

Connection Between Thermodynamics and Dynamics of Simple Fluids in Pores: Impact of Fluid-Fluid Interaction Range and Fluid-Solid Interaction Strength

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Abstract

Using molecular simulations, we investigate how the range of fluid-fluid (adsorbate-adsorbate) interactions and the strength of fluid-solid (adsorbate-adsorbent) interactions impact the strong connection between distinct adsorptive regimes and distinct self-diffusivity regimes reported in [Krekelberg, W. P.; Siderius, D. W.; Shen, V. K.; Truskett, T. M.; Errington, J. R. *Langmuir* **2013**, *29*, 14527–14535]. Although increasing the fluid-fluid interaction range changes both the thermodynamics and the dynamic properties of adsorbed fluids, the previously reported connection between adsorptive filling regimes and self-diffusivity regimes remains. Increasing the fluid-fluid interaction range leads to enhanced layering and decreased self-diffusivity in the multilayer-formation regime but has little effect on the properties within film-formation and pore-filling regimes. We also find that weakly attractive adsorbents, which do not display distinct multilayer formation, are hard-sphere-like at super- and subcritical temperatures. In this case, the self-diffusivity of the confined and bulk fluid has a nearly identical scaling-relationship with effective density.

1 Introduction

The adsorption of light gases by porous materials plays an important role in a wide array of technologies.^{1–5} The measurement of single-component adsorption thermodynamic properties is well-developed, and these measurements can in turn be used to infer the underlying adsorbent (solid) structure and adsorbate-adsorbent (fluid-solid) interactions by utilizing well developed heuristics based on the form of the adsorption isotherm.^{6,7} While such thermodynamic information is critical to determining a material’s adsorptive characteristics, the dynamic properties of the confined fluid, such as diffusion, also impact performance. Although not as well studied as thermodynamic properties, dynamic properties in adsorptive systems have received recent attention.^{8–10} Examples include studies of self-diffusivity in porous adsorbents,^{9,11,12} and simulation of self-diffusivity and development of simplified molecular models of intrapore transport.^{13–15} Other work has investigated transport diffusivity in the Fickian sense¹⁶ and explored nonequilibrium adsorption hysteresis related to intrapore diffusion.^{17,18} Theoretical research has examined the dynamics of pore filling, capillary condensation, cavitation, and pore-network effects using dynamic lattice fluid models.^{19–22} Despite the insights provided by some of these studies, reliable means for predicting and even estimating confined-fluid dynamics remain lacking. While most studies focus separately on thermodynamic and dynamic aspects of fluid behavior in confinement, the connection between the thermodynamics of confined fluids and the corresponding dynamic properties remains a comparatively open topic of investigation. As noted earlier, pure-component adsorption isotherms can be used to infer underlying adsorbent pore structure and adsorbent-adsorbate interactions. Using exhaustive molecular simulation data, we further show in this paper that they can also be used to infer information about the self-diffusivity of confined fluids.

We recently²³ investigated the link between adsorptive thermodynamic properties and confined-fluid mobility in strongly attractive materials. We found that the adsorption isotherms in these systems can be used to classify distinct diffusivity regimes. Specifically,

at temperatures below the bulk critical temperature, three distinct adsorptive regimes are observed in pores with strong fluid-solid interactions:

Film formation occurs at low pressures, where the adsorbate loading (or confined-fluid density, ρ) rapidly increases with applied pressure. Fluid molecules are located in a single layer adjacent to the pore wall.

Multilayer formation occurs at moderate pressures below the capillary condensation pressure, where ρ increases more slowly than in film formation. Fluid molecules sequentially occupy positions interior to the film layer (i.e., particles fill the second, then third, etc., layers).

Pore filling occurs at high pressure above the capillary condensation pressure, where ρ increases slowly with applied pressure. The pore is effectively saturated and added particles occupy positions throughout the pore.

We observed that, in strongly attractive pores, three distinct diffusivity regimes also emerge:

Diffusivity regime 1 (DR1) occurs at low ρ , where self-diffusivity (D) rapidly decreases with increasing ρ .

Diffusivity regime 2 (DR2) occurs at moderate ρ , where D is approximately constant with respect to ρ

Diffusivity regime 3 (DR3) occurs at high ρ , where D decreases with increasing ρ

It was shown that these three diffusivity regimes directly correspond to the three adsorptive regimes. That is, DR1 corresponds to film formation, DR2 corresponds to multilayer formation, and DR3 corresponds to pore filling. Therefore, the isotherm can be used to infer at least the qualitative behavior of the adsorbed fluid's diffusivity.

In this paper, we address an open question from ref. 23: How do the details of the fluid-fluid and fluid-solid interactions impact the connection between adsorptive regimes

and diffusivity regimes? To address this question, we investigate two key parameters: the fluid-fluid interaction range and the fluid-solid interaction strength. The paper is organized as follows. In section 2 we present the simulation methods and model fluid and adsorbents used. Section 3 presents the results of our simulations and discusses the relationship between intrapore self-diffusivity and adsorption thermodynamics. Finally, in section 4, we summarize our key findings.

2 Theoretical Methods

2.1 Adsorbate Model

We use molecular simulations to investigate the properties of argon (Ar) fluid adsorbed into several adsorbents. The argon fluid is modeled using the Lennard-Jones (LJ) potential, truncated by a linear force shift at the cutoff distance r_{cut} :

$$V_{\text{LJ-CFS}}(r) = \begin{cases} V_{\text{LJ}}(r) - V_{\text{LJ}}(r_{\text{cut}}) \\ -V'_{\text{LJ}}(r_{\text{cut}}) \cdot (r - r_{\text{cut}}) & r < r_{\text{cut}} , \\ 0 & r \geq r_{\text{cut}} \end{cases} \quad (1)$$

where

$$V_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2)$$

Numerical values of σ and ϵ for argon are provided in Table 1. For simplicity, these values, as well as the mass of an argon atom m , are used to nondimensionalize our results. The values of fluid-fluid (or adsorbate-adsorbate) cutoff r_{cut} will be one of $r_{\text{cut}}/\sigma = 2.5, 4.0$, or 6.0 . Note that this parameter controls the range of the fluid-fluid interaction. For the sake of brevity, we use the term cutoff (or r_{cut}) to refer to the fluid-fluid interaction range.

2.2 Adsorbent Models

2.2.1 Strongly Attractive Adsorbent

Following ref. 23, we model the adsorption of argon into multiwall carbon nanotube (CNT) using the cylindrical Steele 10-4-3 potential.²⁴ We refer to this system as a strongly attractive adsorbent because the fluid-solid interaction strength is very attractive, as will be shown later. Parameters for the fluid-fluid and fluid-solid interaction are given in Table 1. In this pore, cutoff values of $r_{\text{cut}} = 2.5\sigma$ and 6.0σ were investigated. The former value was also used in ref. 23 and provides continuity with the present work.

2.2.2 Weakly Attractive Adsorbent

For a weakly attractive system, we have chosen a model which mimics argon adsorption in a cylindrical pore bored out of solid carbon dioxide (CO₂). The effective fluid-wall interactions are modeled using a cylindrical 9-3 potential,²⁵ given as

$$\begin{aligned}
 V_{9-3}(r, R) = & 2\pi\rho_s\sigma_{\text{fw}}^3\epsilon_{\text{fw}} \\
 & \times \left[\frac{7\pi}{64} \left(\frac{\sigma_{\text{fw}}}{R} \right)^9 \left[1 - \left(\frac{r}{R} \right)^2 \right]^{-9} \right. \\
 & \times {}_2F_1 \left[-9/2, -7/2; 1, (r/R)^2 \right] \\
 & - \frac{\pi}{2} \left(\frac{\sigma_{\text{fw}}}{R} \right)^3 \left[1 - \left(\frac{r}{R} \right)^2 \right]^{-3} \\
 & \left. \times {}_2F_1 \left[-3/2, -1/2; 1, (r/R)^2 \right] \right] \quad (3)
 \end{aligned}$$

where ${}_2F_1$ is the hypergeometric function. For this adsorbent, we investigated a single cutoff value $r_{\text{cut}} = 4.0\sigma$. The fluid-solid interaction parameters are given in Table 1.

Table 1: Lennard-Jones parameters and relevant physical properties for the Ar-Ar fluid-fluid, the Ar-CNT fluid-solid, and the Ar-CO2 fluid-solid interactions. σ is the LJ diameter, ϵ is the LJ energy scale, and k_B is Boltzmann’s constant.²⁶ ρ_S is the density of the Carbon or CO2, and Δ is the spacing between graphite basal layers used in the 10 – 4 – 3 CNT potential. Cross interaction parameters were derived via Lorentz-Berthelot mixing rules.

Interaction	σ (nm)	ϵ/k_B (K)	ρ_S (nm ⁻³)	Δ (nm)	refs
Ar-Ar	0.3405	119.8	-	-	27,28
Ar-C	0.3403	57.92	114.0	0.3350	29
Ar-CO ₂	0.3725	153.0	20.9406	-	30,31

2.3 System Summary

For convenience, we specify a particular adsorbent and fluid-fluid interaction range value for the argon adsorbate using the notation ADS[r_{cut}], where ADS=CNT or CO2, and r_{cut} is the dimensionless fluid-fluid interaction range. For example, CNT[2.5] specifies the CNT adsorbent model with cutoff value $r_{\text{cut}} = 2.5\sigma$.

The systems studied in this paper are CNT[2.5], CNT[6.0], and CO2[4.0]. The CNT[6.0] system is investigated at pore sizes $R/\sigma = 5.98, 7.77$, and 8.97 and reduced temperature $k_B T/\epsilon = 0.73$ and 1.5 . The CO2[4.0] system is studied at pore sizes $R/\sigma = 3.0, 4.0, 6.0$, and 8.0 and reduced temperatures $k_B T/\epsilon = 0.73, 0.85$, and 1.5 . For the CO2[4.0] system, we focus on the properties at $k_B T/\epsilon = 0.73$ and 1.5 , but the $k_B T/\epsilon = 0.85$ results are only discussed briefly as they are qualitatively similar to those at $k_B T/\epsilon = 0.73$. Although the bulk critical temperature of the model argon fluid depends on the cutoff or fluid-fluid interaction range, for all cutoff values, the reduced temperature of 1.5 is supercritical and the reduced temperatures of 0.73 and 0.85 are subcritical. The dependence of the the bulk critical temperature on the cutoff value is shown in Table 2.³² Note that when referring to super- or subcritical temperatures later, we always mean relative to the bulk critical temperature. The adsorbate loading, or pore-average fluid density ρ , is defined in terms of the pore-size parameter R as $\rho = N/(\pi R^2 L)$, where N is the number of particles, and L is the axial dimension of the cylindrical pores.

Table 2: Critical temperature of Lennard-Jones fluids.³²

r_{cut}/σ	$k_{\text{B}}T_c/\epsilon$
2.5	0.937
4.0	1.207
6.0 ¹	1.291

2.4 Simulation Methods

We employed the same simulation techniques as in ref. 23 and thus do not restate the details here. In short, molecular dynamics (MD) simulations were used to determine the pore-average self-diffusivity in the axial z directions, D_z , and grand-canonical Transition-Matrix Monte Carlo (TMMC) simulations were used to determine thermodynamic properties, such as the adsorption isotherm and isosteric heat of adsorption.³³ Bulk MD and TMMC simulations were also carried out on the LJ fluid (Eqs. (1) and (2)) for the various values of r_{cut} considered. Note that for the case of $r_{\text{cut}} = 6.0$, bulk thermodynamic properties came from TMMC simulations performed on a system truncated at 3.0σ with analytic long-range corrections.³⁴

2.5 Effective parameters

In section 3, we will compare the properties of a wide range of systems. The comparison of the CNT[2.5] and CNT[6.0] system is straightforward because the adsorbent is the same, but the comparison of the CNT and CO2[4.0] systems is less straightforward because the volume available to fluid particles depends on the fluid-solid interactions. Figure. 1a, which compares the fluid-solid interactions of the CNT and CO2 adsorbents at nearly identical values of R , clearly shows that the volume available to fluid particles is larger in CO2 system than in the CNT system.

