Determination of Isosteric Heat of Adsorption by Quenched Solid Density Functional Theory

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Supporting Information

ABSTRACT: The heat of adsorption is one of the most important parameters characterizing energetic heterogeneity of the adsorbent surface. Heats of adsorption are either determined directly by calorimetry or calculated from adsorption isotherms measured at different temperatures using the thermodynamic Clausius–Clapeyron equation. Here, we present a method for calculating the isosteric heat of adsorption that requires as input only a single adsorption isotherm measured at one temperature. The proposed method is implemented with either nonlocal (NLDFT) or quenched solid (QSDFT) density functional theory models of adsorption that are currently widely used for calculating pore size distributions in various micro- and mesoporous solids. The pore size distribution determined from the same experimental isotherm is used for predicting the isosteric heat. The QSDFT method has advantages of taking into account two factors contributing to the structural heterogeneity of adsorbents: the molecular level roughness of the surface and the pore size distribution. The method is illustrated with examples of low temperature nitrogen and argon adsorption on selected samples of carbons of different degree of graphitization and MCM-41 mesoporous silicas of different pore size. The isosteric heat predictions from the NLDFT and QSDFT methods are compared against relevant experiments and the results of Monte Carlo (MC) simulations, with good agreement found in the cases where the surface model adequately reflects the pore surface roughness. Analyses with the QSDFT method show that the isosteric heat of adsorption significantly depends on the molecular level roughness of the adsorbent surface, which is ignored in NLDFT and MC models. The proposed QSDFT method with further verification can be used for calculating the isosteric heat as an additional parameter characterizing the adsorbent surface in parallel with routine calculations of the pore size distribution from a single adsorption isotherm.

1. INTRODUCTION

The isosteric heat of adsorption is the unique characteristic of the adsorbate–adsorbent interaction that is used to characterize the surface properties of adsorbents, catalysts, and other materials.1 In particular, the isosteric heat of adsorption is especially suited for distinguishing between homogeneous and heterogeneous surfaces.2 This ability makes the isosteric heat a useful parameter for characterizing the degree of graphitization in mesoporous materials.9,10 The isosteric heat has also been used to characterize the heat of condensation in mesoporous materials.9,10 The isosteric heat is determined from experiments either directly by calorimetric measurements or indirectly by the thermodynamic isosteric method.3 The latter method is based on the application of the Clausius–Clapeyron equation to the adsorption isotherms measured at different temperatures. The isosteric heat can also be directly computed from the adsorbate–adsorbent interaction potentials for given geometrical models of solid surfaces by grand canonical Monte Carlo (GCMC) simulations.11 The GCMC method utilizes the general statistical mechanical relationship between the differential entropy and enthalpy and the fluctuations of the adsorbate density and energy in the course of simulation. The GCMC method has been employed widely to calculate the isosteric heat of adsorption of simple fluids on carbons,6,12−17 zeolites,18−22 and mesoporous materials.23−26 Most of reported GCMC simulations are based on the idealized models of homogeneous surfaces and pore walls neglecting geometrical and energetic heterogeneity. This is why the simulation results agreed with the experimental only in the case of crystalline surfaces like graphite and highly graphitized carbons.6,24 The importance of direct accounting of surface heterogeneity in GCMC simulations was recently shown by Kowalczyk et al.17 drawing on the example of hybrid reverse MC structural models of highly graphitized and disordered carbon surfaces.
The classical density functional theory (DFT) offers alternative methods for calculating the adsorption heat based on adsorbate–adsorbent interaction potentials and geometrical models of solid surfaces. Balbuena and Gubbins employed the nonlocal density functional theory (NL-DFT) to calculate the isotherms of LJ fluid on nonporous surfaces and in slit pores ranging from 2.5σ_{ff} to 10σ_{ff} at different temperatures and predicted the isosteric heat in individual pores using the Clausius–Clapeyron equation, mimicking the experimental isosteric method. Later, Pan et al. extended this method to calculating isosteric heats of light hydrocarbons and their binary mixtures on carbon. In those works, the isotherms were generated at different temperatures using the pore size distribution (PSD) and determine the isosteric heat by the Clausius–Clapeyron equation, mimicking the experimental isosteric method. Also, Pan et al. extended this method to calculating the isosteric heats of light hydrocarbons and their binary mixtures on carbon. In those works, the isotherms were generated at different temperatures using the pore size distribution (PSD) function. The latter was determined independently by the NL-DFT method from the nitrogen isotherm. An alternative approach was presented by Ustinov et al., who directly calculated the isosteric heat from the free energy functional. This method was applied to the case of N\textsubscript{2} adsorption on graphite and compared to experimental calorimetric results with general agreement. The authors also attempted to account for the surface heterogeneity implicitly by using a specially constructed fluid–solid potential. Recently, Liu et al. calculated the entropy of hydrogen adsorption from optimized free energy functionals on a series of metal–organic frameworks using the modified fundamental measure DFT. Grinev et al. applied the same method to study the temperature dependence of the isosteric heat of methane on graphite.

