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Gas Adsorption in Novel Environments, Including Effects of Pore Relaxation

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Abstract

Adsorption experiments have been interpreted frequently with simplified model geometries, such as ideally flat surfaces and slit or cylindrical pores. Recent explorations of unusual environments, such as fullerenes and metal-organic-framework materials, have led to a broadened scope of experimental, theoretical and simulation investigations. This paper reviews a number of such studies undertaken by our group. Among the topics receiving emphasis are these: universality of gas uptake in pores, relaxation of a porous absorbent due to gas uptake, and the novel phases of gases on a single nanotube, all of which studies have been motivated by recent experiments.

A. Introduction

The field of adsorption has experienced a renaissance due to the development of new materials, advanced technological applications as well as a significant improvement in computational capability. In spite of this progress, there remain some genuinely *fundamental* questions to be answered, such as accuracy of interaction models and validity of assumptions about the substrate's geometry. Our group and many other groups have investigated these problems. In the limited space available here, we describe some of our recent results.

B. Universality and Corresponding States

One kind of universal behavior is reflected in the "law of corresponding states", abbreviated LOCS, which affirms that the equations of state of very different systems (*e.g.*, Ar and Xe) are identical when thermodynamic variables are appropriately scaled.¹⁻³ Thus, the reduced pressure $P^*=P/P_c=F(T^*,\rho^*)$, a *universal function* of the reduced temperature $T^*=T/T_c$ and density $\rho^*=\rho/\rho_c$. Here, the subscript c denotes the value at the critical point. This "law" is based on assumptions that are adequate to describe many systems characterized by van der Waals interactions (Ar, Xe, CH₄,...), but not quantum systems; the difference in the latter case is a larger value of the de Boer quantum parameter, $\eta \equiv h^2/[m\epsilon\sigma^2]$. Here m is the molecular mass, while σ is the hard-core diameter and ϵ is the well-depth of the intermolecular pair potential $v(x)$. The LOCS justifies extrapolation to previously unexplored systems by understanding general behavior to that of just one generic system.

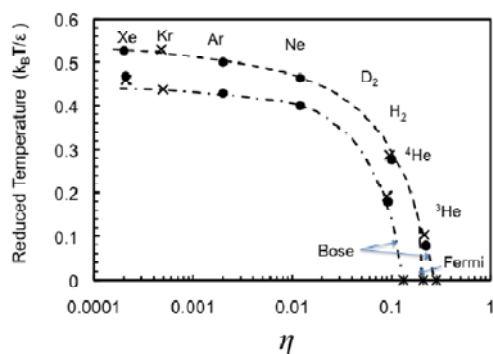


Figure 1. Reduced 2D critical point (dashes) and triple point (dash-dot) temperatures as a function of the de Boer quantum parameter. Points from MgO (x) and graphite (filled circles). Figure adapted from Cheng et al.²

Fig. 1 presents results for 2D critical and triple point temperatures as a function of η . These would have common values if LOCS were valid, but one observes the significant reduction in values for highly quantum systems, like H_2 and He. These differences are attributable to the zero-point energy $E_{zp} \sim \hbar^2 / [m\sigma^2]$, since its importance relative to the potential energy $\langle V \rangle \propto \epsilon$ is given by η . Some years ago, our interest in the LOCS of adsorbed gases was piqued by intriguing behavior of gas adsorption in a variety of activated carbons, reported by Quinn.^{4,5} An example appears in Fig. 2.

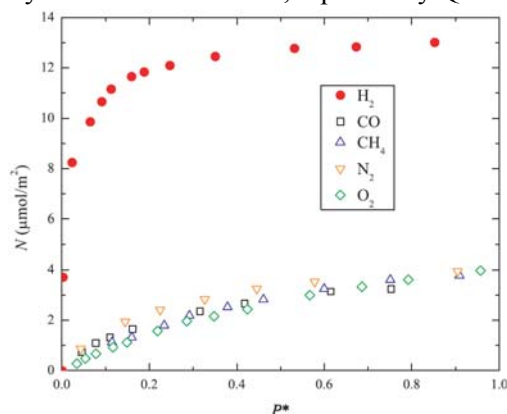


Figure 2. Gas uptake in activated carbon PVDC, as a function of $P^*=P/P_c$ at reduced temperature $T/T_c = 2.36$. Data adapted from Ref. 4.