We therefore need a definition of effective pore size. First consider the effective fluid

particle diameter, defined using the Barker-Henderson construct:³⁵

$$\sigma_{\text{BH}}(T) = \int_0^\infty dr \{1 - \exp[-V_{\text{ff}}^{\text{rep}}(r)/(k_B T)]\}, \quad (4)$$

where $V_{\text{ff}}^{\text{rep}}(r)$ is the repulsive part of the fluid-fluid potential.³⁶ We likewise empirically define the temperature-dependent Barker-Henderson pore radius as

$$R_{\text{BH}}(T; R) = \int_0^R dr \exp[-V_{\text{fs}}^{\text{rep}}(r; R)/(k_B T)], \quad (5)$$

where $V_{\text{fs}}^{\text{rep}}(r)$ is the repulsive part of the fluid-solid potential, following the Weeks-Chandler-Anderson decomposition.³⁶

We define the “available” density as $\rho_{\text{A}}(T; R) = N/[\pi R_{\text{BH}}(T; R)^2 L]$, and the “effective” density as $\rho_{\text{E}} = N/[\pi R_{\text{E}}(T; R)^2 L]$, where $R_{\text{E}}(T; R) = R_{\text{BH}}(T; R) + \sigma_{\text{BH}}(T)/2$. Defined this way, $\sigma_{\text{BH}}(T)$ and $R_{\text{E}}(T; R)$ can be thought of as a mapping between the actual system and an effective hard-sphere fluid confined in a cylindrical pore with hard walls. Figure 1b compares the fluid-solid interactions of the CNT and CO₂ adsorbates to the fluid-fluid LJ interaction in terms of effective size parameters. Note that using these effective parameters leads to overlapping fluid-solid repulsions.

Other measures for the effective pore size, such as a Boltzmann factor criterion, based on both the actual external field V_{ext} and the external potential of mean force $V_{\text{ext}}^{\text{MF}}(r) = -k_B T \log \rho(r)$, were also considered. All investigated methods lead to qualitatively similar, and nearly quantitatively identical, results. The Barker-Henderson pore radius defined in Eq. (5) was used because it depends only on temperature. Note the much deeper minimum in the CNT adsorbent compared to the CO₂ adsorbent. This is why we refer to the CNT system as strongly attractive and the CO₂ system as weakly attractive.

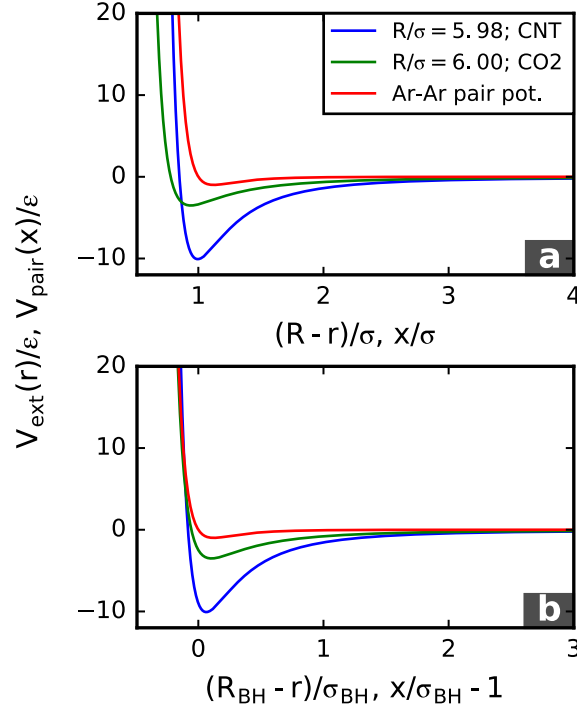


Figure 1: Comparison of potential energy for CNT fluid-solid, CO₂ fluid-solid, and Ar-Ar fluid-fluid interactions. (a) Potentials as a function of unscaled coordinates and (b) potentials as a function of scaled coordinates for $k_{\text{B}}T/\epsilon = 1.5$.

3 Results and Discussion

3.1 Impact of Fluid-Fluid Interaction Range

We begin by investigating the impact of fluid cutoff r_{cut} , which controls the fluid-fluid interaction range, on the properties of argon in strongly attractive CNT pores by comparing the properties of the CNT[2.5] and CNT[6.0] systems. Figure 2 shows the isotherms for both systems at all temperatures and pore sizes considered. Clearly, the qualitative forms of the isotherms are similar between the two cutoff values. At the supercritical temperature of $k_{\text{B}}T/\epsilon = 1.5$ the isotherms are of Type-I Langmuir form. At the subcritical temperature of $k_{\text{B}}T/\epsilon = 0.73$ the isotherms are of Type-IV form, displaying classic hysteresis and strong adsorption at low pressures.

Despite the qualitative similarities, closer inspection reveals distinct quantitative differ-

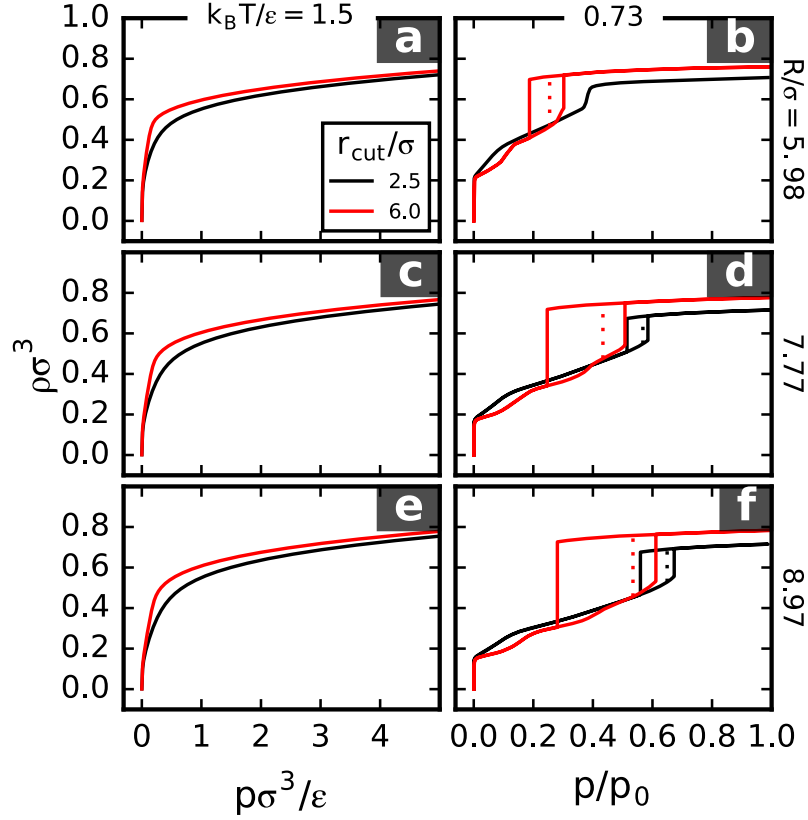


Figure 2: Comparison of CNT[2.5] and CNT[6.0] isotherms. Temperatures and pore sizes are noted along the top of each column and the side of each row, respectively. Note that, at the subcritical temperature of $k_B T/\epsilon = 0.73$ in (b), the pressure is reduced by the bulk saturation pressure p_0 . Dotted lines in (b) indicate coexistence between high and low density phases.

ences as a function of cutoff value. Figure 2 directly compares the isotherms of the CNT[6.0] and CNT[2.5] systems. At $k_B T/\epsilon = 1.5$ (Figs. 2a, c, and e), the longer cutoff leads to a steeper initial fluid loading at low pressures compared to the shorter cutoff. We see that differences in the high-temperature adsorption isotherms between the two cutoffs diminishes at high pressure.

At the subcritical temperature of $k_B T/\epsilon = 0.73$ (Figs. 2b, d, and f), the initial sharp loading, which is a thermodynamic signature of film formation, is nearly identical for the two cutoffs. However, the adsorption isotherms exhibit large differences as a function of cutoff value in other filling regimes. For example, the cutoff impacts the limits of stability

between the low- and high-density fluid branches. Specifically, the desorption and adsorption stability limits shift to lower pressures with increasing cutoff. However, it is clear that the shift is larger for desorption than for adsorption. In fact, for the case of $k_{\text{B}}T/\epsilon = 0.73$ and $R/\sigma = 5.98$ (Fig. 2b), we see that the longer cutoff results in a hysteresis loop, whereas none exists for the shorter cutoff. Also, the fluid loading near the saturation pressure p_0 increases with cutoff. This suggests that increasing the fluid-fluid interaction range leads to increased fluid cohesiveness.

Increasing fluid-fluid interaction range and lowering temperature have similar effects on fluid adsorption. Since the bulk critical temperature T_c increases with cutoff value range (see Table 2), the temperature relative to the bulk critical temperature T/T_c is decreased by increasing the cutoff at fixed T . Therefore, one can view the differences in Fig. 2 as resulting from, effectively, lowering temperature.

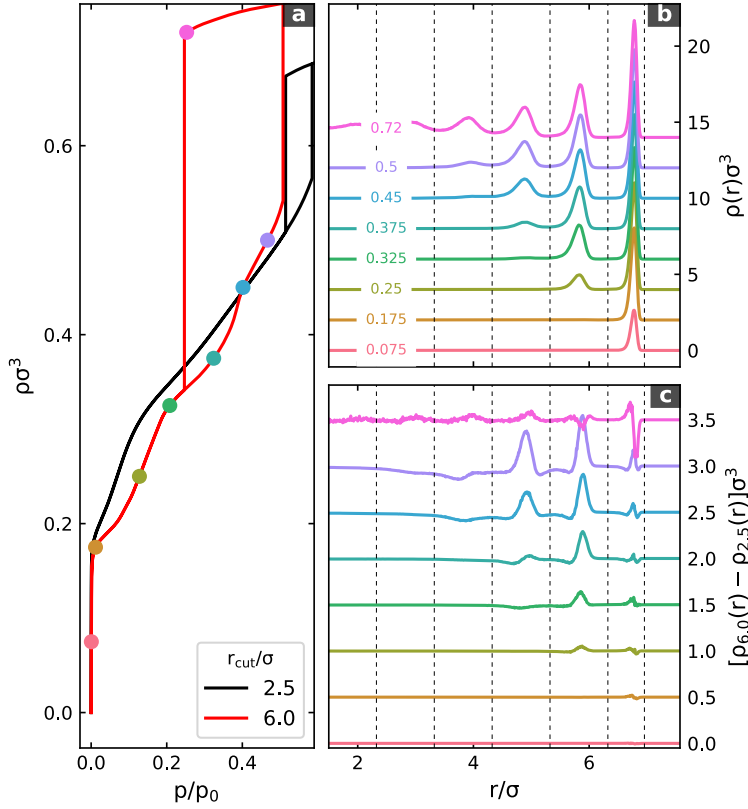


Figure 3: Comparison of structural characteristics of CNT[2.5] and CNT[6.0] systems with $k_B T/\epsilon = 0.73$ and $R/\sigma = 7.77$. (a) Zoomed perspective of isotherms. (b) Density profiles at several pore densities for the CNT[6.0] system. (c) Difference between density profile for the CNT[6.0] and CNT[2.5] systems. The color of each curve in (b) and (c) corresponds to the marker color in (a). Each subsequent curve in (b) and (c) is shifted upward for clarity. The vertical dashed lines in (b) and (c) are the approximate boundaries between each distinct fluid layer.