Of special interest is the work of Olivier, who suggested to use NL-DFT to estimate the isosteric heat of argon adsorption on MCM-41 silica accounting for energetic heterogeneity of the surface. The author employed the NL-DFT model to calculate the surface energy distribution from the experimental isotherm prior to the pressure of capillary condensation, which was then averaged to obtain the integral heat of adsorption on the heterogeneous surface composed of “patches” of given energy. A similar approach, yet by using a lattice DFT model, was used by Kowalczyk et al. to characterize the energetically heterogeneous surface of carbon by nitrogen adsorption. The DFT methods reviewed above had the same deficiency as the GCMC methods—they do not account explicitly for the molecular level roughness of the adsorbent surface, and thus, their applicability is limited to crystalline materials like highly graphitized carbons and MOFs. Noteworthy, calculations of the adsorption heat are much more sensitive to the features of the surface than calculations of the adsorption isotherm. For example, while the NL-DFT method is known to reproduce well capillary condensation isotherms of mesoporous silica with amorphous pore walls, it fails to mimic even qualitatively the isosteric heat variation in the course of polycrystalline (multilayer) adsorption. In this work, we suggest a method for determining the isosteric heat of adsorption based on the quenched solid density functional theory (QSDFT), which accounts directly for the molecular level roughness of the adsorbent surface. The QSDFT model is currently widely used for calculating the PSD from experimental adsorption isotherms on micro- and mesoporous materials, including carbons and silicas. The idea of the proposed method is straightforward: using as input the adsorption isotherm measured at one temperature, T\textsubscript{1}, we first determine the PSD for the sample under consideration and then predict the adsorption isotherm at another temperature T\textsubscript{2} based upon this PSD and determine the isosteric heat by the Clausius–Clapeyron equation. As a complement, we employ NL-DFT and Monte Carlo simulations to calculate the isosteric heat of simple fluids on homogeneous and heterogeneous surfaces and discuss the general applicability of each of these methods to nonporous surfaces and micro-mesoporous materials. Throughout, the importance of surface heterogeneity to determination of the isosteric heat is illustrated. We show that the proposed QSDFT method is capable of predicting the isosteric heat in good agreement with experiments for characteristic samples of carbons and MCM-41 silicas.

The remainder of the paper is organized in the following fashion: the general method for determining the isosteric heat of adsorption from adsorption isotherms (the isosteric method) and from MC simulations is provided in section 2. Section 3 contains examples of isosteric heat calculations on nonporous carbon surfaces and mesoporous MCM-41 silica materials using the QSDFT, NL-DFT, and GCMC methods described in section 2. The adsorbates studied include nitrogen at 77 K and argon at 77 and 87 K. Throughout, comparisons are made between the DFT and GCMC calculations and experimental data from the literature. Conclusions are drawn in section 4.

2. COMPUTATIONAL METHODS AND SIMULATION DETAILS

2.1. Methods for Isosteric Heat Calculations. The isosteric heat of adsorption represents the differential heat of adsorption at given adsorbate pressure and temperature, q\textsubscript{st} = TA(N, P, T), where Δs = s(g) − s(a) is the difference in molar entropies of the adsorbate in the gas (g) and adsorbed (a) states. It obeys the Clapeyron equation

\[ q_{st} = T \Delta s = T \Delta v (dP/dT)_N \]  

(1)

where Δv = v(g) − v(a) is the difference in molar volumes of the adsorbate in the gas and adsorbed states, and the derivative dP/dT is taken at a given adsorbate amount N. Equation 1 may be simplified by assuming that the molar volume of the bulk phase greatly exceeds that of the adsorbed phase v(g) >> v(a). At these conditions, v(a) may be neglected, and an appropriate equation of state may be substituted for v(g). If it is further assumed that the fluid obeys the ideal gas law (v(g) = RT/P), then eq 1 reduces to

\[ q_{st} = R (d(\ln P)/d(1/T))_N \]  

(2)

Equation 2 is referred to as the Clausius–Clapeyron (C–C) equation, which is the foundation of the isosteric method since the derivative d(ln P)/d(1/T) represents the slope of the isotherm—the line of constant adsorption N in ln P–1/T coordinates. In practice, it is enough to measure just two isotherms at close temperatures, T\textsubscript{1} and T\textsubscript{2}, and to calculate the isosteric heat from the finite difference:

\[ q_{st} = R(T_T/T_2 - T_1)(\ln(P_2) - \ln(P_1))_N \]  

(3)

Here, P\textsubscript{1} and P\textsubscript{2} represent the pressures at which both isotherms correspond to the same adsorbed amount (adsorbate loading) N. Equations 2 and 3 are commonly applied to experimental adsorption isotherms to determine the isosteric heat as a function of the adsorption N or pressure P. They are also used for calculating the isosteric heat from the theoretical adsorption isotherms, in particular determined by the DFT models. From the statistical-mechanical perspective, the isosteric heat is related to the fluctuations of the configurational (potential)
energy $U$ and the adsorbed amount $N$ at the conditions of the grand canonical ensemble in the following manner:\textsuperscript{11}

$$q_{\text{ad}} = RT - [(\langle UN \rangle - (U)\langle N \rangle)] / [(N^2) - \langle N \rangle^2] \quad (4)$$

In eq 4, brackets denote ensemble average quantities that can be computed in the course of GCMC simulation. Equation 4 implies the ideal gas approximation, and it is equivalent to the thermodynamic $C - C$ equation (eq 2). That is, provided the identical surface model is employed, both the methods should produce the same results.

