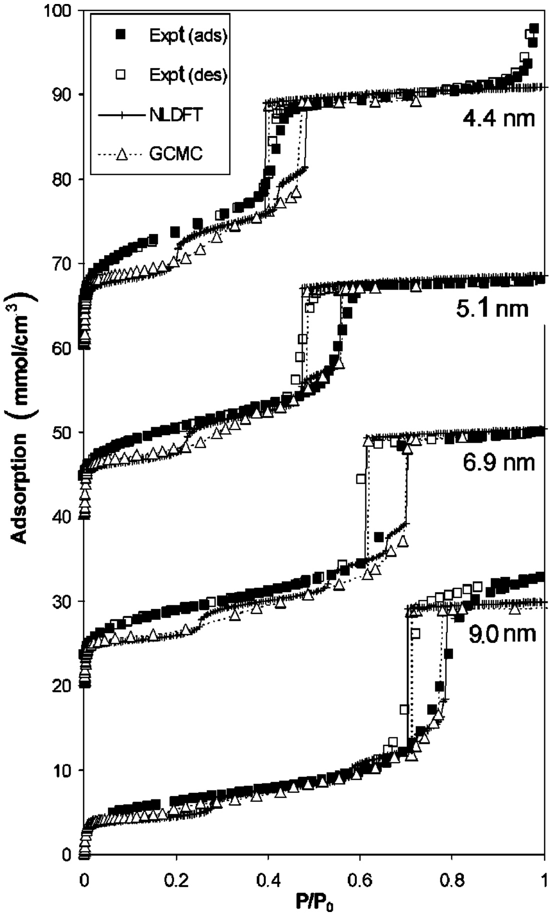

FIG. 4. Isotherms of nitrogen adsorption on several MCM-41-like samples at 77.4 K: experimental data [4,13,14] top to bottom, MC simulation, and NLDFT calculation (pore widths shown on the plot).

In Fig. 4, we compare the experimental isotherm of N_2 adsorption-desorption at 77 K measured on four samples of the MCM-41 type materials [4,14,13], with the NLDFT and MC simulated isotherms in cylindrical pores of 9.0, 6.9, 5.1, and 4.4 nm. The theoretical hysteretic isotherms are bounded by the vertical lines of the vaporlike spinodal (right) and equilibrium (left). For materials with pores wider than ca. 5 nm, both branches of the hysteretic isotherms are in quantitative agreement with the theoretical predictions for the regime of capillary condensation with developed hysteresis. In pores narrower than ca. 4 nm, the adsorption hysteresis is not observed, and both adsorption and desorption isotherms coincide with the theoretical equilibrium isotherm. In intermediate pores, the hysteresis develops as the pore size increases. Desorption is experimentally observed near the theoretical equilibrium transition while the spinodal is not achieved, and condensation occurs between the theoretical equilibrium and the spinodal.

To conclude, NLDFT and MC simulations, with properly chosen parameters of fluid-fluid and fluid-solid intermolecular interactions, quantitatively predict both adsorption and desorption branches of capillary condensation isotherms in the regime of developed hysteresis occurring in cylindrical pores wider than ca. 5 nm. The desorption branch follows the theoretical line of equilibrium transitions while the adsorption branch is close to the theoretical vaporlike spinodal. In the regime of developing hysteresis, in pores of 4–5 nm, the true limit of stability of adsorbed films is not achieved and the observed hysteresis loop gradually narrows as the pore width decreases, and vanishes in pores smaller that ca. 4 nm. However, this critical pore size of adsorption hysteresis significantly exceeds the critical pore size of capillary condensation as the first order phase transition. The latter was estimated as ca. 2 nm [4]. The above values of pore sizes, separating different regimes of capillary condensation, were estimated for sorption of N_2 at 77.4 K in cylindrical channels of MCM-41 materials, and may vary depending on the fluid-substrate pair.

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