Another effect of increasing the cutoff value is the formation of distinct “steps” in the adsorption isotherm at subcritical temperatures and moderate pressures. These steps are shown more clearly in Figure 3a, which provides a zoomed perspective of the isotherms of the CNT systems at $k_B T/\epsilon = 0.73$ and $R/\sigma = 7.77$ from Fig. 2d. We observe steps in the isotherm near $\rho\sigma^3 = 0.325$ and 0.45 . Figure 3b shows that in the density range $0.175 < \rho\sigma^3 < 0.325$ particles accumulate predominately in the second layer (relative to the

fluid-solid interface). At $\rho\sigma^3 = 0.325$, the location of a step in the isotherm, particles begin to accumulate in the third layer. Then, for $0.325 < \rho\sigma^3 < 0.45$ particles predominately accumulate in the third layer. Finally, for densities $\rho\sigma^3 > 0.45$, particles tend to accumulate in the fourth layer. Thus, we see that the steps in the isotherm are due to the filling of individual layers, very nearly one at a time.

This sequential filling of layers is a signature characteristic of the multilayer-formation regime. Closer inspection of Figs. 2b, d, and f and 3a shows that the CNT[2.5] system also displays steps in the isotherm at moderate pressure (near $\rho\sigma^3 = 0.325$ especially), but to a much lesser degree than in the CNT[6.0] system. This suggests that increasing cutoff, or likewise, as discussed earlier, decreasing temperature, enhances layering. To contrast the structure in the CNT[6.0] and CNT[2.5] systems, we examine the difference in the density profiles between the two systems at a given pore loading, shown in Fig. 3c. There are no differences in the density profiles at low loading, but differences do emerge at high loading. In the film-formation regime ($\rho\sigma^3 < 0.2$), where particles are predominately in the layer adjacent to the solid surface, there is very little difference in fluid structure between the two systems. This is expected, as in this regime the fluid-solid interaction controls the fluid properties, and hence the cutoff has little impact. However, as subsequent layers are formed in the multilayer-formation regime ($\rho\sigma^3 > 0.2$), we observe progressively larger differences in fluid structure between the cutoffs. Specifically, the maximum value of the density profile in the second layer increases with cutoff. As the loading is further increased ($\rho\sigma^3 > 0.4$) similar differences are displayed in the third layer. Therefore, increasing the cutoff enhances layering, in the sense that the density of the individual layers is increased. These effects are consistent with the fact that increasing the cutoff has a similar effect on fluid structure as lowering temperature. Finally, in the high loading pore-filling regime ($\rho\sigma^3 = 0.72$), the difference in fluid structure between the two systems is negligible. Therefore, differences in the fluid structure as a function of cutoff only appear in the multilayer-formation regime.

At supercritical temperatures, where properties are predominately dependent on the

fluid-fluid repulsion and the fluid-solid interaction, we expect that the cutoff will have a minimal impact on the resulting fluid structure. Moreover, since there is no multilayer formation at supercritical temperatures, our earlier observations also suggest that fluid-fluid interaction range will have no appreciable impact under these conditions. This is indeed the case at $k_B T/\epsilon = 1.5$, where the density profiles are nearly identical in the CNT[2.5] and CNT[6.0] systems (See Supporting Information Fig. S-2). Therefore, differences in fluid structure arising from the cutoff value are very small in the film-formation and pore-filling regimes, and are apparent only in the multilayer-formation regime.

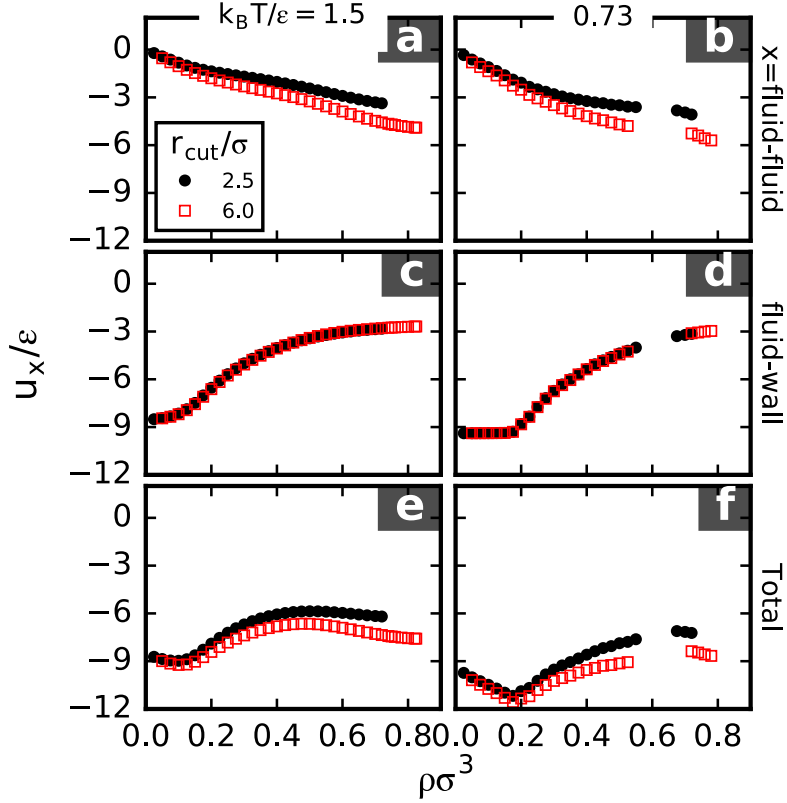


Figure 4: Comparison of the CNT[2.5] and CNT[6.0] potential energy components per particle u_x at $R/\sigma = 7.77$. The potential energy components, fluid-fluid, fluid-wall, and total are noted along each row.

It is now interesting to investigate the impact of the fluid-fluid interaction range on energetic properties. Figure 4 displays the components of the potential energy per particle

in the CNT[2.5] and CNT[6.0] systems at $R/\sigma = 7.77$. Regardless of temperature, the fluid-fluid potential energy is enhanced (i.e., is more negative) by increasing the cutoff. On the other hand, the fluid-solid potential energy is nearly identical between the two systems, emphasizing that the strong fluid-solid interaction dominates the film-layer. Therefore, the observed differences in the total potential energy per particle are due entirely to the differences in cutoff value. What is interesting is that the difference in potential energy increases monotonically with adsorbate loading. This is in contrast to the nonmonotonic difference in structure noted earlier, which is small in the low loading film-formation regime, large in the moderate loading subcritical multilayer-formation regime, and small again in the high loading pore-filling regime. Given this contrast, it is now interesting to investigate how dynamic properties are affected by fluid-fluid interaction range.

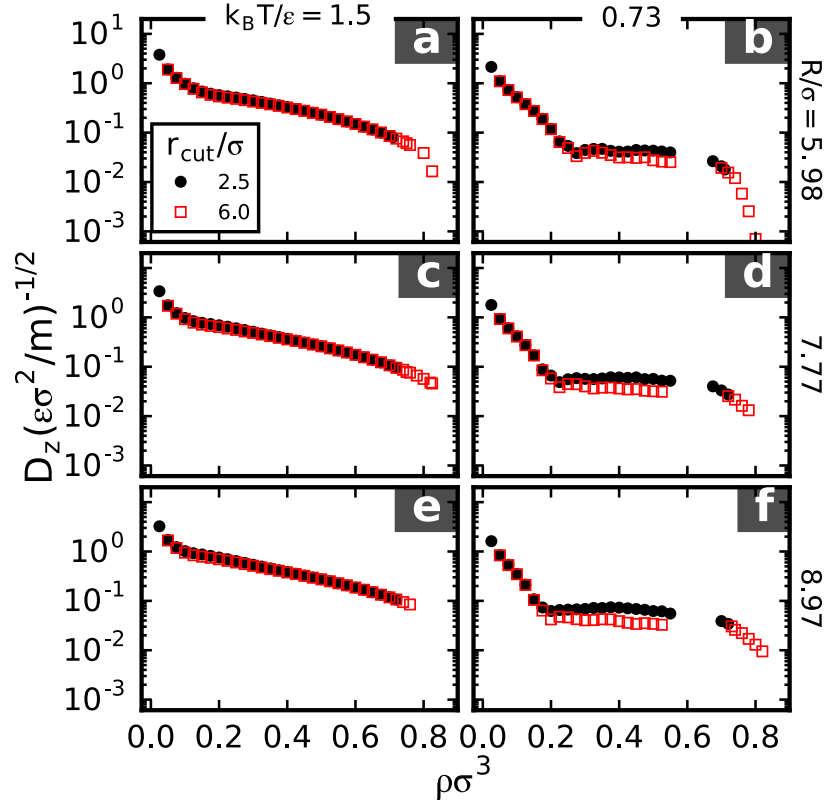


Figure 5: Self-diffusion coefficient vs. fluid density ρ for CNT[2.5] and CNT[6.0] systems. Columns correspond to labeled temperatures, and rows correspond to labeled pore sizes. Symbol type/color corresponds to fluid-fluid interactions range r_{cut} .

Figure 5 compares the CNT[2.5] and CNT[6.0] self-diffusion coefficients as a function of adsorbed fluid density ρ . At the supercritical temperature of $k_B T/\epsilon = 1.5$ the self-diffusivity appears to be insensitive to cutoff. As discussed earlier, even though the cutoff range affects the energetic properties of the system, the structural differences of the confined fluid depend weakly on r_{cut} at supercritical temperatures. This suggests, at least for supercritical temperatures, that the overall fluid structure is closely linked to the self-diffusivity.

Next, consider the subcritical temperature of $k_B T/\epsilon = 0.73$. In this case, the overall dependence of self-diffusion on loading is qualitatively similar for both values of r_{cut} . Thus, like the CNT[2.5] system,²³ the CNT[6.0] system displays three diffusivity regimes DR1, DR2, and DR3 (see Section 1) at subcritical temperatures. In the low loading DR1, the self-diffusivity depends entirely on the film density.²³ As noted earlier, the film density is insensitive to r_{cut} , and we therefore expect the self-diffusivity to likewise be insensitive to cutoff value and Figs. 5b, d, and f shows this to be the case. Following similar arguments and as previously hypothesized in Ref. 23, in the high loading DR3 the self-diffusivity should depend primarily on the packing structure in the pore. As noted earlier, since fluid structure at high loading depends weakly on cutoff, we expect that the self-diffusivity should also depend weakly on cutoff in DR3. Indeed, Fig. 5 shows that this is the case.

At moderate loading and subcritical temperature, we observe that the self-diffusivity is nearly constant, consistent with the previously defined DR2. However, we see that differences in self-diffusivity arise from the cutoff value. As observed earlier, differences in fluid structure arising from r_{cut} are most pronounced in the multilayer-formation regime, where the interior layering is enhanced as r_{cut} is increased. In Figs. 5b, d, and f, we see that increasing r_{cut} decreases the self-diffusivity in DR2. We hypothesize that the enhanced layering due to increasing r_{cut} leads to greater frustration in the layers, which in turn leads to decreased particle mobility. Whereas the quantitative values of self-diffusivity depend on the cutoff, especially in the multilayer-formation regime, the qualitative nature of self-diffusivity does not. We therefore expect the general conclusions of Ref. 23, namely that there is a direct

correspondence between diffusivity regimes and adsorption regimes.

To test this, we compare the locations of the transitions between diffusivity regimes to those between the adsorptive regimes in the same manner as Ref. 23. The transition between the film-formation and the multilayer-formation regimes is defined as the location of the last clearly defined maxima in the isosteric heat of adsorption Q_{st} at low density.^{37,38} We define the transition to pore filling as the point where the density profile at the center of the pore ($\rho(r = 0)$) begins to rapidly increase. Figure 6 compares the transitions between adsorptive regimes and the transitions between diffusivity regimes. We clearly see that DR1 corresponds to film formation, DR2 corresponds to multilayer formation, and that DR3 corresponds to pore filling. Moreover, this correspondence holds at supercritical temperatures as well (See Supporting Information Fig. S-3). Even in the absence of multilayer formation and DR2 regimes under these conditions, we again observe that DR1 corresponds to film formation, and that DR3 corresponds to pore filling. These results show that minor changes to the underlying fluid do not qualitatively change the diffusive characteristics in strongly attractive adsorbents.