When applying eq 4 to a GCMC simulation on open surfaces, one must take care to sample the appropriate adsorption quantities. In the context of most subcritical adsorption simulations, for example the cases of $N_2$ and $Ar$ adsorption at 77 or 87 K considered below, the adsorbed amount (i.e., adsorption excess) and total number of molecules are nearly equivalent. In this case, application of eq 4 is straightforward accounting of the average number of molecules in adsorption simulations, for example the cases of $N_2$ and $Ar$ surfaces, one must take care to sample the appropriate adsorption quantities.

In eq 4, $q_{\text{ad}}$ is the adsorption excess and total number of molecules are nearly equivalent. In this case, application of eq 4 is straightforward accounting of the average number of molecules and total energy in the simulation cell. However, in cases where the unadsorbed molecules may contribute significantly to the total configurational energy, i.e., near-critical or supercritical adsorption (such as the adsorption of $CO_2$, $CH_4$, or other organic molecules), the adsorbed amount $N$ must reflect the excess and not total quantities. For such cases, alternative Monte Carlo methods\textsuperscript{36,39} exist which do not assume the ideality of the adsorbed species. In particular, the method of Do, Do, and Nicholson\textsuperscript{38} calculates the adsorption excess by running two parallel simulations: one standard GCMC adsorption simulation with an adsorbate and adsorbent and a bulk phase simulation with a volume equivalent to that of the accessible volume in the adsorption simulation. This method reduces to eq 4 in the limit of an ideal gas. In this work, we use the isosteric method to compute the adsorption heat from the DFT models and the fluctuation method (eq 4) to compute the adsorption heat from the GCMC simulations. Consistency of the theoretical results obtained by these methods and experimental data is required for validation of the selected molecular model for modeling given adsorbate–adsorbent system.

2.2. Computational Methodology: NLDFT, QSDFT, and GCMC.\thinspace 2.2.1. Density Functional Theory. NLDFT and QSDFT calculations aim to find the equilibrium density distribution $\rho_f(r)$ of adsorbed fluid within the pore volume by minimizing the grand potential $\Omega$ of the system. In NLDFT, the grand potential $\Omega_f$ of adsorbed fluid is a functional of the fluid density $\rho_f(r)$,\textsuperscript{40,41} and the solid–fluid interaction is represented by an external potential $U_{\text{ext}}$:

$$\Omega_f[\rho_f(r)] = E_f[\rho_f(r)] - \int dr \rho_f(r)[\mu_f - U_{\text{ext}}(r)] \quad (5)$$

In eq 5, $U_{\text{ext}}$ represents the adsorption potential exerted on the guest molecules by the solid wall of given curvature, e.g., plane, cylindrical, or spherical, assuming that the pore wall surface is ideally smooth.\textsuperscript{31} The neglect of surface roughness that is inherent to most of nanoporous noncrystalline materials leads to pronounced layering of adsorbed phase, the artificial nature of which was widely discussed in the literature.\textsuperscript{1}

Predictions of NLDFT are well-suited for adsorption on crystalline surfaces such as graphite and mica, where the assumption of molecularly smooth surfaces is reasonable. However, the NLDFT method is less applicable to adsorption on microporous and mesoporous materials like carbons and silicas, experimental isotherms on which do not display layering steps.\textsuperscript{10,42,43} Despite the presence of artificial layering, it should be noted that NLDFT was shown to predict quantitatively the capillary condensation transition on mesoporous materials beyond the multilayer adsorption region.

QSDFT was designed to explicitly account for the molecular level roughness, which results in a monotonic variation of the solid density at the pore wall surface. The nonuniformity of the solid phase density $\rho_s(r)$ reflects the existence of a so-called corona—the solid–void interfacial region, which may extend up to several molecular diameters. In real materials, the pore wall corona contains micropores which have higher adsorption energy that the smooth solid surface. The extent of surface roughness is characterized in QSDFT by one geometrical parameter—the roughness parameter $\delta$, which represents the half-width of the corona. The limit of $\delta \rightarrow 0$ corresponds to ideal smooth surface. In contrast with NLDFT, the grand thermodynamic potential in QSDFT is a functional of both solid $\rho_s(r)$ and fluid $\rho_f(r)$ densities, $\Omega_f[\rho_f(r), \rho_s(r)]$, and the solid–fluid interactions are accounted for by summation of pair interaction potential $u_{sf}(r - r')$ weighted with the given solid and fluid densities, $\int dr' \rho_f(r') u_{sf}(r - r')$; here $r$ and $r'$ are the positions of fluid and solid particles. The equilibrium fluid density $\rho_f(r)$ is found by minimization of the grand thermodynamic potential with respect to the fluid density keeping the solid density fixed or “quenched”

$$\left(\delta \Omega_f[\rho_f(r), \rho_s(r)] / \delta \rho_f(r)\right)_{\rho_s(r)} = 0 \quad (6)$$