Note that four gases (CO , CH_4 , N_2 and O_2) exhibit very similar behavior as a function of reduced pressure P^* , while the H_2 uptake is about a factor of four greater. Quinn’s hypothetical explanation of the “deviant” behavior of H_2 was basically a size effect. In our study⁵, we argued for a completely different explanation: the use of a common reduced temperature $T^*=2.36$ does not ensure identical *relative* energies for the various gases. The Boltzmann factor $\exp[-U(\mathbf{r})/(k_B T)]$ entering statistical probabilities involves a reduced energy, say $D^* = D/(k_B T_c)$, where D is a characteristic energy scale of the specific gas being studied, *e.g.* the well-depth ϵ of the pair potential $v(r)$.⁶ According to LOCS, the ratio D^* should be universal; indeed, $D^* \sim 0.8$ is representative of many “simple” gases on graphite. However, quantum effects depress the T_c for H_2 , so the H_2 /graphite value is $D^* \sim 1.1$, “violating” the LOCS. By plotting data with a common reduced temperature, Quinn was comparing classical gases with a quantum gas which has a much higher Boltzmann factor, greatly enhancing the latter’s uptake, as seen in Fig. 2. The preceding explanation is more than a qualitative argument; it is supported by our simulation results, for which the single fitting parameter was the width of the pore (not known in the experiments). The results agreed well with the experiments, showing that the “non-universal” behavior of H_2 does not need any *ad hoc* small pore conjecture. Thus, films in pores may exhibit behavior analogous to a LOCS; such universality and deviations from it require looking carefully at subtle aspects of the problem.

C. Relaxation of a Porous Medium due to Adsorption

Most studies of physisorption assume that the response of the adsorbent to the adsorbate can be ignored. Such an approach can be justified since the energy of physisorption is small compared to the cohesive energy of most substrates. However, recent studies⁷⁻¹¹ indicate that the approximation may be qualitatively *flawed*, as exemplified in some cases discussed below.

Consider the adsorption of He and H_2 within interstitial channels in a bundle of carbon nanotubes.¹²⁻¹⁴ As seen in Fig. 3, the confining potential and zero-point energy of the gas molecules are both sensitive to the spacing between tubes; huge differences in energy and wave functions arise from a 1% expansion of the nanotube lattice. Thus, there arises an energetic advantage for the lattice of tubes to

expand due to the presence of the gas. As a result of this minute expansion, the heat of adsorption is greatly increased (by as much as a factor of two!) above the value computed in the absence of this relaxation.

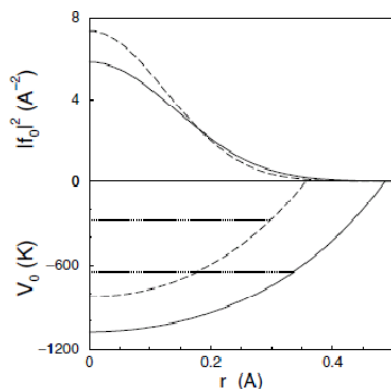


Figure 3. Adsorption potential V_0 as a function of radial distance and resulting ground state energies (horizontal lines) and probability densities $|f_0|^2$ of H_2 within an interstitial channel before (dashed curves) and after (full curves) a 1% expansion of the lattice of nanotubes. From Calbi, Cole and Toigo.¹²

In a recent study¹⁵, we considered the behavior of a graphene sheet, supported by silica, which is exposed to a simple gas; see Fig. 4. The analysis of this problem is straightforward at $T=0$ if one assumes that just a monolayer imbibes between the graphene and the silica. The resulting imbibition criterion exhibits a plausible form: $\epsilon_{3d} = \mu_0 \geq E_{\text{lift}} A/N + \epsilon_{2d} + E_2$. Here A/N is the graphene area per imbibing molecule, E_{lift} is the energy cost per unit area of lifting the graphene off of the silica surface, while ϵ_{2d} and E_2 are the energy per molecule due to in-plane cohesive and substrate interactions, respectively. μ_0 is the chemical potential of the adsorbate's ground state, which equals ϵ_{3d} , the 3D ground state energy per molecule. The criterion is satisfied by all inert gases (other than He) and H_2 . In the He case, $|E_2|$ (the energy gain from interactions) is too small to compensate for E_{lift} .

