Molecular Simulation of Excess Isotherm and Excess Enthalpy Change in Gas-Phase Adsorption

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We present a new approach to calculating excess isotherm and differential enthalpy of adsorption on surfaces or in confined spaces by the Monte Carlo molecular simulation method. The approach is very general and, most importantly, is unambiguous in its application to any configuration of solid structure (crystalline, graphite layer or disordered porous glass), to any type of fluid (simple or complex molecule), and to any operating conditions (subcritical or supercritical). The behavior of the adsorbed phase is studied using the partial molar energy of the simulation box. However, to characterize adsorption for comparison with experimental data, the isotherm is best described by the excess amount, and the enthalpy of adsorption is defined as the change in the total enthalpy of the simulation box with the change in the excess amount, keeping the total number (gas + adsorbed phases) constant. The excess quantities (capacity and energy) require a choice of a reference gaseous phase, which is defined as the adsorptive gas phase occupying the accessible volume and having a density equal to the bulk gas density. The accessible volume is defined as the mean volume space accessible to the center of mass of the adsorbate under consideration. With this choice, the excess isotherm passes through a maximum but always remains positive. This is in stark contrast to the literature where helium void volume is used (which is always greater than the accessible volume) and the resulting excess can be negative. Our definition of enthalpy change is equivalent to the difference between the partial molar enthalpy of the gas phase and the partial molar enthalpy of the adsorbed phase. There is no need to assume ideal gas or negligible molar volume of the adsorbed phase as is traditionally done in the literature. We illustrate this new approach with adsorption of argon, nitrogen, and carbon dioxide under subcritical and supercritical conditions.

1. Introduction

This paper is motivated by the fact that adsorption analysis is hampered by the various assumptions required in the calculation of the adsorption isotherm and the isosteric heat, and most importantly, many assumptions that are not justified, especially when we have to deal with high-pressure adsorption. Here we list some methods and assumptions commonly used in the analysis of adsorption experiments:[1,2]

(1) Void volume is measured by the helium expansion method.

(2) Helium does not adsorb.

(3) Helium and adsorbate access the same set of pores.

(4) Void volume does not change with loading and adsorbent is inert.

(5) Adsorptive behaves as an ideal gas.

(6) Molar volume of the adsorbed phase is much smaller than that of the gas phase.

Many of these assumptions are not strictly correct, but for subcritical fluids they are unlikely to have any significant impact on the calculation as the adsorbed density is very much greater than the adsorptive density. However, for supercritical fluids or subcritical conditions close to the critical point, the adsorptive density may be significant compared to the adsorbed density, and large errors can arise if care is not exercised.

This paper is the first in a number of proposed publications to present a novel approach of analyzing the adsorption problem. We will present a new way to define the adsorbed phase, to calculate the excess adsorbed density or, in other words, to locate a Gibbs dividing surface, in order to determine the pore volume distribution and external surface area and, of course, to determine the isosteric heat. This new approach requires a different way to collect the data. In a subsequent publication we will demonstrate this by reference to the adsorption of argon in Ajax activated carbon under sub- and supercritical conditions and of carbon dioxide at conditions close to the critical point. The derived pore volume distribution is consistent, and the geometrical surface area is physically realistic. The traditional use of the BET (Brunauer–Emmett–Teller) surface area[2] to characterize porous solids (especially microporous solids) should be applied with care, as it might not give the correct geometrical surface area. Furthermore, the use of BET surface area requires an accepted molecular projection area of nitrogen to be 16.2 Å[2]. This value has been questioned by a number of workers[2] and has been challenged in the literature[3] because, for a highly ordered crystalline surface such as graphite, this value is about 15.5 A[2], whereas for cases where the adsorption is highly localized the area could be much greater than 16.2 A[2]. For example, Arnell and Henneberry[4] have reported values as high as 27.7 A[2]. Therefore, the BET surface area, even in the case of nonporous surface, is often arbitrary.

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The isosteric heat of adsorption is given by eq 1a,[5]

$$q_{st} = kT - \frac{f(U,N)}{f(N,N) - \bar{N}_G} \tag{1a}$$

and $\bar{N}_G$ is the number of molecules of an ideal gas that would occupy the adsorption space. Most work on adsorption neglects the second term in the denominator, and the equation is commonly used in the form shown in eq 1b,

$$q_{st} = kT - \frac{f(U,N)}{f(N,N)} \tag{1b}$$

with the assumptions of ideal gas and that the molar volume of the adsorbed phase is smaller than the gas phase. Here, U is the configurational energy of the simulation box, and N is the number of particles. The function f is defined as $f(X,Y) = \langle XY \rangle - \langle X \rangle \langle Y \rangle$, where the notation $\langle \rangle$ represents the ensemble average. Although the second term in the denominator of eq 1a is frequently neglected, its effect can be large if the box size used in the simulation is very large, even if the gas phase is ideal. As the box size increases, the contribution of the denominator in eq 1b also increases, and in the limit of box size to infinity the second term is effectively zero. This is the case because the contribution to the energy of the system is mostly due to the gaseous phase. To overcome this we need to consider the adsorption heat based on the excess amount adsorbed, and it is the aim of this paper to put things into a clearer perspective. The approach to calculate the excess amount will be made in a clear and unambiguous manner. We will illustrate this with adsorption of argon and carbon dioxide on surfaces and in slit pores.

2. Theory

We first summarize the conventional way of calculating the isosteric heat in a molecular simulation and then present a new method to calculate the isosteric heat, based on the excess amount adsorbed. Molecular simulation in the grand (μ,V,T) ensemble gives the absolute amount, that is, the total number of particles in the simulation box, and the total configurational energy of all particles in the box. We shall propose the means to calculate the excess amount on which the isosteric heat is based. With the excess amount and the excess heat the calculation is independent of the box size as long as the box size is large enough to completely contain the adsorbed phase.

2.1. Conventional Method to Calculate the Isosteric Heat. The isosteric heat is commonly understood as the heat released when one molecule of fluid phase is transferred to the adsorbed phase at constant temperature and volume of the simulation box. What this means is that the larger the simulation box the smaller the isosteric heat because of the increased contribution from the gaseous phase. This is not exactly the heat that one would measure from the experiment. The formula that is commonly used in the literature to compute the isosteric heat is eq 1b.

The isosteric heat can be derived from a simple thermodynamic argument. In fact, it should be called isosteric enthalpy of adsorption.[2] It is defined as the difference between the partial molar enthalpy in the gas phase and the partial molar enthalpy in the adsorbed phase:[1,2,5-8]

$$q_{st} = \bar{h}_G - \bar{h}_a \tag{2}$$

Here, the subscript "a" denotes the adsorbed phase and "G" the gas phase. This definition of heat is the enthalpy change of the process of moving one molecule in the adsorbed phase to the gaseous phase. Therefore, it should be called the isosteric heat of desorption. It is commonly used so as to give a positive value for the isosteric heat because the partial molar enthalpy of the adsorbed phase is generally lower than the molar enthalpy of the gas phase.

Assuming the molar kinetic energy does not change when a particle is moved from the gas phase to the adsorbed phase and that the molar volume of the adsorbed phase is negligible; the enthalpies in eq 2 only involve the configurational components. If one assumes the molar adsorbed phase volume is very small, then the partial molar enthalpy is approximately equal to the partial molar configurational energy, that is,

$$\bar{h}_a \approx \bar{u}_a = \frac{\partial U_a}{\partial N_a} \tag{3}$$

where U_a is the configurational energy of the adsorbed phase, and N_a is the number of moles in the same phase. In the grand canonical ensemble, this partial derivative can be obtained from the fluctuation theory:

$$\frac{\partial U_a}{\partial N_a} = \frac{\langle U_a N_a \rangle - \langle U_a \rangle \langle N_a \rangle}{\langle N_a N_a \rangle - \langle N_a \rangle \langle N_a \rangle} \tag{4}$$

Thus, the isosteric heat equation is simply:

$$q_{st} = \bar{h}_G - \frac{\langle U_a N_a \rangle - \langle U_a \rangle \langle N_a \rangle}{\langle N_a N_a \rangle - \langle N_a \rangle \langle N_a \rangle} \tag{5}$$

The partial molar enthalpy of the gas phase can be obtained from a separate GCMC simulation of the bulk phase.