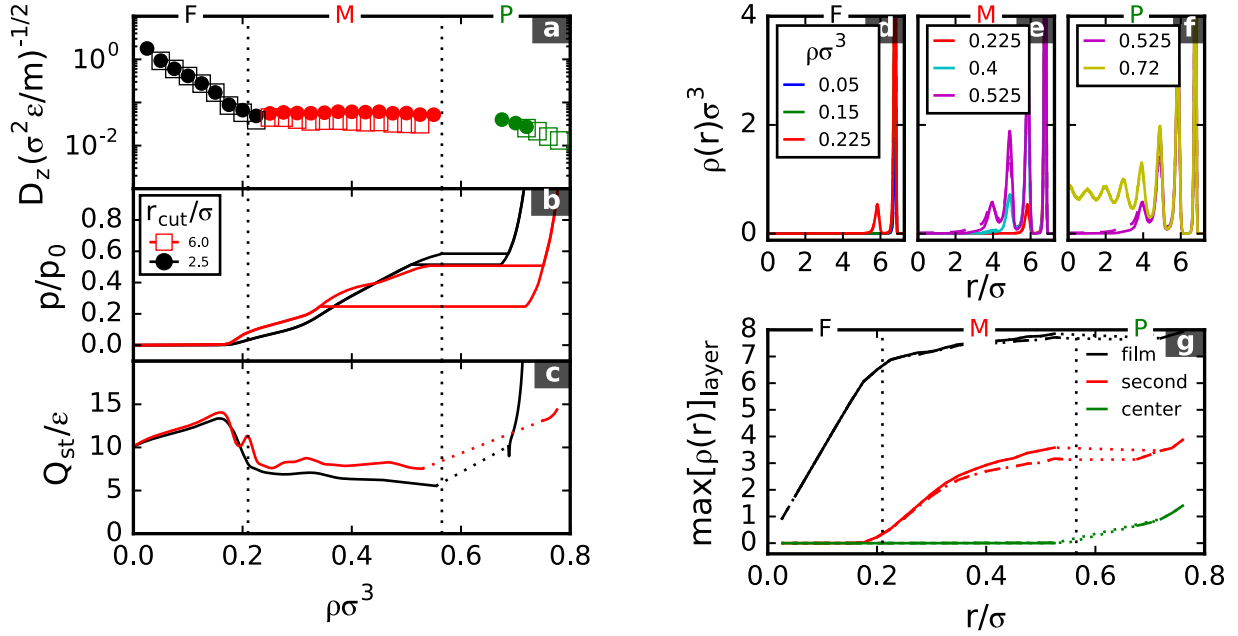


Figure 6: Properties of CNT systems at $k_B T/\epsilon = 0.73$ and $R/\sigma = 7.77$. (a) Self-diffusivity, (b) reduced pressure, (c) isosteric heat of adsorption, and (g) maximum value of density profile in specified layer vs average pore density. In (a), open squares are for $r_{\text{cut}} = 6.0\sigma$ and closed circles are for $r_{\text{cut}} = 2.5\sigma$, and data is color coded according to diffusivity regime: (black) DR1, (red) DR2, and (green) DR3. In (e-g), solid lines are for $r_{\text{cut}} = 6.0\sigma$ and dashed lines are for $r_{\text{cut}} = 2.5\sigma$. In (a), Vertical lines in (a-c) represent the transitions between filling regimes in the CNT[6.0] system, (F) film formation, (M) multilayer formation, and (P) pore filling, denoted along the top of (a).

3.2 Weakly attractive adsorbent

While the previous subsection focused on strongly attractive adsorbents, we now examine whether the connection between diffusivity and adsorptive regimes holds in weakly attractive adsorbents. Figure 7 displays the isotherms for argon adsorption in the weakly attractive CO2[4.0] system. At the supercritical temperature of $k_B T/\epsilon = 1.5$, the isotherms are of Type-I Langmuir form, similar to the supercritical isotherms in the CNT systems. On the other hand, at the subcritical temperature of $k_B T/\epsilon = 0.73$, the isotherms exhibit hysteresis of Type-V form (low adsorption at low pressure), which is indicative of subcritical adsorption in weakly attractive adsorbent.⁷

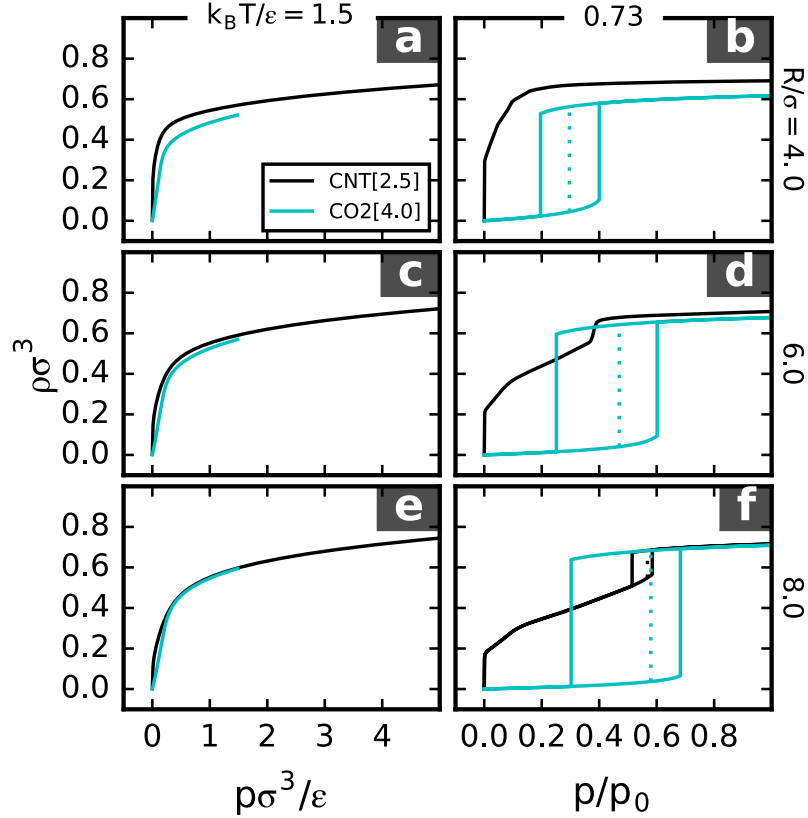


Figure 7: Comparison of the isotherms for the weakly attractive CO2[4.0] system and the strongly attractive CNT[2.5] system. Note that the actual pore sizes for the CO2[4.0] system are $R/\sigma = 4.0, 6.0$, and 8.0 , while those for the CNT[2.5] system are $R/\sigma = 3.99, 5.98$, and 7.77 . Note that at the subcritical temperatures of $k_B T/\epsilon = 0.73$, the pressure is reduced by the bulk saturation pressure p_0 . Dotted lines indicate coexistence between high and low density phases.

Figure 7, which also compares the isotherms in weakly attractive CO2[4.0] and strongly attractive CNT[2.5] pores, clearly shows differences in adsorptive behavior because of fluid-solid interaction strength. Note that the pore sizes being compared do not match exactly, and the fluid-fluid cutoffs are different. However, for qualitative purposes, these differences should have little impact. A comparison of the effective pore sizes (See Section 2.5) for the CNT[2.5] and CO2[4.0] systems is given in Supporting Information Table S-1. At the supercritical temperature of $k_B T/\epsilon = 1.5$, the isotherms depend little on the fluid-solid interaction strength, especially in the case of the larger pores. For the smaller pore size $R/\sigma = 4.0$, where a comparatively large fraction of the adsorbed fluid is in the film layer in the CNT pore (see also Supporting Information Fig. S-6), differences due to changes in fluid-solid interaction strength are apparent. The disparity between the two systems is much starker at the subcritical temperature of $k_B T/\epsilon = 0.73$. While the high-pressure behavior is similar, the low to moderate pressure behavior is very different in the two adsorbents. Instead of the rapid increase in loading at very low applied pressures indicative of film formation in CNT pores, we observe a very slow increase in loading with increasing pressure in the CO2[4.0] pores. This indicates that film formation is either not present or is very weak in the CO2[4.0] pores.

Figure 8 compares the density profiles in CO2[4.0] and CNT[2.5] pores at the supercritical temperature of $k_B T/\epsilon = 1.5$ and $R/\sigma \approx 8.0$. Although the isotherms in the two pores are very similar, the density profiles display clear differences. While the individual peak locations, and, hence, the layer locations, are similar, the peak heights are lower, and the peak widths are wider in the CO2[4.0] pore relative to in the CNT[2.5] pore. That is, individual fluid layers are more diffuse in the weakly attractive CO2[4.0] pore than in the strongly attractive CNT[2.5] pore. These effects are qualitatively similar at the subcritical temperature of $k_B T/\epsilon = 0.73$ (See Supporting Information Fig. S-5) Note that the CO2 system does not display the sequential layer filling at moderate loading associated with multilayer formation.

These structural differences suggest that the weakly attractive CO2 adsorbent is funda-

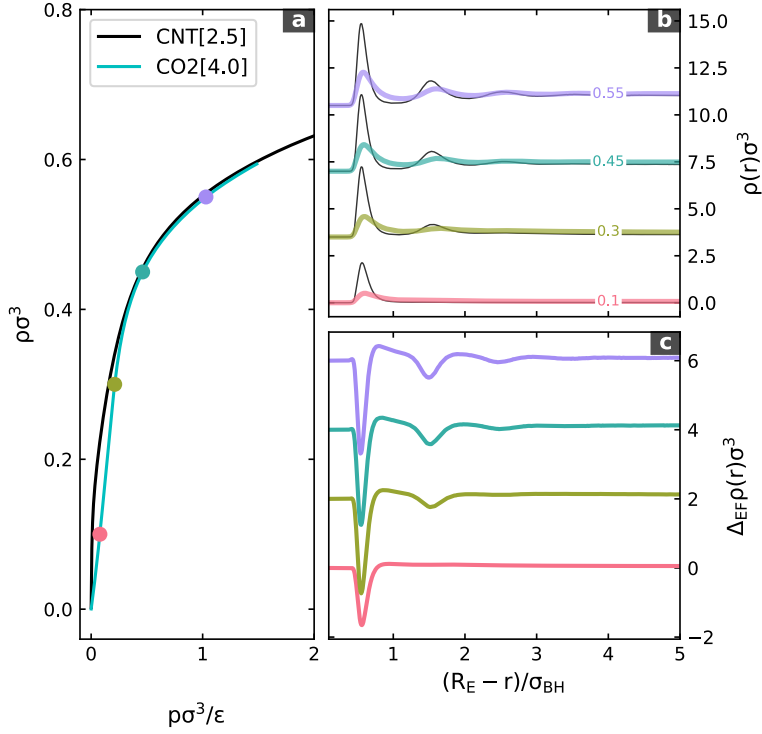


Figure 8: Comparison of the CO2[4.0] system at $k_{\text{B}}T/\epsilon = 1.5$ and $R/\sigma = 8.0$ to the CNT[2.5] system at $k_{\text{B}}T/\epsilon = 1.5$ and $R/\sigma = 7.77$. (a) Zoomed perspective of isotherms. (b) Density profiles at several pore densities. Colored lines are for CO2[4.0] system, and black lines are for CNT[2.5] system at corresponding densities. (c) Difference between density profiles of CO2[4.0] and CNT[2.5] systems. The color of each curve in (b) and (c) corresponds to the marker color in (a). Each subsequent curve in (b) and (c) is shifted upward for clarity. Note that in (b) and (c) the scaled variable $(R_{\text{eff}} - r)/\sigma_{\text{BH}}$ is used (See Section 2.5)

mentally different from the strongly attractive CNT adsorbent. Since it is clear that the CO2 adsorbent interacts weakly with the adsorbate it is interesting to see how the structure of argon in CO2 pores compares with that of hard spheres in hard-wall cylindrical pores, where there are no attractive interactions between the fluid particles and the solid wall. Figure 9 compares the density profiles of argon in CO2[4.0] pores to those of hard spheres in hard-wall cylindrical pores (data taken from Ref. 39) at similar effective densities and effective pore sizes (see Section 2.5). At low loading, the weakly attractive CO2[4.0] system has an enhanced film density compared to the purely repulsive hard-sphere system. However, at high loading, the structure in the two systems is very similar regardless of temperature, sug-