This functional derivative leads to the Euler–Lagrange equation for the fluid density $\rho_f(r)$ at given chemical potential $\mu_f$ and temperature $T$

$$\rho_f(r, \mu_f, T) = \Lambda^{-3} \exp[e^{(1)}(r, [\rho_f(r)], \mu_f)] - \beta \int dr' \rho_f(r') u_{sf}(r - r') \times \rho_f(r') u_{sf}(r - r') \rho_f(r - r')$$

Details of the treatment of the direct correlation function $e^{(1)}$ for NLDFT and QSDFT can be found in prior publications.\textsuperscript{36,37}

Integration of the fluid density provides the mean density of adsorbed fluid that is proportional to the adsorption isotherm

$$N_{\text{DFT}}(p/p_0, T) = a \int \rho_f(r, \mu_f, T) dr \quad (8)$$

Here, $a$ is a dimensional factor converting the isotherm into proper reduced units, like adsorption per unit area, or per unit pore volume, or per gram of adsorbent. $D$ denotes the size of the model pore–pore width in the case of slit pores or diameter in the case of cylindrical or spherical pores. Note that eq 8 presents the isotherm as a function of the reduced pressure, $p/p_0$ and thus implies a proper conversion from the chemical potential $\mu_f$ in the case of ideal gas $\mu_f = RT \ln(p/p_0)$. The adsorption isotherm $N_{\text{DFT}}(p/p_0, T)$ on a nonporous surface corresponds to the limit of large $D$, and it serves as a reference isotherm for checking the consistency of the selected fluid–solid potential.

Determination of Pore Size Distribution by the DFT Method. A set of theoretical isotherms $N_{\text{DFT}}(p/p_0, T; D)$ calculated for a range of pore sizes $D = D_{\text{min}} - D_{\text{max}}$ is referred to as a kernel. Kernels of theoretical isotherms are used to determine the PSD function, $f(D)$, from the experimental isotherm, $N_{\text{exp}}(p/p_0, T)$, by solution of the generalized adsorption equation.
Equation 9 presents the experimental isotherm as the convolution of the DFT kernel and the PSD function. The sought PSD function, \( f(D) \), is determined by deconvolution of integral eq 9 using one of the computational schemes based on Tikhonov’s regularization with certain constraints, in particular, by the quick non-negative least-squares method. The method presented below to calculate the isosteric heat from theoretical DFT isotherms is dependent upon the pore morphology of the adsorbent as well as the level of surface heterogeneity. In general, we distinguish between nonporous and micro-mesoporous materials as well as homo- and heterogeneous surfaces, examples of which include carbons of different degree of graphitization and MCM-41 silica. Noteworthy, in calculations presented below, the isosteric heat is determined for constant absolute adsorption (the quantity calculated in DFT and GCMC simulations), as opposed to constant adsorption excess (the quantity measured in experiments). However, the distinction between absolute and excess adsorption quantities is negligible as a consequence of the subcritical nature of Ar and N\(_2\) adsorption, and as such, it may be neglected with minimal effect.

**Nonporous Materials.** In case of a nonporous material, one may calculate the isosteric heat utilizing two or more isotherms calculated by the DFT model for a nonporous surface \( N_1(p/p_0, T_1), N_2(p/p_0, T_2), \ldots \) before calculating isosteric heat of adsorption using eq 2 or 3. A schematic of this process is provided in the Supporting Information, section B.
section for the isosteric heat of N₂ and Ar adsorption on several carbons of varying degrees of graphitization.

**Micro-Mesoporous Materials.** In the case of micro-mesoporous materials, the isosteric heat depends on the PSD. To account for this effect, we suggest the following method, which requires a single experimental isotherm, \( N_a(P_a,T_1) \) measured at temperature \( T_1 \). First, the experimental isotherm is used to predict the PSD \( f(D) \) by deconvolution of the integral adsorption \( q(D) \) with the DFT kernel \( N_{DFT}(P,T,D) \) at given temperature. Second, we predict the experimental isotherm at another temperature \( T_2 \) using the HRMC method\(^{17,52} \) based upon radial density morphology of disordered carbon surfaces were derived from pores. Atomistic structural models of graphitized and morphologically disordered carbon surfaces of varying degrees of graphitization. Some of the earliest experiments (WAXS) on Madagascar graphite.\(^{17} \) In the case of micro-mesoporous materials, the isosteric heat depends on the PSD. As shown in the Results and Discussion section, these simulations, nitrogen molecules and Ar atoms were modeled by single-site \((12,6)\) Lennard-Jones particles to correspond to the single-site models used in the DFT calculations. The \( N_2-N_2 \) and \( N_2-C \)-carbon and Ar−Ar and Ar−silica parameters were taken from refs\(^{49–51} \). Details of the simulations and a table with the molecular interaction parameters are given in the Supporting Information, section C.