Remember that up to this point we have not defined our adsorbed phase. This will be presented in Section 2.2, but in the meantime if we take the adsorbed phase as the whole volume in the simulation box, then this can cause a problem because there can be particles in the box that have practically zero solid–fluid potential. What that really means is that the configurational energy obtained from the simulation is not the configurational energy of the adsorbed phase. The only exception to this would be when we deal with an ideal gas where there is no interaction among the "free" particles, and therefore the configurational energy of the box is simply that of the adsorbed particles. Other than this, we have to develop a general framework for adsorption such that the ideal gas is merely a special case that can be easily accommodated within this general framework. Another motivation for doing this is the need to have theoretical adsorption capacity and heat that can be readily compared with experimental data.

2.2. A New Method to Calculate the Isosteric Heat Based on Excess Quantities. For a theory to have any practical value, it must be possible for results derived from molecular simulations to be used directly when comparing with experimental results. This means that we must develop a new molecular simulation approach that will give us directly the excess adsorbed quantity and the isosteric heat based on this excess amount. The adsorbed phase is defined naturally in this development. Most importantly, the way we calculate exc-
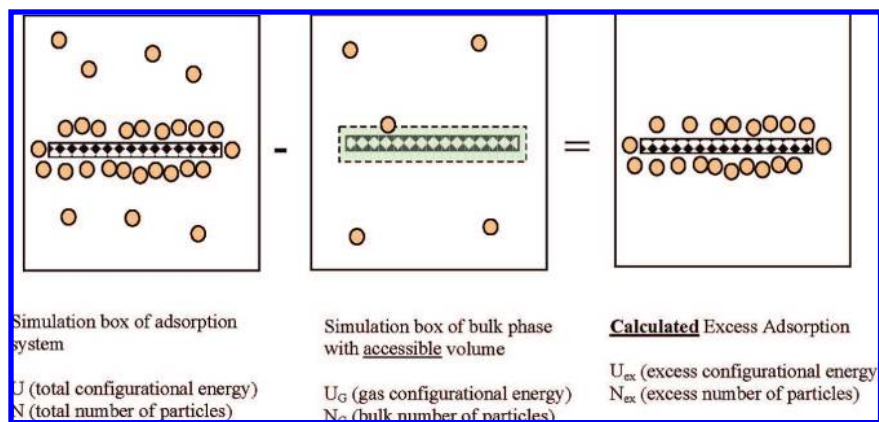
Figure 1. The schematic diagram of the calculated excess amount and the excess energy using the reference of gaseous properties occupying the accessible volume.

ess in the molecular simulation should be the same as the calculation we would conduct experimentally.

Isosteric Heat of Adsorption. Although isosteric heat has been used constantly in the literature in the calculation of the amount of heat released per unit change in the particles added to the adsorbed phase, it has been used almost in a mechanical manner. We will show its derivation for the general case first and then deduce the result to the diluted conditions. We start with a clear definition of the differential enthalpy of adsorption.[1,2,5–8] It is defined as the change of the total enthalpy of the system per unit change in the number of particles added to the excess adsorbed phase at constant temperature and total number of particles:

$$\Delta\bar{h}_{ex} = \left(\frac{\partial H}{\partial N^{ex}}\right)_{T,N} \tag{6}$$

where H is the total enthalpy of the system and is related to that of the gaseous reference phase, H_G; the solid adsorbent, H_s; and the excess enthalpy, H_{ex}, by eq 7 (Figure 1).

$$H = H_{ex} + H_G + H_s \tag{7}$$

The excess enthalpy, H_{ex}, then depends on the way we define the gaseous reference enthalpy and the solid enthalpy. The variable H_s is the enthalpy of the solid whose region extends to the boundary of the accessible volume (where the gas–solid potential energy passes through zero). We define the gaseous reference enthalpy, H_G, as the enthalpy of the hypothetical gas phase occupying the accessible region of the simulation box having the same density as the bulk gas.

Similar to the excess enthalpy defined in eq 7, the excess internal energy, number, and volume are defined by the following,

$$U = U_{ex} + U_G + U_s \tag{8a}$$

$$N = N_{ex} + N_G + N_s \tag{8b}$$

$$V = V_{ex} + V_G + V_s \tag{8c}$$

where N_G is the number of particles in the system occupying the accessible volume of the simulation box at the same density

as the bulk. The number of adsorbate particles in the solid phase is zero ($N_s = 0$) because of the extremely large positive solid-fluid potential energy. The excess volume is zero ($V_{ex} = 0$) by virtue of the definition of the system volume being the sum of the accessible volume, V_G, and the solid volume. Note that we define the solid volume as one extending all the way to the boundary where the solid–fluid potential energy is zero. A similar concept of "available volume" has recently been proposed by Mittal et al.[9] and was shown to be particularly valuable in the context of self-diffusivity calculations.

The key important parameter in this approach is the accessible volume of the simulation box, and it can be obtained by carrying out a Monte Carlo integration by inserting particles at random positions within the box with a random orientation. If the solid–fluid potential of that particle is nonpositive then we count the insertion as a success; otherwise it is a failure. We repeat this procedure N times. If the number of success is $N_{success}$, then the accessible volume is $(N_{success}/N)V_{box}$.

Inserting eq 7 into eq 6, and keeping the total number of particles in the system constant (i.e., $dN_{ex} = -dN_G$; this statement means that one particle is leaving one phase to enter the other phase), we find

$$\Delta\bar{h}_{ex} = \left(\frac{\partial H_{ex}}{\partial N_{ex}}\right)_T - \left(\frac{\partial H_G}{\partial N_G}\right)_T \tag{9}$$

Since $V_{ex} = 0$, the excess enthalpy is the same as the excess internal energy, and we rewrite the above equation as follows:

$$\Delta\bar{h}_{ex} = \left(\frac{\partial U_{ex}}{\partial N_{ex}}\right)_T - \left(\frac{\partial U_G + \partial pV_G}{\partial N_G}\right)_T \tag{10}$$

in which we have also written the enthalpy of the reference gaseous phase in terms of internal energy and pressure. Combining the excess energy and the energy of the reference gaseous phase to recover U, we get:

$$\Delta\bar{h}_{ex} = \left(\frac{\partial U}{\partial N_{ex}}\right)_T - \left(\frac{\partial pV_G}{\partial N_G}\right)_T \tag{11}$$

This is the fundamental equation of the change of the enthalpy of the complete simulation box with respect to the excess

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number. We can define the isosteric heat as the negative of this quantity to give a positive value of isosteric heat, that is,

$$q_{st} = \left(\frac{\partial p V_G}{\partial N_G}\right)_T - \left(\frac{\partial U}{\partial N_{ex}}\right)_T \quad (12)$$

For an ideal gas, $(\partial p V_G/\partial N_G) = kT$, eq 12 becomes $q_{st} = kT - (\partial U/\partial N_{ex})_T$, which is the equation applicable only for low-density adsorption of subcritical fluids. This is very restrictive as many real adsorption systems involve not only nonideal gases but also high-pressure conditions that make this special case of only limited value.