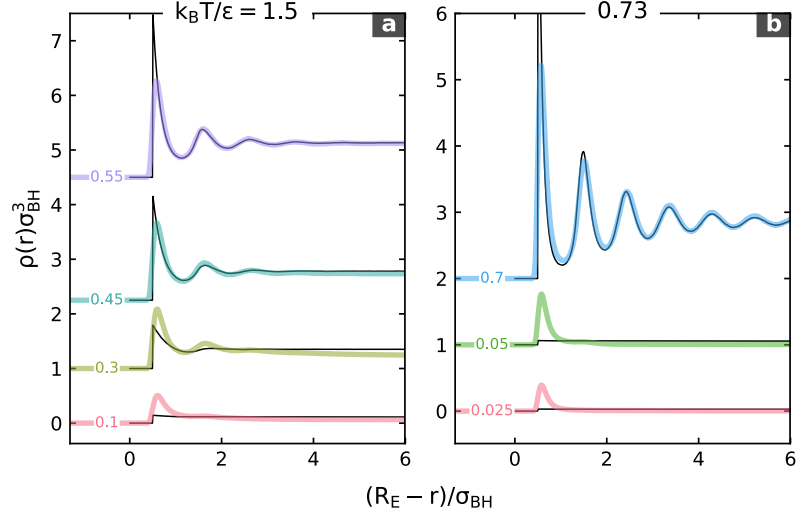


Figure 9: Comparison of density profiles of the CO2[4.0] system (colored lines) to the hard-sphere in purely repulsive cylindrical pore system (corresponding black lines). CO2[4.0] data is at $R/\sigma = 8.0$ and fluid densities $\rho\sigma^3$ denoted in the figure. The effective parameters for CO2[4.0] (See Section 2.5) are for $k_B T/\epsilon = 1.5$: $R_E/\sigma_{BH} = 7.67$ and $\rho_E/\sigma_{BH}^3 = 0.109, 0.327, 0.490, 0.599$; and for $k_B T/\epsilon = 0.73$: $R_E/\sigma_{BH} = 7.46$ and $\rho_E/\sigma_{BH}^3 = 0.030, 0.059, 0.828$. Hard-sphere data (corresponding black lines) is at $R/\sigma = 7.5$ and for (a): $\rho\sigma^3 = 0.1, 0.325, 0.5, 0.6$; and for (b): $\rho\sigma^3 = 0.025, 0.05, 0.825$. Note that for the hard-sphere system $R_E = R$, $\rho_E = \rho$, and $\sigma = \sigma_{BH}$.

gesting that the high density structures in the CO2[4.0] system are dominated by repulsive interactions.

On the other hand, at low loading, the fluid structure of argon in CO2 pores lies somewhere between that of hard spheres in purely repulsive hard-wall pores, and that of argon in strongly attractive CNT pores. By this we mean that, at low densities, although the fluid layering near the fluid-solid interface in CO2 pores is less pronounced than in CNT pores, (Fig. 8 and Supporting Information Fig. S-5), it is more pronounced than hard spheres in hard-wall pores (Fig. 9). We also compared the fraction of particles in the pore that could be found in the fluid layer adjacent to the solid surface, which we denote as χ_1 , in the CNT[2.5], CO2[4.0], and hard sphere systems (see Supporting Information Figs. S-6 and S-7). For the case of pore size $R/\sigma \approx 8.0$, at a loading $\rho_E\sigma_{BH}^3 \approx 0.1$ and the supercritical temperature

$k_B T/\epsilon = 1.5$, $\chi_1 = 0.95$ for the CNT[2.5] system, $\chi_1 = 0.45$ for the CO2 system, and $\chi_1 = 0.2$ for the hard sphere system. However, at the subcritical temperature $k_B T/\epsilon = 0.73$, $\chi_1 \approx 1.0$ for the CNT[2.5] system, $\chi_1 = 0.8$ for the CO2 system, and again $\chi_1 = 0.2$ for the hard sphere system. Therefore, at low loading, the layer adjacent to the solid surface is enhanced in the CO2 system relative to a purely repulsive system, and this enhancement grows with decreasing temperature behaving like the CNT system in this respect.

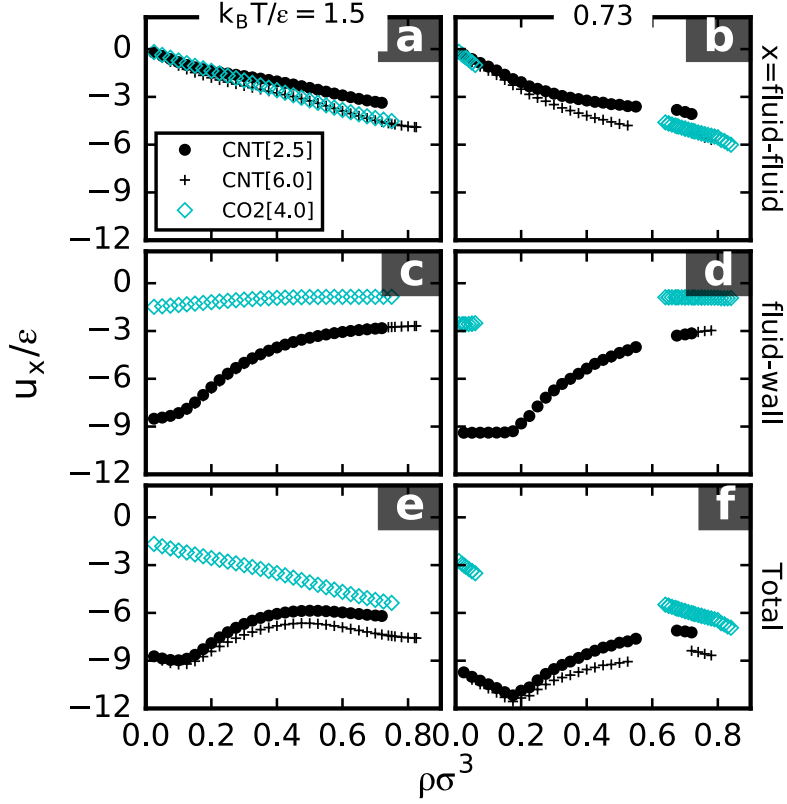


Figure 10: Comparison of CO2[4.0] and CNT[2.5] potential energies at $R/\sigma \approx 8.0$. The potential energy type, fluid-fluid, fluid-wall, and total are noted along each row.

We now turn to the comparison of energetic properties in weakly attractive CO2 pores to those in the strongly attractive CNT pores. Figure 10 compares components of the potential energies of the CO2[4.0] and CNT systems at $R/\sigma \approx 8.0$. Unsurprisingly, the fluid-fluid interaction energies are very similar, particularly when comparing the CO2[4.0] and CNT[6.0] systems. The fluid-wall potential energy is, of course, significantly different in

the two systems. In particular, we see that the fluid-wall potential energy is a weak function of loading in the CO₂ system. Thus, this contribution to the total potential energy plays a diminished role in the CO₂ system compared to in the CNT system. We note that the isosteric heat of adsorption in the CO₂[4.0] system (see Supporting Information Fig. S-8) likewise does not show a local maximum over the range of state points investigated, which is indicative of a transition from film formation to multilayer formation or pore filling.

Therefore, because the usual thermodynamic signatures of film formation, such as a rapid increase in loading at low applied pressure, and a maximum in the isosteric heat of adsorption, are not present, we cannot say that there is a true film formation regime in the CO₂ pores. However, we clearly observe that the density of the fluid layer adjacent to the solid surface is enhanced in the CO₂ system relative to hard spheres in hard-wall pores (see Fig. 9 and Supporting Information Fig. S-7). Thus, we term the moderate density enhancement observed in the weakly attractive CO₂ system as *weak* film-formation to differentiate it from the more dramatic density enhancement associated with true film formation observed in the strongly attractive CNT system. Moreover, as noted earlier, the CO₂ system does not display multilayer-formation regime. This is expected, as systems which display multilayer formation also display thermodynamic signatures of film formation, which is lacking in the CO₂ system.

Given the earlier noted differences in energetic and structural characteristics between the CO₂[4.0] and the CNT adsorbents, it is interesting to contrast the argon self-diffusivities in these systems. Figure 11 displays the self-diffusivities in CO₂[4.0] pores as a function of effective density. We see that the self-diffusivity is very normal, in the sense that it behaves similar to what one would expect for a simple bulk fluid: an initial rapid decrease in self-diffusivity at low densities, an exponential decrease in self-diffusivity at moderate densities, and a rapid decrease in self-diffusivity at high densities. This suggests that, at least qualitatively, we can identify the diffusivity regimes 1 and 3 (DR1 and DR3). Notice that there is no region of nearly constant diffusivity indicative of DR2.

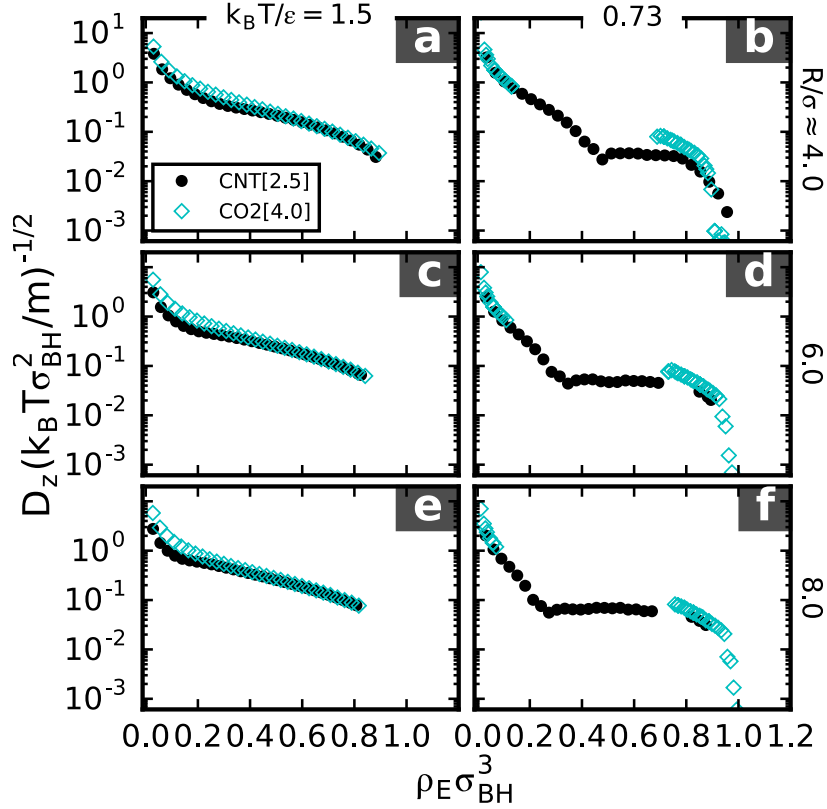


Figure 11: Comparison of the self-diffusion coefficients in the CO2[4.0] and CNT[2.5] systems. Self-diffusivity, nondimensionalized by the effective particle size σ_{BH} , is displayed as a function of the effective “hard-sphere” density $\rho_E \sigma_{\text{BH}}^3$ (see Section 2.5). Reduced temperatures are noted along the top of each column, and approximate pore sizes are noted along each row. Note that the actual pore sizes for the CO2[4.0] system are $R/\sigma = 4.0, 6.0$, and 8.0 , and those for the CNT[2.5] system are $R/\sigma = 3.99, 5.98$, and 7.77 .