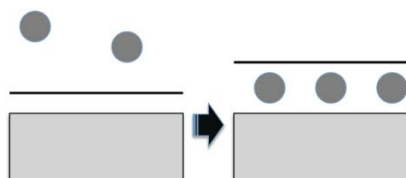


Figure 4. Schematic depiction of the imbibition transition. Initial state (left) of gas above graphene, supported on silica, transforms to a monolayer film intercalated between the graphene and the silica (right).

We recently considered the behavior of gas confined within a graphitic slit pore, of width w .¹¹ For Ar and ^4He we found large pressures ($P_{\text{wall}} \approx 100$ bar) exerted on the wall, as seen in Fig. 5. Because of the strongly attractive substrate potential, a high density film is formed in the region near the repulsive part of the adsorption potential. Newton's third law then ensures a large reaction force P_{wall} causing the pore to expand, to an extent depending on the elastic energy of the pore. Note in Fig. 5 that capillary condensation (CC) causes a precipitous drop in P_{wall} , reaching negative values (tension). The explanation is that the fluid has a strong energy incentive to undergo CC, reducing the liquid-vapor interfacial energy.

D. Universality in Substrate Relaxation

The effects discussed above for carbon materials and graphene/silica are expected to be large and strongly nonlinear in the case of an easily expanded MOF material. Li et al.¹⁶ first coined the term "gate-opening pressure" (P_{GO}) to describe a sharp discontinuity observed for subcritical gas adsorption to flexible MOFs. Similar P_{GO} s, along with abrupt gate-closing pressures (P_{GC} s), were seen by Kitaura et al.¹⁷ for *supercritical* adsorption of N_2 , O_2 , CH_4 at 298 K to $\text{Cu}(\text{dhbc})_2(4,4'\text{-bpy})$ (dhbc = 2,5-dihydroxybenzene dicarboxylate; N_2 and CH_4 data reproduced in Fig. 6). The width of the hysteresis loop was attributed to displacement of π - π stacked layers and stabilization of the expanded crystal by the

adsorbate. An osmotic potential ensemble model,¹⁸ which extends the grand canonical ensemble by accounting for the possibility of a flexible host, was applied to the unusual S-shaped isotherms characteristic of gate-opening, fitting the flat portion of the isotherm to extract adsorbate-free interaction energies of the rigid host.

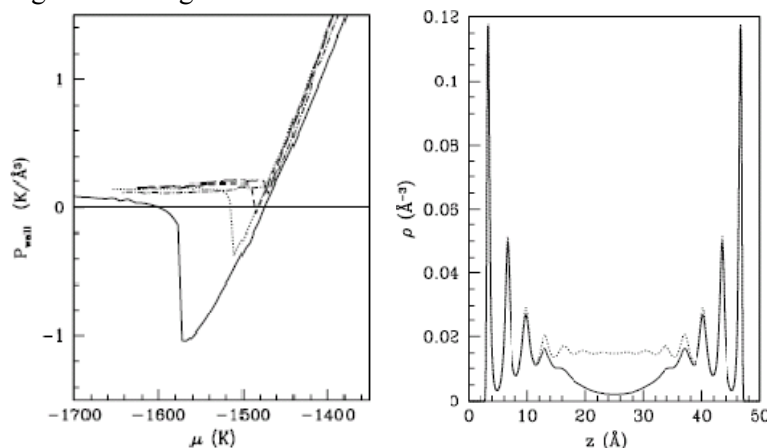


Figure 5. (left panel) Wall pressure exerted by Ar as a function of chemical potential μ . From lowest to highest, curves correspond to $w=30, 40, 50, 70$ and 80\AA . The conversion of pressure is $1\text{K}/\text{\AA}^3 \sim 138\text{ atm}$. (right panel) Film density for Ar in a pore of width 50\AA , at pressures just below (full curve) and above (dashed curve) the capillary condensation transition. From Ancilotto et al.¹¹