To understand how the adsorbed phase behaves, we investigate the change of the excess energy with the change in the excess amount, that is,

$$-\left(\frac{\partial U_{ex}}{\partial N_{ex}}\right)_T \quad (13)$$

We introduce the negative sign to make this quantity positive, simply for convenience. We shall come back to this quantity later.

Now back to our general equation for the isosteric heat (eq 12). It must be noted that even when we deal with ideal gas, the first term on the RHS of this equation is kT, but the second term involves N_{ex}, not N as done so often in the literature (for example, eq 1b). It is essential that we account for N_{ex} in the calculation of the enthalpy change because if the simulation box is very large and the number of particles in the free phase is very large, then that would make the second term on the RHS of eq 1a very small. This is not logical because that would make the isosteric heat depend on the box size!

Application of the Fluctuation Formula. The fundamental equation to compute the enthalpy change in adsorption is eq 12. We will now show that how we to compute this term from the grand canonical Monte Carlo simulation. First we rewrite this equation as follows:

$$\Delta\bar{h}_{ex} = \left[\frac{\partial U}{\partial(N - N_G)}\right]_T - \left(\frac{\partial p V_G}{\partial N_G}\right)_T \quad (14)$$

and apply the chain rule of differentiation with respect to the chemical potential to get eq 15,

$$\Delta\bar{h}_{ex} = \frac{(\partial U/\partial\lambda)_T}{(\partial N/\partial\lambda)_T - (\partial N_G/\partial\lambda)_T} - V_G\frac{(\partial p/\partial\lambda)_T}{(\partial N_G/\partial\lambda)_T} \quad (15)$$

where $\lambda = \mu/kT$, with μ being the chemical potential. From the Gibbs−Duhem equation, the change of the pressure with chemical potential at constant temperature is simply ρ, that is, $(\partial p/\partial\lambda)_T = \rho kT$. Substituting this into eq 15, we obtain an equation that is suitable for the application of the fluctuation formula in grand canonical ensemble:

$$\Delta\bar{h}_{ex} = \frac{(\partial U/\partial\lambda)_T}{(\partial N/\partial\lambda)_T - (\partial N_G/\partial\lambda)_T} - \frac{N_G kT}{(\partial N_G/\partial\lambda)_T} \quad (16)$$

This equation suggests that we need to carry out two separate GCMC simulations. One is the simulation of a bulk phase with

accessible volume V_G, and the other is the simulation of the adsorption system having a volume V. From the GCMC simulations of these two boxes, we can obtain the following fluctuation variables:

$$\left(\frac{\partial U}{\partial\lambda}\right)_T = f(U, N); \left(\frac{\partial N}{\partial\lambda}\right)_T = f(N, N); \left(\frac{\partial N_G}{\partial\lambda}\right)_T = f(N_G, N_G) \quad (17)$$

Therefore, the final formula for the differential enthalpy change is:

$$\Delta\bar{h}_{ex} = \frac{f(U, N)}{f(N, N) - f(N_G, N_G)} - \frac{N_G kT}{f(N_G, N_G)} \quad (18)$$

This is the general formula for the enthalpy change, and it is applicable to any fluids and to any conditions. For ideal gases, this equation reduces to:

$$\lim_{P \to 0} \Delta\bar{h}_{ex} = \frac{f(U, N)}{f(N, N) - f(N_G, N_G)} - kT \quad (19)$$

It is noted that the denominator of the above equation includes $f(N_G, N_G)$, and it is essential that the contribution of the gaseous phase be taken out in the calculation of the isosteric heat. Although this has been recognized before,[5] this has frequently been ignored in the literature.

As we have indicated earlier, two separate simulations must be carried out: one is the main simulation box of the adsorption system, and the other is the hypothetical box of bulk gas with a volume equal to the accessible volume of the simulation box. This accessible volume could be small in the simulation because the number of particle in this reference gas phase box is too low for good statistical purposes. We can improve this by simply running the simulation of the reference gas phase with a larger box with larger volume, say V'_G. The number of particles resulting from the simulation is N'_G and the associated variables are $U'_G, f(N'_G, N'_G)$ and $f(U'_G, N'_G)$. Having these, the equation that is used for the calculation of the enthalpy change in adsorption is:

$$\Delta\bar{h}_{ex} = \frac{f(U, N)}{f(N, N) - (V_G/V'_G)f(N_G, N_G)} - \frac{N'_G kT}{f(N'_G, N'_G)} \quad (20)$$

Note that V_G is the accessible volume whereas V'_G is the volume that we use to simulate the bulk gas phase and can be equal to or different from the accessible volume V_G. Equation 20 is our fundamental equation, and it is valid for any system and any conditions. In the limit of dilute conditions of the bulk gas phase (ideal gas), we have:

$$\lim_{P \to 0} \frac{N'_G}{f(N'_G, N'_G)} = 1$$

and the above equation (eq 20) reduces to eq 1a. Therefore, eq 1a is strictly valid only for an ideal gas. For adsorptive gases that do not conform to ideal behavior, the ratio $N_G/f(N_G, N_G)$ will deviate from unity. We will discuss this in greater detail in Section 3.

To understand how the different energies of interaction contributed to the enthalpy change in adsorption, we can break down the energy in terms of its various components, say $U = \sum_j U_j$, and the contribution of the component j is simply:

$$\frac{f(U_j, N)}{f(N, N) - (V_G/V'_G)f(N_G, N_G)} \tag{21}$$

Calculation of the Pressure. The inputs to the two separate grand ensemble simulations (adsorption box and reference gaseous box) are the temperature, the physical box size (i.e., within the limits set by the positions of outer layer adsorbent atoms or by periodic boundaries), and absolute activity $z = \exp(\mu/kT)/\Lambda^3$. The outputs from the GCMC of the reference gas box are bulk gas density and pressure. The pressure can be found from the pressure virial[10] or from the method suggested by Harismiadis et al.,[11] which is convenient for complex intermolecular potentials of nonsimple molecules. These authors suggested a method based on the canonical ensemble in which, in the thermodynamic limit, the pressure is the negative change of the Helmholtz free energy with respect to volume at constant number of particles and temperature. This can be built in to a simulation in the Grand Canonical (μ,V,T) ensemble. By making a small change in volume from V to V' (usually we make a 1% change), the pressure can be computed from:

$$p = \frac{kT}{\Delta V} \ln\left\langle \exp\left[N \ln\left(\frac{V'}{V}\right) - \frac{U' - U}{kT}\right]\right\rangle \tag{22}$$

where $\langle \cdot \rangle$ is the ensemble average in the canonical ensemble and ΔV must be constant in magnitude as well as in sign in the evaluation of the above average. We can carry out two independent volume perturbations of the same magnitude, but different in sign, and obtain pressure as the arithmetic average of the following two pressures:[12,13]

$$p' = \frac{kT}{\Delta V'} \ln\left\langle \exp\left[N \ln\left(\frac{V'}{V}\right) - \frac{U' - U}{kT}\right]\right\rangle \tag{23a}$$

$$p'' = \frac{kT}{\Delta V''} \ln\left\langle \exp\left[N \ln\left(\frac{V''}{V}\right) - \frac{U'' - U}{kT}\right]\right\rangle \tag{23b}$$

where $\Delta V' = V' - V$ and $\Delta V'' = V'' - V$. The configuration energies U' and U'' correspond to V' and V'', respectively. It could be useful that pressure can be computed for various values of δV, and linear extrapolation of a straight line fitting through these points to $\delta V = 0$ will give a more reliable estimate of pressure. The procedure of arithmetic average has been addressed by Kofke and co-workers,[12−14] and they raised an issue of asymmetry of increasing and decreasing the volume. Readers are referred to their publication for further details.