Figure 11 also compares the self-diffusivities of argon in CO2[4.0] and CNT[2.5] pores. Note that the effective density (See Section 2.5) puts the two systems on equal footing. At the supercritical temperature of $k_B T / \epsilon = 1.5$ (Figs. 11a, d, and g), although the two systems display qualitatively similar self-diffusivity characteristics as a function of effective density, significant quantitative differences are also apparent. In particular, at low densities, the self-diffusivity in CNT[2.5] pores displays a more rapid decrease with increasing density than the corresponding self-diffusivity in CO2[4.0] pores. As discussed earlier, at high temperature and low loading the fraction of the fluid in the layer adjacent to the solid interface (χ_1) is much smaller in the CO2 system than in the CNT system. Therefore, the fluid in the CO2 system

is not restricted to the layer adjacent to the surface, and hence the fluid is less frustrated and displays higher mobility than in the CNT system. However, as the temperature is decreased, the fluid in the CO2 system is increasingly restricted to the layer adjacent to the solid. Therefore, the fluid structure in the CO2 and CNT systems at low loading becomes more similar as temperature is decreased. We therefore expect the difference in self-diffusivity to diminish as temperature is decreased. Inspection of Fig. 11 shows that this is indeed the case. Specifically, the self-diffusivity in the two systems at $k_B T/\epsilon = 0.73$ (Figs. 11b, d, and f) and low loading is nearly identical.

For the larger two pore sizes ($R/\sigma \approx 6.0$ and 8.0) shown in Fig. 11, the behavior of argon self-diffusivity in the two adsorbents is similar. In particular, at $k_B T/\epsilon = 1.5$, the self-diffusivities in the two systems are nearly identical at high loading. At lower temperatures, the diffusivity characteristics are at least qualitatively similar. This is somewhat surprising given that the density profiles (Fig. 8 and Supporting Information Fig. S-5) are so different.

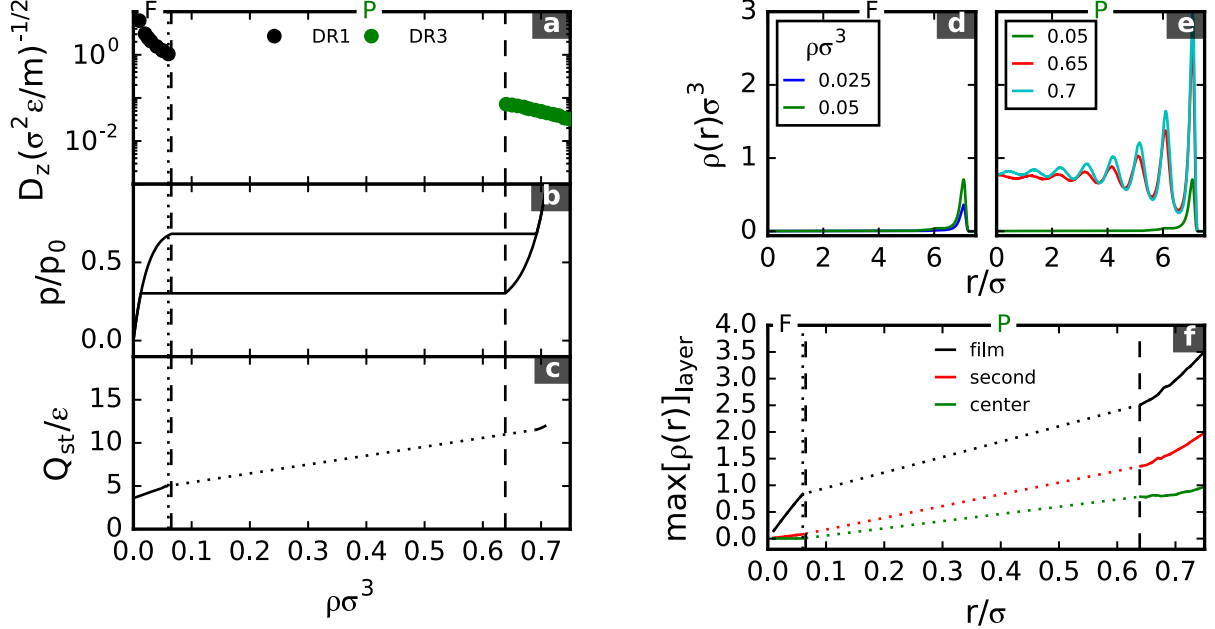


Figure 12: As Fig. 6, for the CO2[4.0] system with $k_B T/\epsilon = 0.73$ and $R/\sigma = 8.0$. Dashed lines in (a-c) mark limits of stability between low- and high-density branches.

The lack of thermodynamic signatures of film-formation and multilayer-formation regimes

in the CO₂ adsorbent makes it questionable whether it is appropriate to apply the framework linking adsorptive regimes to diffusivity regimes of Ref. 23 to this system. Figure 12 (see also Supporting Information Fig. S-10) attempts to compare the diffusivity regimes to the adsorptive properties of the CO₂[4.0] system. As noted earlier, the CO₂ system does not display the usual thermodynamic signatures of film formation. We have instead identified *weak* film formation, which indicates density enhancement near the fluid-solid interface relative to a purely repulsive system. Specifically, states which show a near-zero maximum value of the density profile in the second layer from the interface are termed weak film-formation. All other states are termed pore filling. With this identification, we can say that the link between diffusivity regimes and adsorptive properties is at least consistent with that observed in the CNT system. By this, we mean that the rapid decrease in self-diffusivity at low fluid loading (DR1) corresponds to adsorbed-fluid structures with particles *mostly* occupying locations near the fluid-solid interface ($> 80\%$, see Supporting information Fig. S-6), and that the decrease in self-diffusivity at high loading (DR3) corresponds to adsorbed-fluid structures with particles occupying positions throughout the pore.

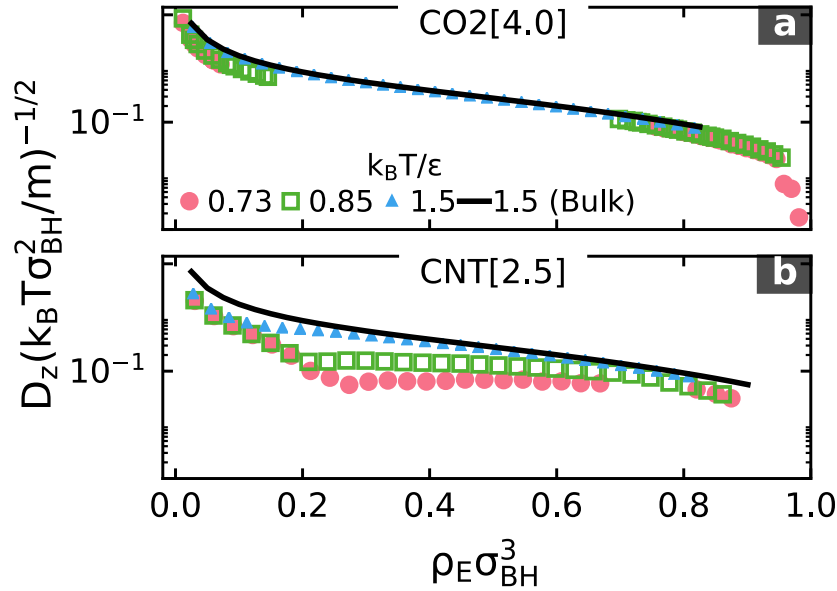


Figure 13: Scaled self-diffusivity as a function of effective density in (a) CO₂[4.0] system at $R/\sigma = 8.0$ and (b) CNT[2.5] system at $R/\sigma = 7.77$. Solid line is bulk argon at $k_B T/\epsilon = 1.5$.

Rather than trying to fit the weakly attractive CO2[4.0] system into the same framework as the strongly attractive CNT system, our results hint at another useful framework. As discussed earlier, the density profiles in CO2[4.0] pores are in many ways more similar to those of hard spheres in hard-wall pores than to those in a strongly attractive pores. Recent work has shown that the relationship between self-diffusivity and thermodynamic measures is the same for bulk hard-sphere fluids and hard-sphere fluids in hard-wall confinement.^{40–47} Such “scaling” relationships provide a means to predict the dynamic properties of confined fluids from knowledge of the bulk thermodynamic–dynamic relationship and confined fluid thermodynamics. While several thermodynamic measures have been shown to give such a scaling relationship, the simplest is the average pore density.

To test whether such a scaling relationship exists, we consider the self-diffusivity as a function of the effective pore density ρ_E , defined in Section 2.5. Figure 13a shows that for the CO2[4.0] system, the self-diffusivity of the adsorbed fluid is well described by the bulk argon fluid at the same effective density. We observe (see Supporting Information Fig. S-11) deviations only at the highest investigated effective densities, with these deviations depending on both pore size and, for the smallest pore size, temperature. Still, the vast majority of the data is well described by the bulk relationship.

Given that the bulk-fluid scaling relationship describes the self-diffusivity in the CO2 system quite well, it is interesting to see whether the relationship also describes the self-diffusivity in the CNT system, shown in Figure 13b (see also Supporting Information Fig. S-12). Clearly, the bulk fluid fails to describe the argon self-diffusivity in the CNT system. Even at the supercritical temperature of $k_B T/\epsilon = 1.5$, where repulsions become relatively more important, the scaling still breaks down at low loading where the film layer dominates. The only regime where the bulk curve appears to describe the confined data is for large pores at high loading, in the pore filling regime where packing physics dictates the overall properties.

Therefore, while the properties in the weakly attractive CO2 system are consistent with

the qualitative link between adsorptive regimes and diffusivity regimes reported in Ref. 23, they also display a much more useful, and quantitatively predictive, relationship between thermodynamics and self-diffusivity. In particular, the relationship between self-diffusivity and effective density of fluid adsorbed into CO₂ pores is the same as for the bulk fluid. This scaling relationship fails to describe the properties of fluid adsorbed into strongly attractive CNT pores. Thus, for strongly attractive systems which display film and multilayer formation, one can turn to the qualitative framework of Ref. 23 to describe self-diffusivity, but for weakly attractive systems, one can turn to more quantitative scaling relationships based on bulk-fluid properties.

4 Conclusions

We have investigated how fluid-fluid interaction range, and fluid-solid interaction strength impact the previously reported²³ connection between thermodynamics and self-diffusivity in adsorptive systems, which found that distinct filling regimes (film formation, multilayer formation, and pore filling) correspond to distinct diffusivity regimes (DR1, DR2, and DR3). We find that increasing the fluid-fluid interaction range leads to small changes to properties in the multilayer-formation regime, but has little effect on the film-formation and pore filling regimes. In the multilayer-formation regime, increasing fluid-fluid interaction range leads to more well defined fluid layers, and a corresponding decrease in self-diffusivity. However, we find that the increasing fluid-fluid interaction range has no effect on the qualitative relationship between filling regimes and diffusivity regimes of Ref. 23

On the other hand, we find that weakly attractive pores exhibit fundamentally different behavior compared to strongly attractive pores. In particular, weakly attractive pores do not display film or multilayer formation. In fact, the fluid structure in weakly attractive pores is in many ways more similar to hard spheres in hard-wall pores than a simple fluid in strongly attractive pores. While the properties in weakly attractive pores are consistent with the framework of Ref. 23, the similarity of this system to hard-spheres in hard-walls suggests a more useful framework to describe dynamics in terms of thermodynamic measures. Specifically, the self-diffusivity in weakly attractive pores has the same scaling-relationship with effective density as the bulk fluid.

These results suggest that the relationship between adsorption thermodynamics and in-pore self-diffusion exists as a spectrum between strongly attractive and weakly attractive systems. On one hand, the dynamic properties of fluids in strongly attractive systems can be described, at least qualitatively, in the framework of Ref. 23. On the other, the dynamic properties of fluids in weakly attractive systems can be described by thermodynamic-dynamic scaling relationships based on metrics as simple as the effective density. This study opens many questions for future research to address. One important question is, how does a

fluid in an adsorbent with moderate fluid-solid interaction strength behave? In particular, does such a system display characteristics of one extreme, or both? For example, such a system might exhibit multilayer formation and follow a bulk-fluid scaling relationship. Another open question is how the pore-averaged self-diffusivity investigated here depends on spatially dependent dynamics. In particular, the observation that increasing fluid-fluid interaction range leads to enhanced layering and decreased self-diffusivity suggests that pore-averaged dynamics are related to individual layer dynamics. It is our hope that a detailed understanding of positional dependent dynamics will lead to a quantitative link between fluid structure and dynamics.