In an attempt to determine if the LOCS can be applied to this gate-opening phenomenon, we extended experimental measurements of N_2 adsorption to $\text{Cu}(\text{dhbc})_2(4,4'\text{-bpy})$ to additional temperatures (Fig. 6).¹⁹ Prior N_2 adsorption data at 298K is reproduced within experimental error; however, adsorption is not flat prior to the gate-opening pressure. As temperature is decreased to 195K, N_2 capacity increases 40% relative to that at 298K, and converges with the capacity of CH_4 that was originally reported at 298K. This increase suggests additional expansion, more efficient packing, or that rigidity is T dependent. The convergence of N_2 and CH_4 at similar T^* suggests some applicability of the LOCS; however, other gases suggest that there are at least two discrete values of adsorbate capacity,¹⁷ rather than a continuous function of T^* . The temperature dependence of gate-opening pressure does not fully correlate with chemical potential, as suggested by the osmotic potential model, and the imbibition transition model for graphene-silica, described above. The behavior discussed here cannot be explained by treatment of the phenomenon as a simple superposition of adsorption to a simple first ('closed') structure and a second ('open') structure, a common assumption. Additional studies are forthcoming.¹⁹

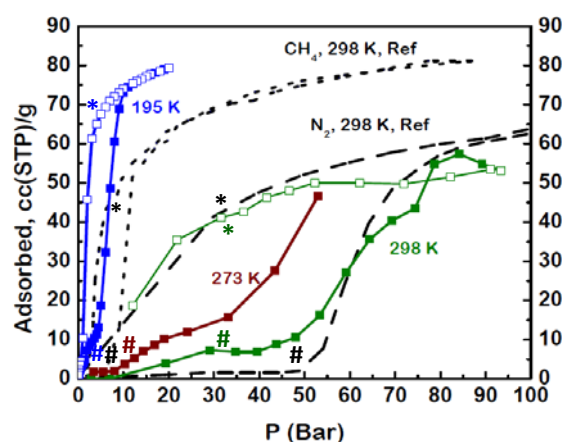


Figure 6: Adsorption (filled) and desorption (open) to $\text{Cu}(\text{dhbc})_2(4,4'\text{-bpy})$ for N_2 (squares) at various temperatures, as shown, plotted with N_2 at 298K (dashed) and CH_4 at 298 K (dotted) from¹⁷. Both gate-opening (#) and gate-closing (*) are a function of temperature, as is adsorption capacity. Only adsorption data was collected at 273K for N_2 . Reduced T^* for N_2 and CH_4 are 1.55 at 195 and 298K, respectively. However other data¹⁷, suggest capacity is not a simple function of T^* .

E. Adsorption on a Single Nanotube

Recent studies by Wang et al.²⁰ using a resonance technique have yielded adsorption isotherms of gases on an *individual* carbon nanotube (NT); a quasi-1D system. Most previous studies of adsorption on

NTs were done on nanotube bundles, in which case the interpretation is complicated by unknown geometry or disorder. In order to gain a microscopic understanding of the new data, we carried out classical grand canonical Monte Carlo (GCMC) simulations of Ar and Kr gas on a single NT.²¹ We found *qualitative* agreement of simulation results with the experiment for Ar, but an apparent significant disagreement for Kr. The Ar data (over the experimental temperature range, $T > 66$ K) revealed evidence of gas condensation and eventual solidification, to a non-epitaxial phase, of high monolayer density with coverage parameter $\varphi \approx 0.24$, consistent with our Ar simulation results. Here the coverage parameter φ is the number of adsorbate atoms per carbon atom. On the other hand, although the Kr simulations with a zigzag NT found an essentially discontinuous increase in the function of $\varphi(P)$, the commensurate phase in the simulations has 50% more atoms than that deduced from the experimental data. Fig. 7 compares isotherms at 77.4K, from experiments²⁰ and simulations.²¹ The zigzag NT (18,0) has radius $R = 0.705$ nm, which lies within the range (0.5-1.5 nm) fabricated in the Wang experiment, in which R was not measured. The isotherms show two distinct differences: (1) the transition pressure (0.04 Torr in experiments *vs.* the simulation value, 0.08 Torr, and (2) the coverage parameter after the transition ($\varphi = 1/6$ in experiments and $1/4$ in simulations).