Behavior of the Adsorbed Phase. It is useful to investigate how the adsorbed phase behaves; for example, for how it changes with temperature, we have to consider the change of the excess energy with the change of the excess amount (eq 13). Let us now develop an equation for computation from the GCMC simulation of the two boxes that we have discussed. First we rewrite eq 13 as follows:

$$-\left(\frac{\partial U_{ex}}{\partial N_{ex}}\right)_T = -\left(\frac{\partial U - \partial U_G}{\partial N - \partial N_G}\right)_T \tag{24}$$

Taking the chain rule of differentiation with respect to chemical potential, we get the following:

$$-\left(\frac{\partial U_{ex}}{\partial N_{ex}}\right)_T = -\left(\frac{\partial U/\partial\lambda - \partial U_G/\partial\lambda}{\partial N/\partial\lambda - \partial N_G/\partial\lambda}\right)_T$$

Finally, we apply the fluctuation variables from a grand canonical to get the required expression for computation:

$$-\left(\frac{\partial U_{ex}}{\partial N_{ex}}\right)_T = -\left[\frac{f(U, N) - f(U_G, N_G)}{f(N, N) - f(N_G, N_G)}\right] \tag{25}$$

As before, if we run the GCMC of the reference gas phase with a different volume, V'_G; the relevant formula is then

$$-\left(\frac{\partial U_{ex}}{\partial N_{ex}}\right)_T = -\left[\frac{f(U, N) - (V_G/V'_G) \times f(U'_G, N'_G)}{f(N, N) - (V_G/V'_G) \times f(N'_G, N'_G)}\right] \tag{26}$$

To investigate how various contributions to adsorption affect this, we simply replace U with the component U_j if we wish to know how component j affects the adsorbed phase.

Slope of the Adsorption Isotherm. Although mean particle number and heat of adsorption can be readily obtained as we have shown, the slope of the isotherm can also be obtained with the fluctuation variables. Let us start with the change of the particle in the simulation box with respect to pressure, $\partial N/\partial p$. Applying the chain rule of differentiation with respect to the chemical potential, eq 27 is obtained.

$$\frac{\partial N}{\partial p} = \frac{\partial N/\partial\lambda}{\partial p/\partial\lambda} \tag{27}$$

From standard thermodynamics, $\partial p/\partial\lambda = \rho kT = (N_{G1}/V_G)kT$, and using the fluctuation variable for $\partial N/\partial\lambda$ as $\partial N/\partial\lambda = f(N,N)$, the above equation reduces to eq 28.

$$\frac{\partial N}{\partial p} = \frac{f(N, N)}{(N_G/V_G)kT} \tag{28}$$

If we are interested in the change of the excess amount with respect to pressure, the necessary equation is:

$$\frac{\partial N_{ex}}{\partial p} = \frac{f(N, N) - f(N_G, N_G)}{(N_G/V_G)kT} \tag{29a}$$

If the bulk gas simulation is done with a different volume, V_G, from the accessible volume, eq 29a is replaced by eq 29b.

$$\frac{\partial N_{ex}}{\partial p} = \frac{f(N, N) - (V_G/V'_G)f(N'_G, N'_G)}{(N'_G/V'_G)kT} \tag{29b}$$

This equation states that the excess amount would reach a maximum when

$$f(N, N) = f(N_G, N_G) \tag{30a}$$

or

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$$f(N, N) = (V_G/V'_G)f(N_G, N_G) \qquad (30b)$$

This point is the point where the denominator of the excess isosteric heat is zero, giving an infinite excess isosteric heat.

3. Results and Discussion

We will illustrate our theory with the adsorption of argon, nitrogen, and carbon dioxide in graphitic slit pores and in cylindrical carbon nanotubes. Various temperatures are chosen to represent the sub- and supercritical conditions. The potential model for argon is taken to be a single site LJ model with the collision diameter of 0.3405 nm and the reduced well depth of interaction energy of 119.8 K. For nitrogen and carbon dioxide we used the TraPPE models,[15] which describe nitrogen as a collection of two dispersive sites and three partial charge sites and carbon dioxide as a collection of three dispersive sites and three partial charge sites. For nitrogen, the separation distance between the two dispersive sites is 1.1 Å, and the molecular parameters are $\sigma = 3.32$ Å and $\varepsilon/k = 36$ K. The three partial charges lie on the molecular axis, with the positive charge at the center ($0.964e^-$) and two negative charges ($-0.482e^-$) on the same positions as the dispersive sites. For linear carbon dioxide the separation distance between carbon atom and an oxygen atom is 1.16 Å, and the three partial charges lie exactly on the same positions as those of dispersive sites. The molecular parameters of carbon atom are $\sigma = 2.8$ Å and $\varepsilon/k = 27$ K, and those of oxygen atoms are $\sigma = 3.05$ Å and $\varepsilon/k = 79$ K. The magnitudes of the three partial charges are -0.35, 0.7, and $-0.35e^-$, with the positive charge at the carbon atom.

For the solid–fluid potential we model the surface of a slit pore as a Steele structureless model and the surface of a cylindrical pore as a continuum surface with the potential energy taking the form of hypergeometrical function.[16]

3.1. Subcritical Adsorption of Argon and Nitrogen. Let us start our discussion by first revisiting the usual adsorption of subcritical fluids in characterization. For the subcritical fluids at temperatures well below the critical point, we expect the ideal gas behavior and the dominance of the adsorbed phase over the gaseous phase, that is, the molar volume of the adsorbed phase is much smaller than that of the gaseous phase. Figure 2 shows the adsorption isotherms of argon at 77 and 87.3 K in a graphitic slit pore ($H = 0.8$ nm) with the absolute isotherms are shown as symbols and the excess ones as solid lines. The width H is defined as the distance between one plane passing through the carbon atoms of the outermost layer of one wall and the corresponding plane of the opposite wall. The excess amount is defined as the difference between the amount in the pore and the hypothetical amount occupying the accessible at the same density as the bulk gas phase, that is,

$$N_{ex} = N - N_G = N - V_{acc}\rho_G \qquad (31)$$

If we use the accessible volume to define the pore density, the absolute pore density is $\rho = N/V_{acc}$, and the excess pore density is $\rho_{ex} = \rho - \rho_G$.

It comes as no surprise that there are no differences between the absolute and excess isotherms (shown in Figure 2), due to the very low density in the gas phase at these temperatures, which are well below the critical point.

We can check the ideal gas behavior by studying the ratio $N_G/f(N_G,N_G)$ as a function of pressure, and this is shown in Figure 3.
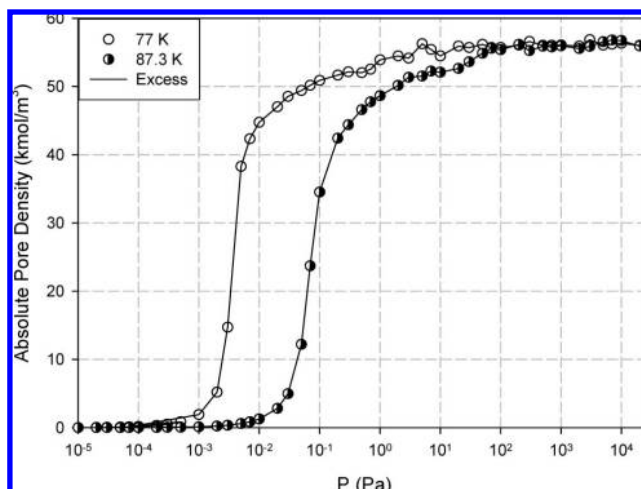

Figure 2. Adsorption isotherms of argon in 0.8 nm graphitic slit pore at 77 and 87.3 K. Symbols are for absolute isotherms, and the solid lines are for excess isotherms.
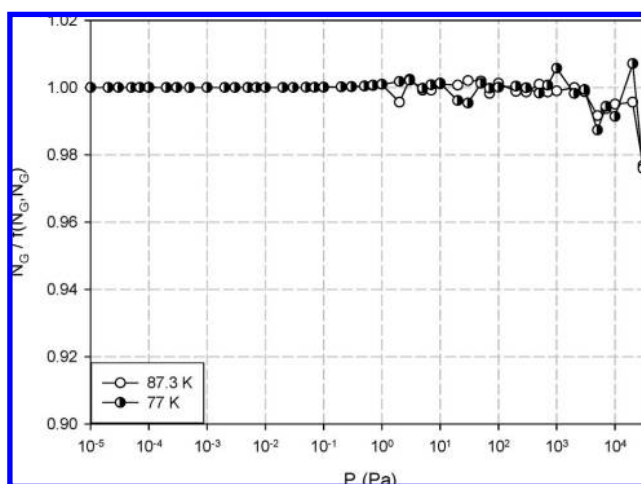

Figure 3. Behavior of $N_G/f(N_G,N_G)$ as a function of pressure for argon at 77 and 87.3 K.