5 Acknowledgments

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Supporting Information

Isotherms for the CNT[6.0] system, structural characteristics of the CNT[2.5] and CNT[6.0] systems, diffusivity and adsorptive regimes of the CNT[2.5] and CNT[6.0] systems, effective pore sizes of the CNT[2.5] and CO2[4.0] systems, Isotherms for the CO2[4.0] system, structural comparison of the CO2[4.0] and CNT[2.5] systems, film fraction vs loading for the CO2[4.0] and CNT[2.5] systems, isosteric heat of adsorption for the CO2[4.0] and CNT[2.5] systems, axial self-diffusion coefficient vs loading for the CO2[4.0] system, diffusivity and adsorptive regimes of the CO2[4.0] and CNT[2.5] systems, scaled self-diffusivity vs effective density for the CO2[4.0] and CNT[2.5] systems.

`Supporting_information.pdf` provides supporting figures and tables.

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Graphical TOC Entry



SUPPORTING INFORMATION TO “CONNECTION BETWEEN THERMO-
DYNAMICS AND DYNAMICS OF SIMPLE FLUIDS IN PORES: IMPACT OF
FLUID-FLUID INTERACTION RANGE AND FLUID-SOLID INTERACTION
STRENGTH”

Fluid-fluid interaction range

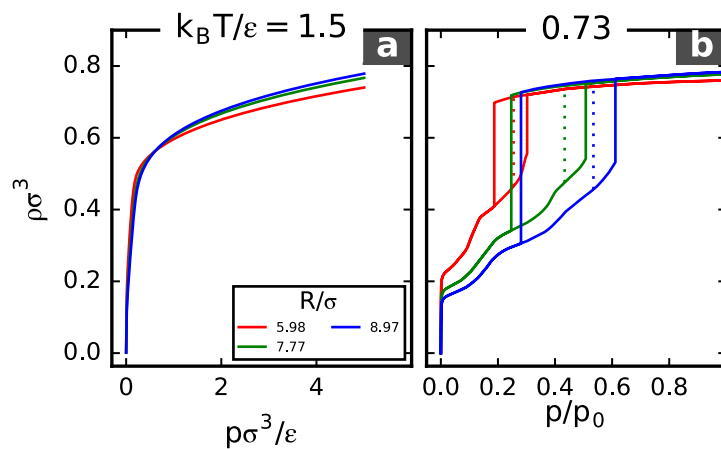


FIG. S-1. Isotherms for the CNT[6.0] system. Note that, at the subcritical temperature of $k_B T/\epsilon = 0.73$ in (b), the pressure is reduced by the bulk saturation pressure p_0 .

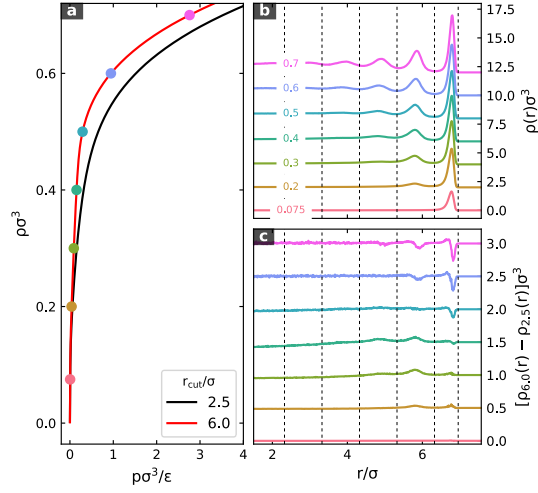


FIG. S-2. Comparison of structural characteristics of CNT[2.5] and CNT[6.0] systems with $k_B T/\epsilon = 1.5$ and $R/\sigma = 7.77$. (a) Zoomed perspective of isotherms. (b) Density profiles at several pore densities for CNT[6.0] system. (c) Difference between density profile with $r_{\text{cut}} = 6.0\sigma$ and $r_{\text{cut}} = 2.5\sigma$. The color of each curve in (b) and (c) corresponds to the marker color in (a). Each subsequent curves in (b) and (c) is shifted upward for clarity. The vertical dashed lines in (b) and (c) are the approximate boundaries between each distinct fluid layer.

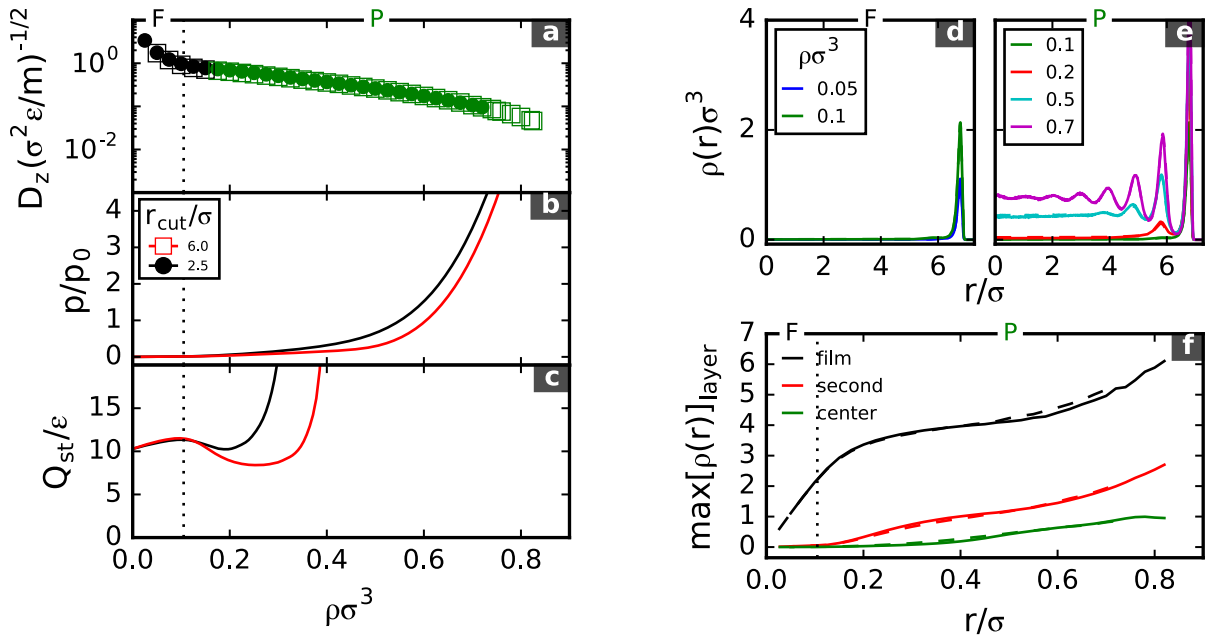


FIG. S-3. Same as Figure 6 in main text, but with $k_B T/\epsilon = 1.5$ and $R/\sigma = 7.77$.

Weakly attractive adsorbent

TABLE S-1. The effective pore sizes used in comparing the CNT[2.5] and CO2[4.0] systems.

$k_{\text{B}}T/\epsilon$	R/σ		$R_{\text{BH}}(T; R)/\sigma_{\text{BH}}(T)$	
	CNT[2.5]	CO2[4.0]	CNT[2.5]	CO2[4.0]
0.73	3.99	4.0	3.456	3.557
1.50	3.99	4.0	3.552	3.663
0.73	5.98	6.0	5.398	5.507
1.50	5.98	6.0	5.545	5.665
0.73	7.77	8.0	7.145	7.455
1.50	7.77	8.0	7.339	7.666

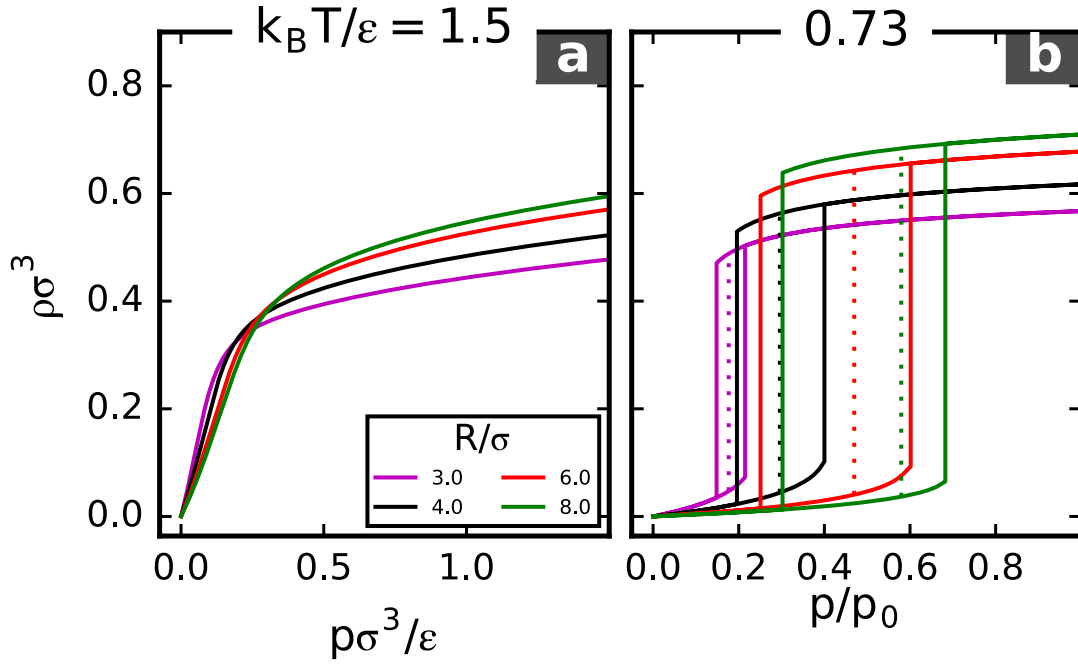


FIG. S-4. Average pore-density ρ of fluid for CO2[4.0] systems versus bulk pressure of fluid in equilibrium with the pore p for fluid in at reduced temperatures noted along top of each subfigure. Note that at the subcritical temperatures in (b), the pressure is reduced by the bulk saturation pressure p_0 . Dotted lines in (b) indicate coexistence between high and low density phases.

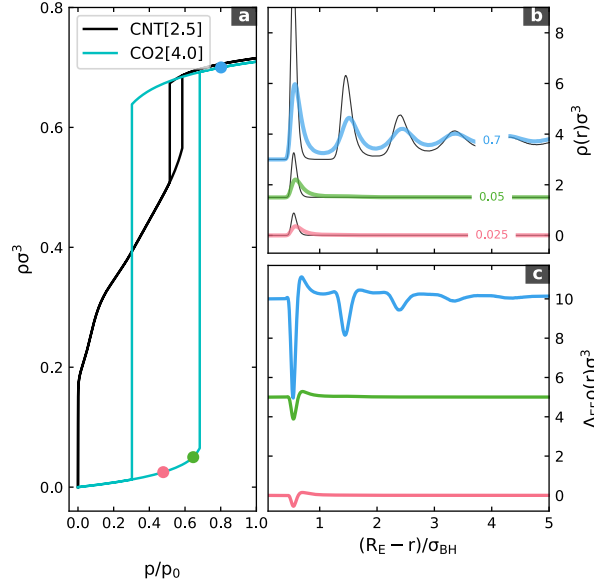


FIG. S-5. Comparison of the CO2[4.0] system at $k_B T/\epsilon = 0.73$ and $R/\sigma = 8.0$ to the CNT[2.5] system at $k_B T/\epsilon = 0.73$ and $R/\sigma = 7.77$. (a) Zoomed perspective of isotherms. (b) Density profiles at several pore densities. Colored lines are for CO2[4.0] system, and black lines are for CNT[2.5] system. (c) Difference between density profiles of CO2[4.0] and CNT[2.5] systems. The color of each curve in (b) and (c) corresponds to the marker color in (a). Each subsequent curve in (b) and (c) is shifted upward for clarity. Note that in (b) and (c) the scaled variable $R_{\text{eff}} - r$ is used (See Section 2.5 of main text)

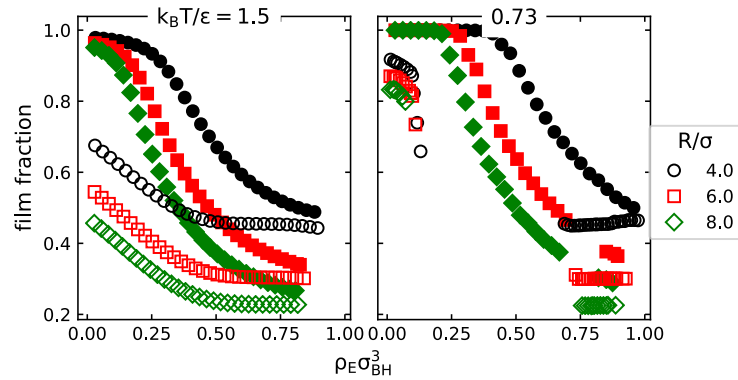


FIG. S-6. Comparison of fraction of fluid in film layer ($N_{\text{film}}/N_{\text{total}}$) versus loading for CNT[2.5] system (filled symbols), and for CO2[4.0] system (open symbols).