MC simulations were done with atomistic models of carbon pores. Atomistic structural models of graphitized and morphologically disordered carbon surfaces were derived using the HRMC method\(^{17,52} \) based upon radial density distribution determined from wide-angle X-ray scattering experiments (WAXS) on Madagascar graphite.\(^{17} \) In the case of the morphologically disordered surface, the intrawall ultramicropores were also generated using temperature-quenched Monte Carlo simulations. Notably, in these GCMC models it is implicitly assumed that intrawall ultramicropores are accessible to nitrogen molecules.\(^{17} \) In contrast, a structureless cylindrical layer of oxygen atoms served as a model for the silica mesopores. A structureless model for mesoporous silica was chosen in this case to contrast with the QSDFT method, which explicitly accounts for surface roughness. As shown in the Results and Discussion section, these contrasting methods illustrate the fundamental effect of surface heterogeneity on the behavior of the isosteric heat in porous systems. Further details of the carbon and silica structural models are given in the Supporting Information, section C.

### 3. RESULTS AND DISCUSSION

**Highly Graphitized Carbon.** It is known that the isosteric heat of N₂ and Ar on graphite is highly sensitive to the degree (temperature and extent) of graphitization. Some of the earliest experimental studies of isosteric heat utilized Cabot Sterling graphite (2700 °C) due to the extreme homogeneity of its surface.\(^{2,4,5} \) Figures 1A and 1C present the adsorption isotherms of N₂ at 77.4 K and Ar adsorption at 87.3 K on Sterling carbon from the works of Terzyk et al.\(^{53} \) and Kiselev et al.\(^{5} \) Both N₂ and Ar adsorption on Sterling display similar features. Monolayer formation on the surface occurs in the relative pressure range between \( 10^{-4} < p/p_0 < 10^{-3} \) for N₂ and \( 10^{-3} < p/p_0 < 10^{-2} \) for Ar and is accompanied by a sharp uptake of adsorbate followed immediately by a level plateau region over 1–2 decades of pressure. Subsequent layering transitions are denoted by additional plateaus, which occur at pressures incrementally closer to the saturation pressure.

The NLDFT isotherms plotted in Figure 1A,C were calculated on large “slit” pores to avoid capillary condensation and approximate adsorption on a nonporous graphic surface. The GCMC adsorption isotherms were performed on a model graphic surface reconstructed by the hybrid reverse Monte Carlo (HRMC) method to fit the radial distribution function (RDF) of Madagascar graphite; see details in the recent paper.\(^{17} \) Figure 1 illustrates that NLDFT and GCMC both reproduce the adsorption behavior of N₂ (Figure 1A) and Ar (Figure 1C), which indicates the high level of homogeneity of the experimental surfaces. Note that NLDFT, which implies an ideal plane surface and completely ignores the density fluctuations, produces artificial steps, corresponding to the second and third layer formation that are not observed in experiments and leveled in GCMC simulations.

In Figure 1B,D, the isosteric heat calculated by NLDFT via the C–C equation (eq 3) is compared with the results of GCMC calculations based on the fluctuation eq 4 and experimental N₂ measurements from Beebe,\(^{7} \) Joyner and Emmett,\(^{5} \) and Rouquerol et al.\(^{5} \) and Ar measurements from Avgul and Kiselev.\(^{7} \) In addition, we present the literature theoretical results of the isosteric heat calculations obtained for N₂ (Figure 1B) by Ustinov et al.\(^{30} \) from the NLDFT free energy functional and for Ar (Figure 1D) by Do et al.\(^{15} \) from GCMC simulations.

In both cases, the calculated and experimental data are in almost quantitative agreement, despite significant differences in samples, instrumentation, and experimental methods. At low adsorbate loading (\(<10 \mu mol/m^2\)), the isosteric heat increases with the amount adsorbed. This behavior corresponds to the monolayer formation. At approximately monolayer coverage, the isosteric heat experiences a maximum. For N₂, this maximum is sometimes\(^{5,7} \) accompanied by a very pronounced peak which is speculated to arise from a two-dimensional phase transition which occurs on the graphite surface.\(^{5,7,15} \) This transition is characterized by the spacial rearrangement of N₂ molecules on the surface from a disordered fluid-like state to a “localized” or solid-like (crystalline) state.\(^{5} \) It has been proposed that the predominance of this peak can act as an indicator of the level of graphitization,\(^{15} \) with less graphitized samples exhibiting smaller peaks. Notably, neither NLDFT nor GCMC simulations replicate this peak, which may be a consequence of representing N₂ by a simple Lennard-Jones fluid and the mean-field approximation of NLDFT. However, in the case of Ar adsorption this peak is significantly reduced,\(^{5} \) and NLDFT and GCMC reproduce the isosteric heat well in this range. After their respective maxima, additional layering effects are seen in both N₂ and Ar adsorption, as evidenced by small undulations in the isosteric heat occurring at roughly 20 and 30 \( \mu mol/m^2\). NLDFT and GCMC both produce similar undulations, though not necessarily at the same adsorbate loadings.\(^{15} \)