A value of unity of this function indicates an ideal gas, and it is indeed the case for argon at 77 and 87.3 K. There is only a small deviation from unity when pressure approaches the vapor pressure (by about 2%), and it can be concluded that argon behaves like an ideal gas at these temperatures. We note that this ratio is slightly less than unity when pressure approaches the saturated vapor pressure. This deviation will be more significant when we deal with supercritical pressure, and this will be discussed later with argon, nitrogen, and carbon dioxide adsorption under supercritical conditions.

To investigate the relative contribution of the adsorbed phase and that of the hypothetical gas phase that would occupy the accessible volume in the confined space of 0.8 nm graphitic slit pore at the same density as the bulk gas phase, we investigate the ratio

$$\frac{f(N,N)}{f(N_G,N_G)} \text{ or } \frac{f(N,N)}{(V_G/V'_G)f(N'_G,V'_G)}$$

that appears in the denominator of the isosteric heat equation (eq 18). This ratio will be very large if the traditional equation for isosteric heat, which has been used in the literature, is acceptable because of the dominance of the adsorbed phase contribution. In Figure 4, we plot this ratio as a function of pressure, and it is seen that this ratio is indeed much greater
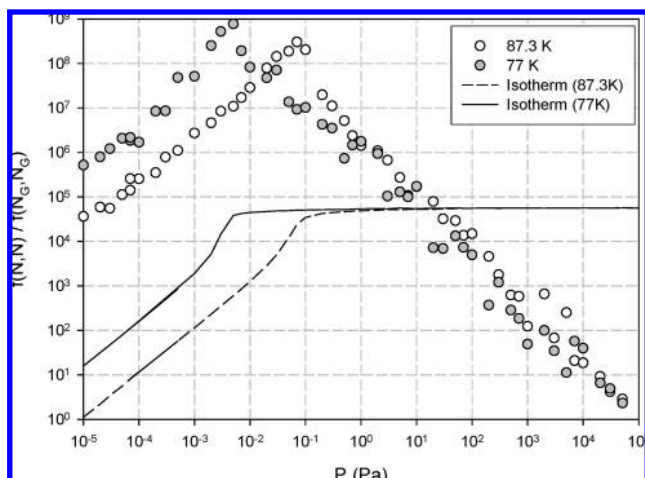
Figure 4. Behavior of $f(N,N)/f(N_G,N_G)$ with pressure. The isotherms (the bottom two plots) are shown in the same figure to show how this ratio varies with amount adsorbed.
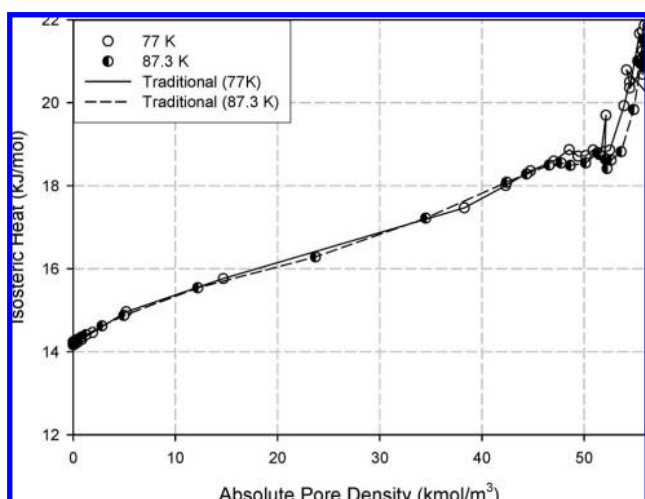

Figure 6. Isosteric heat of argon and nitrogen adsorption in 0.8 nm graphitic slit pore at 77 K.

Figure 5. Isosteric heat of argon adsorption in 0.8 nm graphitic slit pore at 77 and 87.3 K. Symbols are from the heat equation in this paper (eq 18), and lines are from the commonly used equation (1b) in the literature.

Figure 7. Adsorption isotherm of argon in 0.8 nm graphitic slit pore at 180, 200, 298, and 400 K (The unfilled symbols are for absolute isotherms while the filled symbols are for excess isotherms).

than unity, supporting the use of eq 1b for argon at 77 or 87.3 K. At low pressures, where the adsorbed amount is less than the saturation amount, this ratio is on the order of 10^6. As saturation is approached the ratio decreases, but it is still greater than unity.

Having seen that the gas behaves very much like an ideal gas (Figure 3) and the dominance of the adsorbed phase (Figure 4), it is not surprising to find that the correct heat equation presented in this paper (eq 18) agrees well with the heat equation for ideal gas commonly used in the literature (eq 1b), as seen in Figure 5 for the subcritical conditions of 77 and 87.3 K where we plot the isosteric heats versus the absolute pore density. Large fluctuations are observed at high loadings, and this is due to the difficulty in inserting particles in the pore having dense fluids during the Monte Carlo simulation.

The behavior of nitrogen at 77K is the same as that seen so far for argon at 77 and 87.3 K. We only show the isosteric heat in Figure 6 as an illustration of the similarity between nitrogen and argon adsorption under subcritical conditions.

3.2. Supercritical Adsorption of Argon. The difference between the new equation for the isosteric heat (eq 18) and the common equation (eq 1b) traditionally used in the literature is
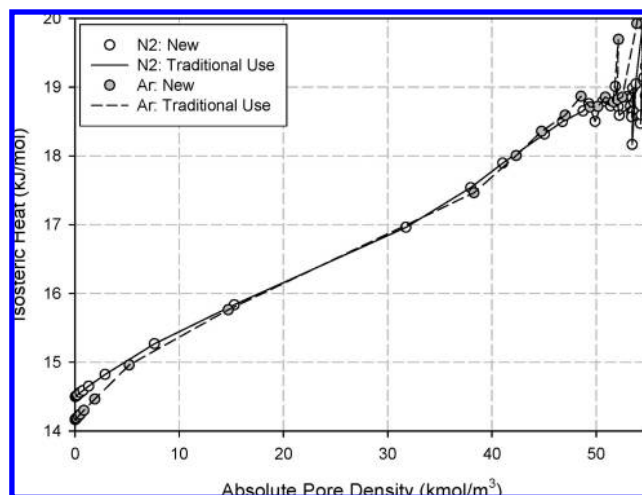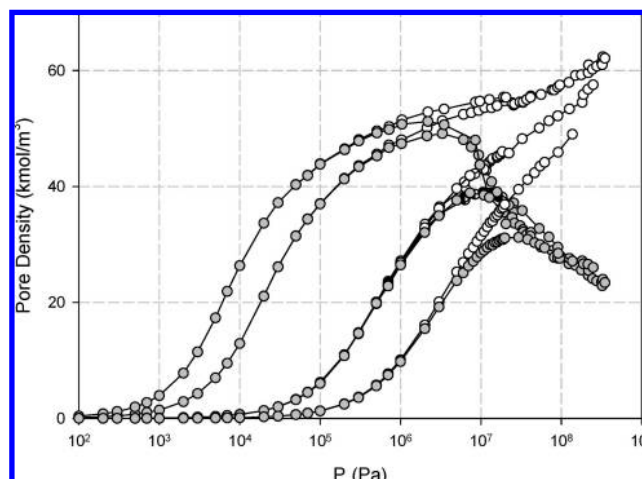
manifested with supercritical fluids that are known not to behave as an ideal gas at the selected temperatures, and the contribution from the gas phase can be comparable to that from the adsorbed phase. This is shown in Figure 7 with argon adsorption in 0.8 nm graphitic slit pore at 180, 200, 298, and 400 K.