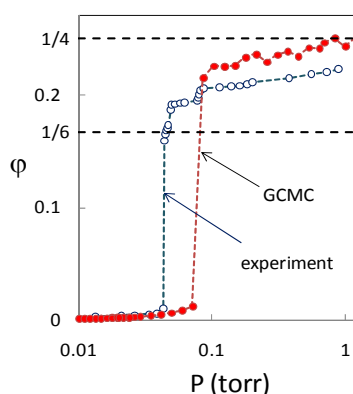


Figure 7. The isotherm at 77.4K for Kr on a single NT obtained from experiments of Wang et al.²⁰ and the isotherm at 77.4K for Kr on zigzag NT (18,0) obtained from GCMC.²¹

In order to understand this discrepancy we consider the dependence on curvature of the (commensurate-incommensurate) CS-IS transition of Kr. On flat graphite, the Kr solid is $a\sqrt{3} \times a\sqrt{3} R30^\circ$ (1:6) CS phase and there is a transition to a IS phase at higher density.²² As a graphene sheet “rolls up” to form a NT, the separation between sites near the gas-surface potential minima increases. This weakens the interaction between atoms above $\sqrt{3}$ sites and encourages the formation of higher density phases.²³ However, for a single small R tube studied in our simulations, the 1:6 CS phase is *not* favored. Our observed 1:4 CS phase has only half of the atoms on the most attractive sites and the other half on the less attractive (bridge/saddle-point) sites. This newly observed commensurate phase is not possible on flat graphite due to the small nearest neighbor spacing (0.326 nm), but it becomes favored for small R due to the increase of interatomic spacing to 0.422 nm. To explore the dependence of Kr phases on the NT chirality, we studied an armchair NT (12,12) of radius $R = 0.814$ nm. At low T (< 70 K) we found a condensed phase of $\varphi = 0.25$ again, but it is a IS phase in which the nearest neighbor distance (~ 0.4 nm) is close to the natural Kr spacing, not the 1:4 CS phase found in zigzag NT (18,0).

To study the dependence on R over a wider range, we computed the classical ground state energy E/N of hypothetical ordered structures on NTs by potential energy minimization. The results of the three lowest energy CS configurations are shown in Fig. 8 for zigzag ($n,0$) NTs and exhibit the preferential stability of the IS phase except for $17 < n < 30$, in which case the 1:4 CS phase is the most stable phase. For the armchair NTs the IS phase is always favorable. This finding is consistent with the simulation results.

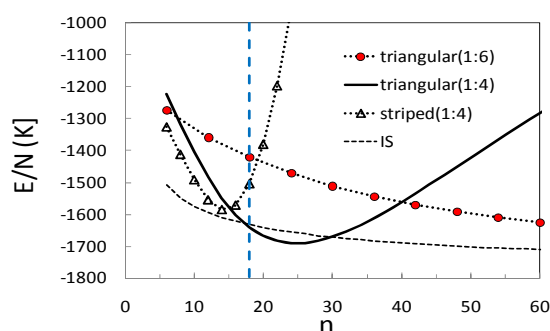


Figure 8. Total energy of a Kr monolayer on a zigzag nanotube($n,0$) as a function of the index n . The average adsorption distance of Kr over carbon atoms on the zigzag(18,0) $R_{ad}=R+0.346$ nm is assumed for all cases, where R is the nanotube radius. The broken vertical line indicates the zigzag (18,0) nanotube studied in simulations. Refer to Ref. 21 for lattice structures of CS phases.

Based on our findings the experimental observation of the 1:6 CS phase suggests that the NTs have much larger radius than assumed. Lacking explicit information about the experimental tube, it is unfortunately not possible to make more detailed quantitative comparison.

Acknowledgments

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