**Effect of the Surface Roughness.** To illustrate the importance of accounting for the surface roughness, we compare in Figure 2 the isosteric heat of N₂ at 77 K on carbon surfaces calculated with NLDFT (smooth surface model) and QSDFT (molecularly rough surface model) at different values of the roughness parameter \( \delta = 0.5, \ldots , 3.0 \, \text{Å} \).
the limit of zero coverage, \(N/N_{\text{mono}} \ll 1\), the isosteric heat \(q_{\text{st}}\) increases with increasing surface roughness. This behavior is expected as any surface heterogeneities are energetically favorable and promote adsorption. As such, increased roughness should correspond to higher heats of adsorption. For any degree of surface roughness, the QSDFT isosteric heats monotonically decrease during the monolayer formation (\(N < 10 \mu\text{mol/m}^2\) in Figure 2) that is explained by the gradual filling of the micropores and surface indentations within the pore wall corona with fluid. This behavior is in striking contrast to the nonmonotonic behavior of the isosteric heat on smooth surfaces (Figure 1) due to the abrupt layering transition characteristic to NLDFT (Figure 2, black line). Another characteristic feature of both the theoretical and experimental isotherms due to the surface roughness is the dampening of further layering transitions beyond \(p/p_0 = 0.1\).

**Molecularly Rough Carbon.** In Figure 3A, we demonstrate the application of QSDFT to mimic \(N_2\) adsorption on a molecularly rough carbon surface of reference carbon designated as LMA-10.\(^{54}\) Here, the roughness parameter \(\delta = 0.5 \text{ Å}\) was adjusted to produce a reasonable fit of the adsorption isotherm, which is representative of a morphologically disordered carbon surface. The surface roughness (even so small as a half molecular diameter) smoothens the layering transition centered on \(p/p_0 = 1 \times 10^{-3}\). This gradual transition contrasts with the sharp uptake that accompanies \(N_2\) adsorption on highly graphitized Sterling at the same pressure (Figure 1). The QSDFT and experimental isotherms are compared to the results of GCMC simulations that were performed on a model heterogeneous surface generated by the hybrid reverse MC (HRMC) method.\(^{53}\) The GCMC adsorption isotherm behaves similarly to the experimental and QSDFT isotherms, strongly indicating a particular degree of surface roughness.

The QSDFT and GCMC calculated isosteric heats are presented in Figure 3B. For comparison, we also plot, due to the lack of relevant experimental data for LMA-10 carbon, the calorimetric measurement data\(^{7}\) collected on a Sterling carbon which was graphitized at a lower temperature (1500 °C) than the Cabot Sterling sample (2700 °C) that was used above as example of highly graphitized surface (see Figure 1). The isosteric heat on this carbon (black circles) monotonically decreases and lacks the prominent monolayer peak present for highly graphitized surfaces. Interestingly, the isosteric heat as calculated by GCMC is in reasonable agreement with the experimental except for the initial region of low submonolayer coverage, despite the fact that the HRMC model was tailored to a different carbon.\(^{7,54}\) This similarity may indicate similar levels of surface roughness. The elevated GCMC isosteric heats at low coverage are likely related to high-energy adsorption in the micropores present in the HRMC model of LMA-10. QSDFT is able to capture the transition from surface coverage to multilayer adsorption, and agrees well with the experiments and GCMC at higher surface loading. However, the divergence from GCMC and experiments in submonolayer region, which corresponds to the gradual filling of surface micropores, indicates the limitations of the QSDFT model, which does not entirely capture the specifics of surface micropore morphology.\(^{52}\)

**Mesoporous MCM-41 Silica.** The adsorption and isosteric heat behavior of fluids adsorbing to mesoporous materials differs qualitatively from that of nonporous materials such as the carbons considered above. In particular, the phenomena of capillary condensation and/or evaporation, which are dependent upon the pore geometry\(^{55–57}\) and pore network topology,\(^{58–60}\) have a profound effect on the isosteric heat.\(^{55}\) In certain mesoporous materials such as MCM-41, the effects of capillary condensation and evaporation can be easily distinguished; these processes are often assumed to occur independently in the individual pore domains of the material due to the topological regularity of the pore structure that possesses a crystallographic symmetry.

We start from the example of \(Ar\) adsorption on a sample of MCM-41 silica with a reported mean pore diameter of 4.2 nm.\(^{54}\)
studied by Oliver,\textsuperscript{10} which was the first attempt of application of NLDFT for predicting the isosteric heat from the adsorption isotherm accompanied by accurate measurements. The author measured Ar adsorption at several different temperatures and calculated from the slope of the isotherms the isosteric heat in a wide range of adsorption pressures from $p/p_0 < 1 \times 10^{-2}$ to the saturation pressure ($p/p_0 \sim 1$) (Figure 4). Prior to capillary condensation, the isosteric heat monotonically decreases from its maximum value at zero coverage, achieves a plateau, and then near the completion of pore filling shows a characteristic peak which is typical for mesoporous materials. Olivier suggested to describe the isosteric heat behavior prior to capillary condensation ($p/p_0 > 0.4$) by using the surface energy distribution recovered from the convolution of the kernel of NLDFT isotherms calculated for different fluid–solid interaction parameters for a plane adsorbent surface. Here, we use a different approach. The energetic heterogeneity of the surface is effectively accounted for by the molecular level surface roughness in the QSDFT model.