The absolute adsorption isotherm exhibits a steady increase because of the compressibility of the supercritical fluid even in the confined space. On the other hand the excess isotherm shows a clear maximum beyond which it decreases with pressure because the second term in eq 31 becomes significant. The maximum in the excess isotherm is due to the comparable contribution from the gas phase. We note that the maximum shifts to higher pressure for higher temperatures and the maximum excess is lower. Up to 1×10^9 Pa (10 000 atm), the excess amount remains positive, which is in contrast to what has been reported in the literature.[17] This is due to the use of the accessible volume in the calculation of the excess, whereas in the literature the helium void volume is used, and this volume can be greater than the actual geometrical volume because of the possibility of helium adsorption. A classic example is the study of Malbrunot et al. in 1992,[17] when they used helium expansion at ambient temperatures to measure void volume of activated carbon. Because helium adsorbs in fine pores they overestimated the void volume and hence the excess amount
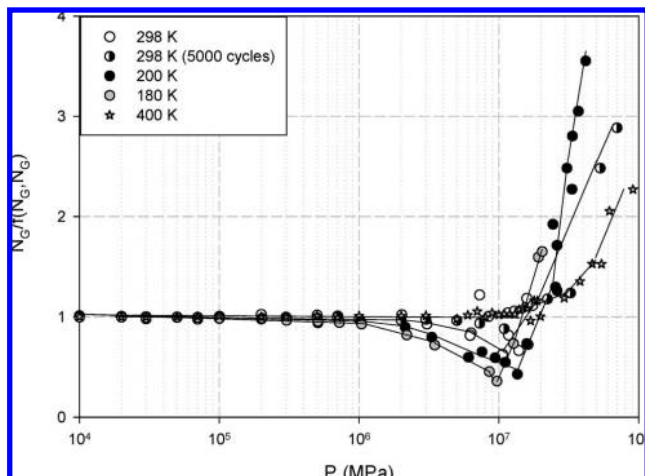
Figure 8. A measure of ideal gas for supercritical conditions at a number of temperatures.
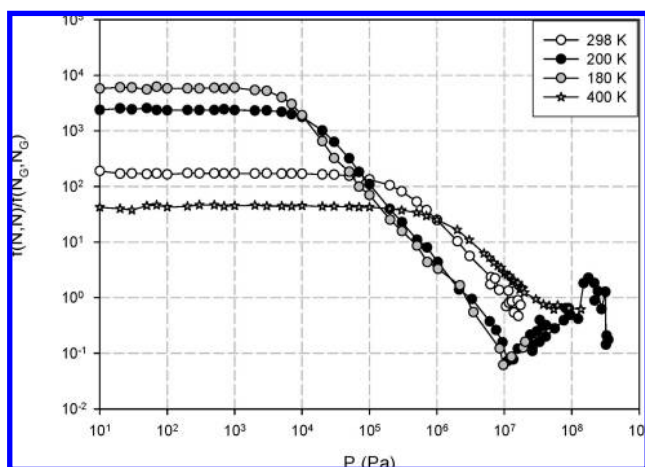

Figure 9. Relative contribution between the gas phase and the adsorbed phase for argon adsorption in 0.8 nm graphitic slit pore at 77, 87.3, 200, and 298 K.
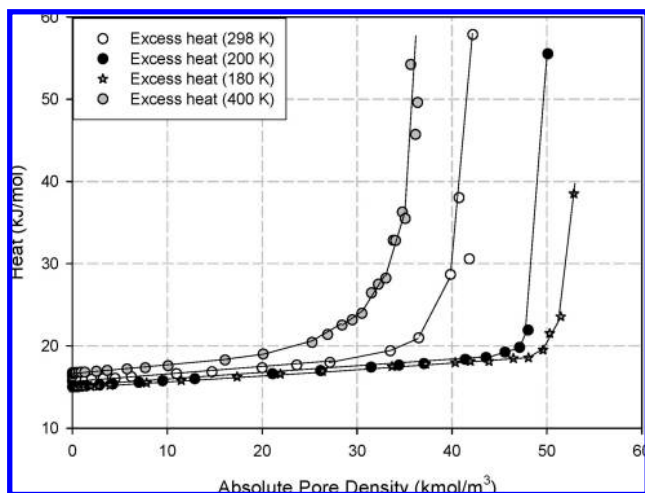

Figure 10. Plots of excess isosteric heat (using eq 18) as a function of absolute pore density for argon adsorption in 0.8 nm graphitic slit pore at 180, 200, 298, and 400 K.
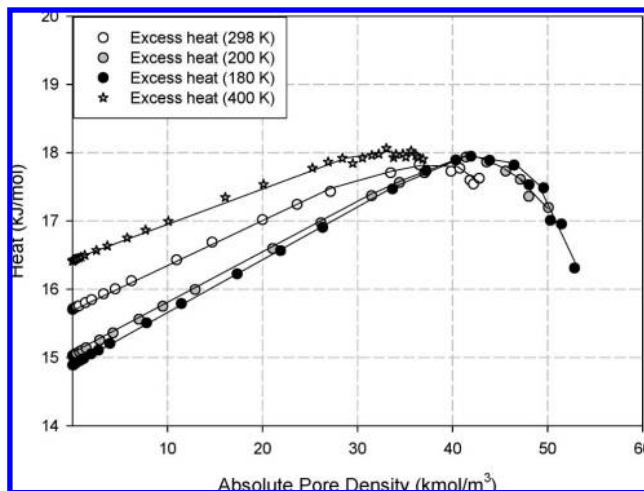

Figure 11. Plots of isosteric heat (using eq 1b) as a function of absolute pore density for argon adsorption in 0.8 nm graphitic slit pore at 180, 200, 298, and 400 K.
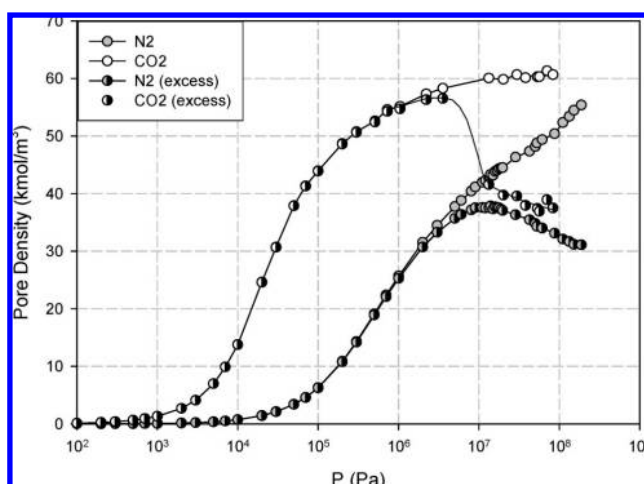