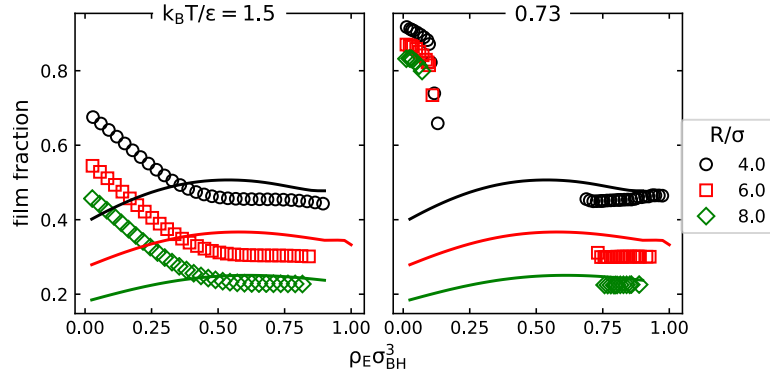


FIG. S-7. Same as Fig. S-6, but comparing CO2[4.0] system (open symbols) with hard-spheres in hard-wall pores (lines). Note that the size of the hard-wall pores are $R/\sigma = 3.5, 5.0$ and 7.5 , which roughly correspond to the effective pore sizes for the CO2[4.0] system (see Table S-1).

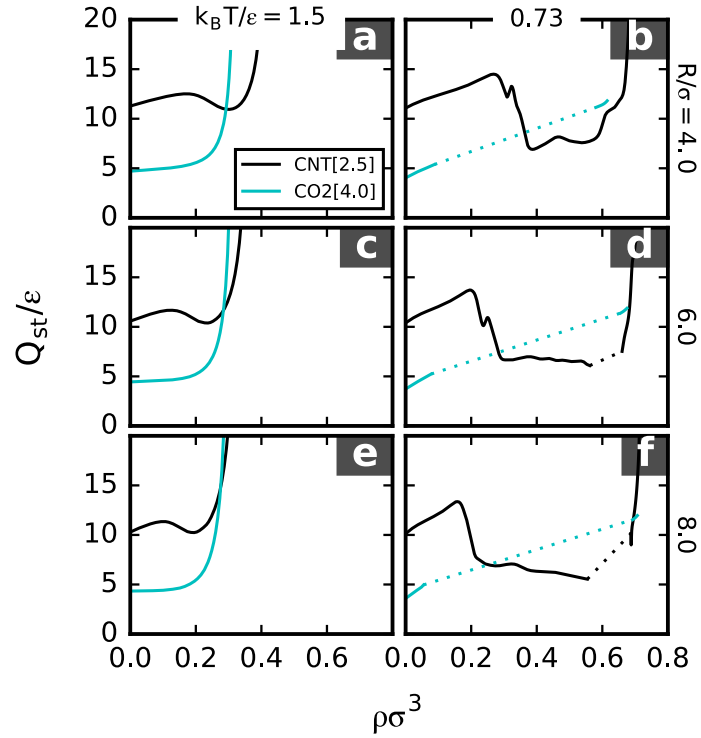


FIG. S-8. Comparison of the isosteric heat of adsorption Q_{st} for the CO2[4.0] and CNT[2.5] systems.

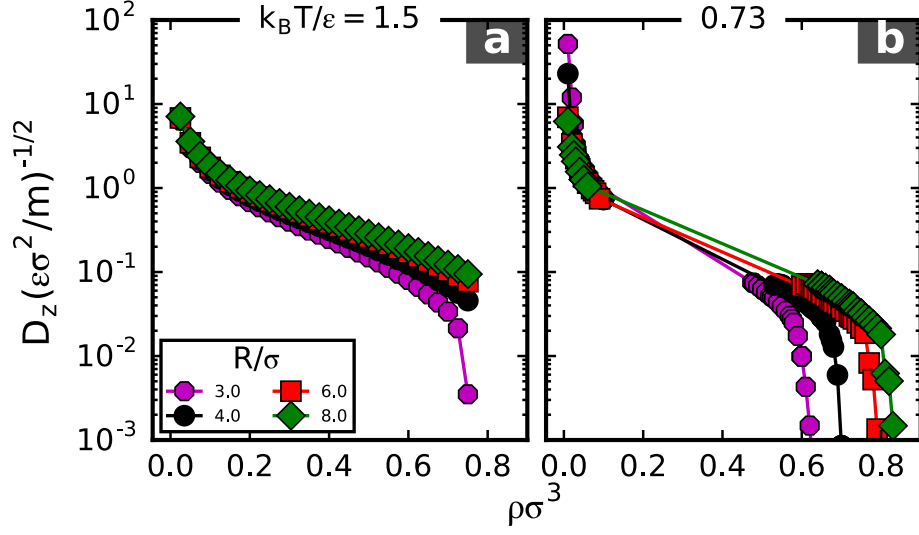


FIG. S-9. Axial self-diffusion coefficient D_z versus fluid density ρ of the CO2[4.0] system.

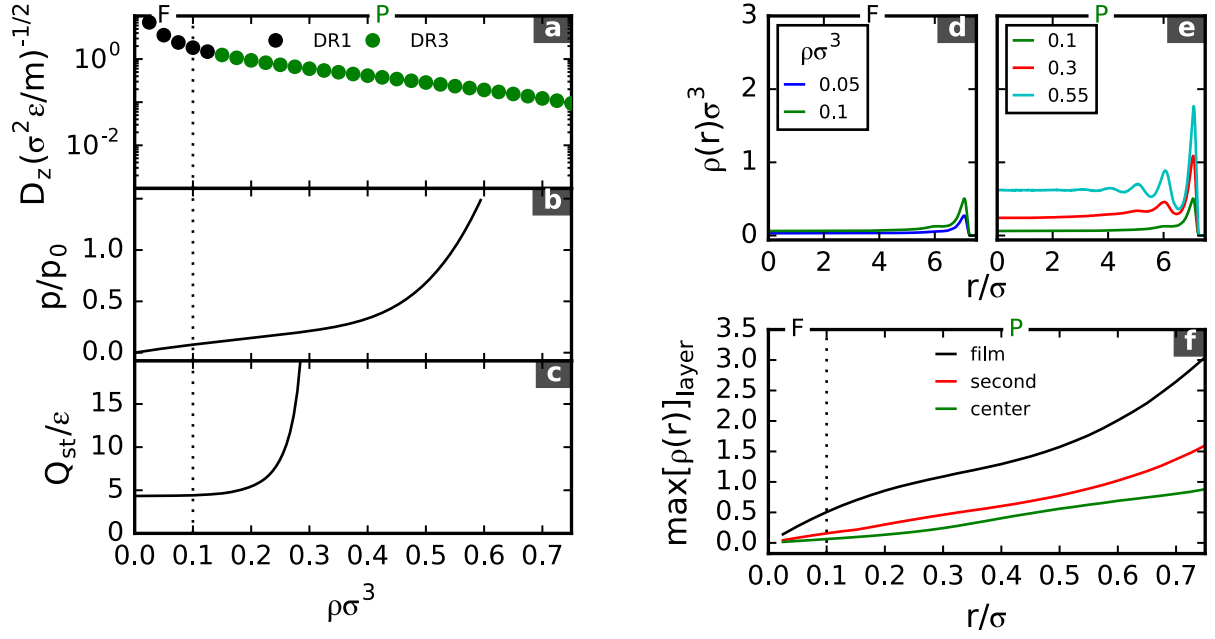


FIG. S-10. As Fig. 6 in main text, for the CO2[4.0] system with $k_B T / \epsilon = 1.5$ and $R/\sigma = 8.0$.

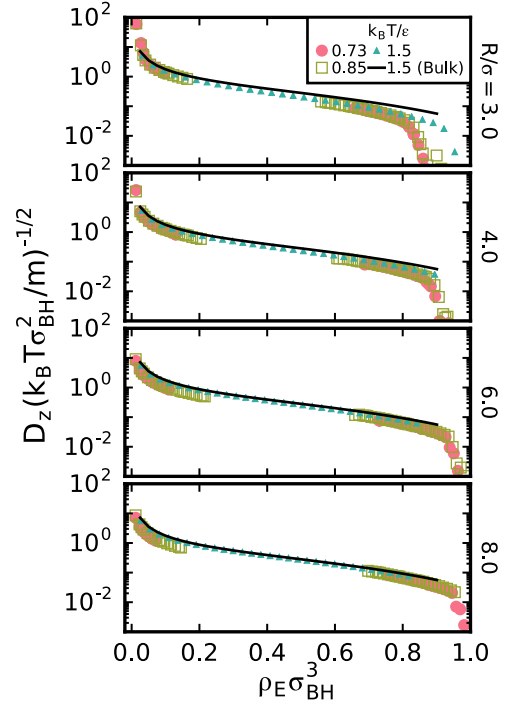


FIG. S-11. Scaled self-diffusivity as a function of effective pore-density in the CO2[4.0] system.

Solid line is bulk Ar at $k_B T / \epsilon = 1.5$

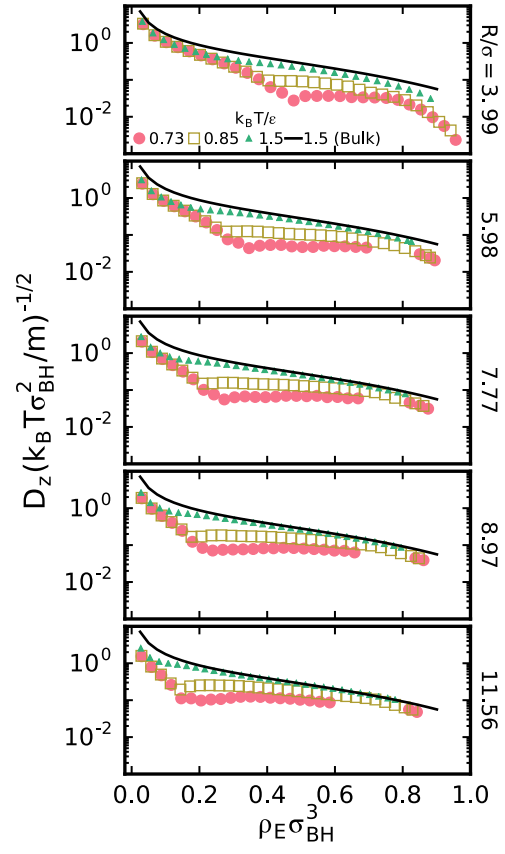


FIG. S-12. Scaled self-diffusivity as a function of effective pore-density in the CNT[2.5] system. Solid line is bulk Ar at $k_B T / \epsilon = 1.5$