In Figure 4, we present the adsorption isotherm and isosteric heat for Ar adsorption on MCM-41 at 87 K calculated by the QSDFT model for a cylindrical pore model. First, we performed the calculations for a single silica pore of 4.2 nm. At this pore size, the experimental and theoretical adsorption isotherms are in excellent agreement in the region prior to capillary condensation (Figure 4A), which indicates that the QSDFT cylindrical pore model is an accurate representation of the MCM-41 surface and its interaction with Ar. The QSDFT isotherm exhibits a prominent type H1 hysteresis loop, which overstates minor hysteresis present to a degree in the experimental data. The isosteric heat in Figure 4B (4.2 nm, dotted line) was calculated by the C–C equation from the QSDFT isotherms at 77 and 87 K. In Figure 4B and in the subsequent examples below, the ordinate for the isosteric heat of adsorption is normalized to the adsorbed amount at relative pressure $p/p_0 = 0.8$, termed $N_{0.8}$ as a convention. This convention ensures that the isosteric heat effects (as calculated by the C–C equation using $T_1 = 77$ K and $T_2 = 87$ K) are normalized to a point prior to the freezing transition present in Ar adsorption below its triple point.\textsuperscript{7}

The calculated isosteric heat agrees in general with the experimental and is typical of mesoporous silica: prior to the capillary condensation, in the range $N/N_{0.8} < 0.4$, the isosteric heat is monotonically decreasing, corresponding to the gradual building up of layers of adsorbate on a molecularly rough surface (similar to the nonporous carbon example shown above (Figure 3)). After the onset of capillary condensation ($N/N_{0.8} > 0.4$), the isosteric heat is a constant, which is due to the effect of capillary condensation in the mesopores.\textsuperscript{25} This isosteric heat reflects the latent heat (enthalpy of condensation/evaporation) in the pores, which is slightly larger than the bulk value $\sim 6.53$ kJ/mol. As the capillary condensation is completed, the isosteric heat exhibits a second characteristic peak in contrast with a bell-shaped peak observed experimentally.

Second, we took into account the PSD which is another factor, in addition to the surface roughness, contributing to the pore structure heterogeneity. The PSD was determined by the QSDFT method from the best fit to the experimental desorption isotherm at 87 K (Figure 4A). The isosteric heat was then calculated by the C–C equation from the adsorption and desorption isotherms at 77 and 87 K predicted with this PSD (Figure 4B). Noteworthy, the experimental isotherm is truncated below $p/p_0 = 0.03$ due to the limit of accuracy in the data digitization. As such, the PSD method is restricted to pressures larger than this value. For this reason, the QSDFT isosteric heat using the PSD method is truncated at $N/N_{0.8} = 0.2$.

The use of the PSD improves agreement with the experiment, especially in the region of complete pore filling, where the contributions from the pores of different size smoothen the isosteric heat peak. Both the single-pore and PSD-derived isosteric heats slightly overestimate the isosteric heat in the region of multilayer adsorption prior to capillary condensation ($0.4 < N/N_{0.8} < 0.9$). In the region between the onset of capillary condensation and complete mesopore filling $0.4 < N/N_{0.8} < 0.9$, the isosteric heats calculated from the adsorption and desorption branches are almost identical. However, the single pore model cannot capture the fine details of the isosteric heat peak at the onset of pore emptying along the desorption branch in the same manner as the PSD model.

We next consider three MCM-41 samples, for which the experimental isosteric heats were calculated by the C–C equation from the isotherms measured at 77 and 87 K.\textsuperscript{8} The behavior of fluid in these samples is affected by the pore size and temperature of adsorption. While the Ar isotherm on the sample with widest pores (C-50, 4.5 nm) has a developed H1

Figure 4. (A) Ar adsorption isotherm (87 K) on 4.2 nm MCM-41.\textsuperscript{10} Experiments are compared with the QSDFT isotherm calculated in a single cylindrical pore of width 4.2 nm and the QSDFT isotherm that takes into account the PSD determined from the experimental desorption. (B) Isosteric heat of adsorption of Ar (87 K) on MCM-41 mesoporous silica; comparison of the results of the single pore and PSD QSDFT methods and experiments from Olivier.\textsuperscript{10}
hysteresis at both temperatures 77 and 87 K (Figure 5), in samples with smaller pores (AM-5 and MG-26, 3.8 and 4.2 nm, respectively) the hysteresis is prominent only at 77 K, and it diminishes at 87 K (see full isotherms in Supporting Information, section D).

The theoretical isosteric heats from QSDFT calculations (taking into account the PSD, as described above) are presented in Figures 5 and 6 in comparison to the experimental data.9 We also present the results of GCMC calculations for smooth-walled cylindrical silica pores of similar pore size to demonstrate the necessity of accounting for the surface roughness in the region of adsorbed film formation.