Figure 12. Adsorption isotherms of nitrogen and carbon dioxide in 0.8 nm graphitic slit pore at 298 K.
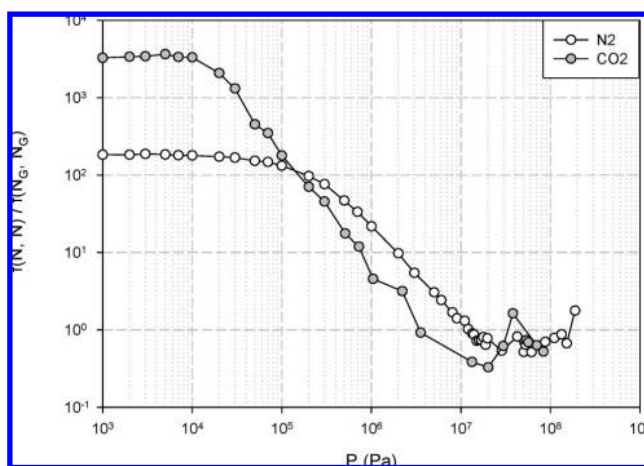

Figure 13. Ratio $f(N,N)/f(N_G,N_G)$ of nitrogen and carbon dioxide in 0.8 nm graphitic slit pore at 298 K.

becomes negative at high pressures. They finally recognized this helium adsorption and rectified the situation by carrying out helium expansion at much higher temperatures.[18] As a result, the excess amount becomes positive, and it is only negative when pressure is extremely high (on the order of 5 000 atm). It

is suspected that even if high temperatures were used in helium expansion there would still be a modest adsorption and the calculated helium-void volume would probably still be greater than the actual geometrical volume. The use of He adsorption in the determination of excess adsorption has been discussed by Gumma and Talu.[19] We believe that the accessible volume
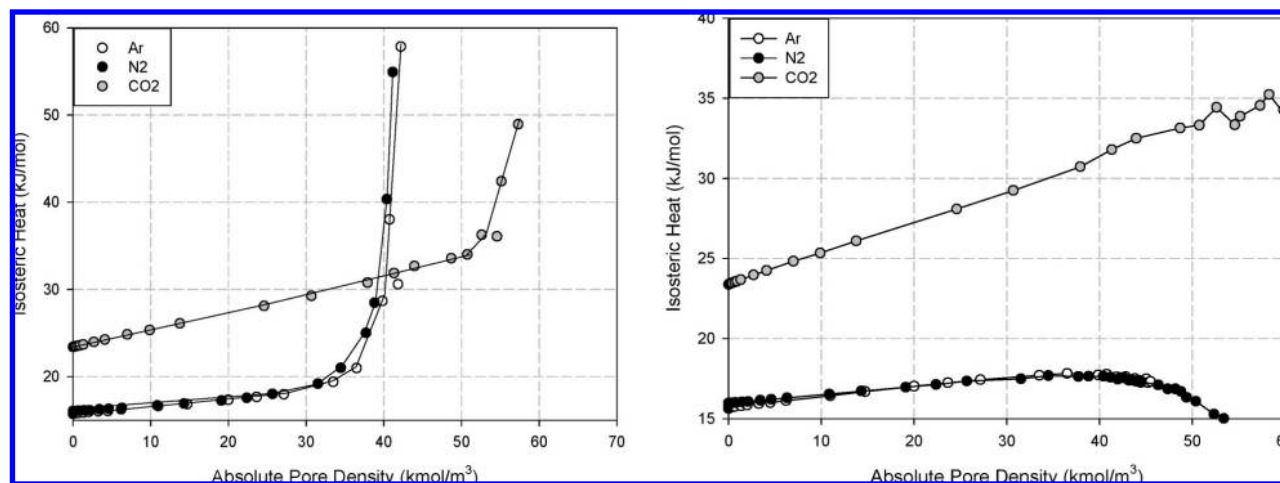
Figure 14. Isosteric heat of argon, nitrogen, and carbon dioxide in 0.8 nm graphitic slit pore at 298 K. Left hand figure is from eq 18 and the right-hand figure is from eq 1b.
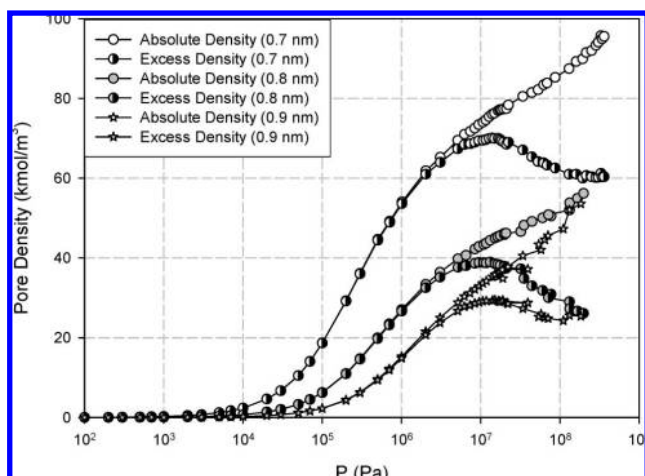

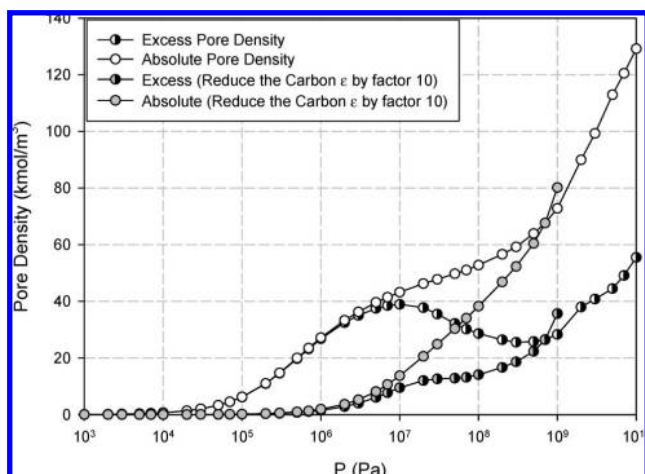**Figure 15.** Adsorption isotherms of argon in 0.7, 0.8, and 0.9 nm graphitic slit pores at 298 K.

Figure 16. Adsorption isotherms of argon in 0.8 nm graphitic slit pores at 298 K. The bottom two curves are isotherms when the well depth of carbon atom in the graphene layer is reduced by 10.

is a better choice to calculate the excess amount because the use of accessible volume avoids negative excess amounts. We will discuss in further details in the following section. A negative excess amount means that the adsorbed density is less than the bulk gas density, and this is contrary to physical intuition, even in the confined space of small pores, because in

addition to the external pressure the exertion of the solid−fluid potential should enhance the density. Therefore, the adsorbed density should always be greater than the bulk gas density, that is, the excess amount should always be positive. It is important to recognize the significance of the accessible volume, and as we have shown in our recent publication,[20] using the accessible volume, the Henry constant is always positive in circumstances where, using traditional helium expansion volume, the Henry constant is negative at high temperatures. Furthermore, by using the accessible volume the isosteric heat of adsorption at zero loading becomes well-defined, whereas the heat using the helium void volume can become infinite and even negative at high temperatures. Combining all these observations, we reach the conclusion that the accessible volume is an important adsorption variable and that it should be determined for the adsorbate under consideration. Different adsorbates will have different accessible volume, and this is expected because large adsorbates can not access fine pores that small adsorbates can. Thus, the use of helium to measure void volume can lead to inconsistencies because (i) it can adsorb and (ii) He may access ultrafine pores that other adsorbates can not.

When does the supercritical gas deviate from the ideal gas behavior? This is seen in Figure 8, where we plot $N_G/f(N_G,N_G)$ versus pressure for argon adsorption at the same temperatures used in Figure 7. We see that once the pressure has reached 1 MPa, (about 10 atm) there is significant deviation from the ideal gas. This deviation is quite interesting. For temperatures that are not too high, this deviation becomes less than unity, reaches a minimum, and then increases sharply as pressures greater than 10 MPa. At high pressures, where the system is very dense, clusters are formed.[21,22] Because these clusters cannot readily interchange among each other, the fluctuation variable $f(N,N)$ is proportional to the number of clusters (i.e., less than N), resulting in a ratio $N_G/f(N_G,N_G)$ greater than unity. However, at moderate pressures this ratio has a minimum that is less than unity. The same occurs for subcritical fluids when pressure approaches the vapor pressure (see Figure 3). Another point that we observe is that this minimum disappears at high temperatures (see the curve corresponding to 400 K in Figure 8).

To see the relative contribution of the gas phase to the total adsorption we investigate $f(N,N)/f(N_G,N_G)$, and this is shown in Figure 9 as a function of pressure. A value of unity of this ratio indicates the equal fluctuations of the adsorbed and gas phases. From this figure we see the importance of the gas phase when
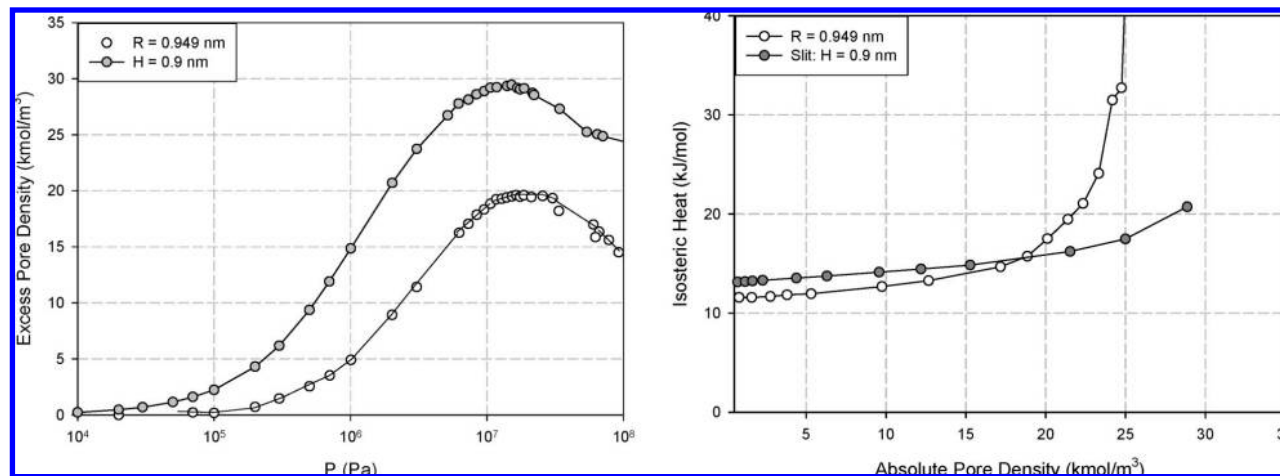
Figure 17. Adsorption excess isotherm and isosteric heat of argon adsorption in SWCNT at 298 K with a radius of 0.949 nm. The corresponding variables for 0.9 nm slit pores are also shown in the same figures for comparison.

the pressure has reached about 10 MPa. Comparing the magnitude of this ratio under supercritical conditions with that for subcritical conditions in Figure 4, we can see the dominance of the adsorbed phase for subcritical conditions.

In Figure 10 we plot the isosteric heat calculated using the correct equation (eq 18) versus the absolute pore density. The plot of isosteric heat versus the excess density should not be used because it is not a well-behaved variable, as it exhibits a maximum.

The excess heat becomes infinite at this maximum, but this singularity does not pose any problem because the integral energy that is the integral of the heat with respect to density is a well-behaved function.

To show the difference between the heats calculated from the correct equation (eq 18) and from the incorrect equation (eq 1b), we show in Figure 11 the heat calculated from eq 1b. The pattern of the heat curve is different from that seen in Figure 10.

We further support what we have observed thus far for the simple molecule argon with adsorption of nitrogen and carbon dioxide to represent fluids with quadrupoles. We choose them because, like argon, nitrogen and carbon dioxide are commonly used fluids in solid characterization. Figure 12 shows the isotherms of these fluids at 298 K. The ratios $N_G/f(N_G,N_G)$ and $f(N,N)/f(N_G,N_G)$ are shown in Figure 13, and the heats are shown in Figure 14. Once again we conclude that all behaviours seen with argon earlier are repeated here, and we reinforce our correct equation for the heat (eq 18) and the use of accessible volume to calculate the excess amount. We note also that, like argon, the excess amount of nitrogen and carbon dioxide is always positive despite that they both pass through a maximum. This suggests that the pore density is always denser than the bulk density, at least for pressures up to 1000 atm. Further discussion on this will be presented later when we study adsorption in pores of different widths.

Effects of Pore Width. As we discussed earlier, the excess amount is positive if the accessible volume is used. There have been arguments in the literature that the excess amount can be negative because the pore density has reached saturation and therefore any further increase in the bulk density would give a linear asymptote with a slope of void volume and would give negative excess (see eq 30a). We test this assertion for pores of different sizes and choose 0.7, 0.8, and 0.9 nm. Figure 15 shows the adsorption isotherms for these pores, and we observe no sign of the isotherm approaching the negative excess region,

but we do see that after the excess amount has passed the maximum the isotherm has a modest minimum and then slightly increases. This supports our earlier argument that excess amount should not be negative, as it is most likely that molecules inside the pore are better compressed (even with the restriction of the confined space) than those outside because of the solid−fluid potential of carbon pores. One then wonders, would negative excess be observed if the solid−fluid potential were made weaker? To test this hypothesis we reduced the reduced well depth (ε/k_B) of carbon atom on the surface by a factor of 10, from 28 K to 2.8 K and ran the simulation to extremely high pressure. Figure 16 shows the adsorption isotherm of argon at 298 K in 0.8 nm graphitic slit pore for up to 100 000 atm; we do not observe negative excess. This suggests that if one uses the appropriate accessible volume corresponding to the adsorbate under question, then one will not observe negative excess no matter how weak the surface is.

Effects of Pore Shape. We finally perform simulations of adsorption of argon in a carbon nanotube to test the effects of pore shape, and once again what we observed for slit pores. The following figures show the pore density and the isosteric heat for adsorption inside a single SWCNT of radius 0.949 nm. The radius is defined as the radius of a circle passing through the centers of all carbon atoms. Adsorption in a 0.9 nm slit is also shown in the same figure for comparison.

4. Conclusions

In this paper we propose a novel approach to the treatment of adsorption data, in which the volume occupied by a reference fluid (conventionally helium) is replaced by an accessible volume occupied by the adsorptive: This volume is readily calculated by Monte Carlo integration using a molecule of the adsorptive to probe those regions of the adsorbent where the adsorption potential is not positive. We have shown that a number of logical consequences follow from this choice: first, the adsorption isotherm can never become negative, which is a reasonable expectation since the adsorbate, under the influence of the adsorption field, will always be in a state of greater compression than the external phase. Second, the heat of adsorption is independent of the size of the simulation box for both sub- and supercritical adsorption and again does not become negative or infinite under extreme conditions.

These general observations are supported by a number of simulations using argon, nitrogen, and carbon dioxide in slit

pores and in nanotubes at several temperatures. Our simulations demonstrate that a new framework for collecting and handling adsorption data is highly desirable; especially where supercritical systems are being investigated. In future work we shall address the issue of how experimental data can be processed in order to achieve this goal.

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