Analysis of the larger-pore sample C-50 was carried out on both the adsorption and desorption branches of the isotherm. Notably, the predicted isotherms at 77 K reasonable well describe the experimental hysteretic isotherms, thus allowing for calculations and comparisons of the isosteric heats for both adsorption and desorption isotherms. Agreement with experimental data for the isosteric heat is observed in the whole range of loadings, taking into account the inherent uncertainties of the application of the numerical differentiation according to the C–C equation to the experimental data at low loadings. Noteworthy, at the onset of the complete filling region $N/N_0 > 0.9$, the QSDFT model is able to capture the experimental data exhibiting the characteristic peak. For comparison, we performed the GCMC simulation for a single cylindrical smooth-wall pore of 5.02 nm internal diameter (Figure 5B, triangles). The apparent deviations show the necessity of taking

Figure 5. (A) Ar adsorption and desorption isotherms (Ravikovitch et al.9) on MCM-41 sample C-50 measured at 77 and 87 K alongside the QSDFT fitted (87 K) and predicted (77 K) isotherms for both adsorption and desorption branches. (B) Experimental and theoretical isosteric heats of Ar adsorption on C-50 for adsorption and desorption branches. The GCMC calculation performed for a single cylindrical smooth-wall pore of 5 nm show the necessity of taking into account the surface roughness in the adsorbed film region prior to capillary condensation.

Figure 6. Adsorption and isosteric heat analysis for the desorption of Ar at 77.4 and 87.3 K on the MCM-41 samples AM-5 (A, B) and MG-26 (C, D). Experimental data taken from Ravikovitch et al.9 Characteristic GCMC calculations shown for sample MG-26 (D).
into account the surface roughness in the adsorbed film region prior to capillary condensation. In the capillary condensation region, GCMC agrees well with the experiments and QSDFT, yet significantly overestimates the isosteric heat peak in the complete filling region.

In Figure 6, we present similarly calculated desorption isotherms and respective isosteric heats for smaller pore samples AM-5 and MG-26. In general, the behavior of the isosteric heat calculated with the QSDFT and GCMC methods and agreement with experimental data are similar to the sample C-50 described above. These examples confirm the capabilities of the QSDFT model, which takes into account both the surface roughness and PSD structural heterogeneities. The examples shown above confirm the capabilities of the QSDFT model, which takes into account both the surface roughness and PSD structural heterogeneities.

4. CONCLUSIONS
The main result of this work is the proposed QSDFT method for calculating the isosteric heat from the adsorption isotherm measured at one temperature. The QSDFT method takes into account two factors contributing to the structural heterogeneity of adsorbents: the molecular level roughness of the surface and the PSD. The latter is calculated from the same adsorption isotherm with the same QSDFT model used for generation of the kernel of reference adsorption isotherms in pores of different sizes. The QSDFT kernels have been developed for various adsorbate—adsorbent systems, such as N₂, Ar, and CO₂, on micro- and mesoporous carbons and silicas with different pore morphology (slit-shaped, cylindrical, and spheroidal pores). These kernels are currently widely used for calculating PSDs in various micro- and mesoporous solids.

The proposed QSDFT method is illustrated with examples of low temperature nitrogen and argon adsorption on selected samples of carbons of different degree of graphitization and MCM-41 mesoporous silicas of different pore size. It is shown that the isosteric heat depends on the molecular level roughness of the adsorbent surface and the PSD. The isosteric heat predictions from the QSDFT method are compared against relevant experiments and the results of the nonlocal density functional theory and Monte Carlo simulations, with good agreement found in the cases where the surface model adequately reflects the pore surface roughness. For smooth surfaces of highly graphitized carbon, the NLDFT model, which ignores the surface roughness, is found in good agreement with the experimental data and GCMC simulations. However, even a minor degree of surface roughness, corresponding to the QSDFT roughness parameter as small as 0.5 Å, changes the qualitative behavior of the dependence of the isosteric heat on the loading, in agreement with experimental observation for carbons of lower degree of graphitization. QSDFT calculations performed for surfaces of increasing roughness parameter show a monotonic increase of the isosteric heat at zero coverage, which is capable of mimicking the effect of the presence of surface micropores, despite the lack of explicit high-energy adsorption potential sites. This behavior confirms the utility of QSDFT for molecularly rough surfaces.

The capabilities of the QSDFT method were demonstrated on Ar adsorption on a series of MCM-41 materials with different pore sizes. It was shown that the use of the pore size distribution calculated from the desorption branch of the experimental isotherm allowed for quantitative predictions of the isosteric heat in the whole range of loadings from the monolayer to multilayer and from capillary condensation to complete pore filling, including the characteristic peak of adsorption heat observed upon the completion of pore filling in the process of adsorption and prior to the onset of capillary evaporation in the process of desorption.

The proposed QSDFT method can be used for calculating the isosteric heat as an additional parameter characterizing the adsorbent surface in parallel with routine calculations of the pore size distribution from an adsorption isotherm measured at one temperature. At the same time, it should be noted that while the proposed method has shown to be applicable to nonporous (carbon) and mesoporous (MCM-41) materials, further verification is needed to determine the utility of this method for broader classes of adsorbents.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b04119.

(A) QSDFT kernels for Ar adsorption on silica; (B) details of isosteric heat calculation algorithm using one isotherm; (C) DFT and GCMC model parameters; (D) PSD and hysteresis loops for MCM-41 samples (PDF)

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