

Relationship between pore-size distribution and flexibility of adsorbent materials: statistical mechanics and future material characterization techniques

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Abstract Measurement of the pore-size distribution (PSD) via gas adsorption and the so-called “kernel method” is a widely used characterization technique for rigid adsorbents. Yet, standard techniques and analytical equipment are not appropriate to characterize the emerging class of flexible adsorbents that deform in response to the stress imparted by an adsorbate gas, as the PSD is a characteristic of the material that varies with the gas pressure and any other external stresses. Here, we derive the PSD for a flexible adsorbent using statistical mechanics in the osmotic ensemble to draw analogy to the kernel method for rigid materials. The resultant PSD is a function of the ensemble constraints including all imposed stresses and, most importantly, the deformation free energy of the adsorbent material. Consequently, a pressure-dependent PSD is a descriptor of the deformation characteristics of an adsorbent and may be the basis of future material characterization techniques. We discuss how, given a technique for resolving pressure-dependent PSDs, the present statistical mechanical theory could enable a new generation of analytical tools that measure and characterize certain intrinsic material properties of flexible adsorbents via otherwise simple adsorption experiments.

Keywords Molecular simulation · Adsorbent material · Pore-size distribution · Adsorption kernel · Metal organic framework · Flexible material

1 Introduction

Metal-organic frameworks (MOF) have recently emerged as a new class of porous materials with potentially widespread use in gas adsorption applications (Li et al. 1999; Ferey 2008; Furukawa et al. 2010; Zaworotko 2008). MOFs are modular, crystalline materials composed of metal ions and organic linkers that have the particularly advantageous properties of high internal surface area, large pore volume per unit mass, and frequently high-affinity for gas adsorbates (Wilmer et al. 2012; Farha et al. 2012). A subset of MOFs are highly flexible and deform in response to a stress (Neimark et al. 2010; Ghysels et al. 2013; Sarkisov et al. 2014), which can be imposed by exposure to an adsorbate gas (Neimark et al. 2011). The prototypical example of MOF flexibility is the group of MIL-53 materials with coaxial pores arranged in a wine rack motif that undergoes various transitions between “large pore” and “narrow pore” configurations (Serre et al. 2002; Millange et al. 2002; Liu et al. 2008). More recent work has identified a flexible MOF (DUT-49) that exhibits spontaneous desorption during a pressure increase owing to a structural transformation of the MOF from high to low porosity, i.e., “negative gas adsorption” (Krause et al. 2016; Evans et al. 2016). Flexible MOFs have been proposed as porous media for advanced separation technologies owing to their essential adsorption capability combined with size-based sieving properties that depend on the thermodynamic conditions of the separation (Li et al. 2012). The development of flexible materials for such separations is largely empirical at

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present, based mostly on the measurement of adsorption isotherms. While useful, adsorption isotherms alone do not provide sufficient insight into the physics of why a material deforms as observed. More specific and tailored design of flexible adsorbents requires analytical tools that do not exist at present (Neimark et al. 2010, 2011; Thommes 2015). Furthermore, the thermodynamics of adsorption in flexible adsorbents are only beginning to be described in fundamental terms (Coudert et al. 2011; Bousquet et al. 2012; Shen and Siderius 2014; Balzer et al. 2015; Coudert et al. 2015; Kowalczyk et al. 2016). Consequently, there is currently wide opportunity to study the thermodynamics of flexible adsorbents from a fundamental point of view with the secondary aim of developing new analytical tools for characterizing these materials. Interest in flexible materials extends beyond MOFs, as elastic deformation is observed in other adsorbents including carbonaceous sorbents, porous glasses, porous coordination polymers, and zeolites (Thommes et al. 2015). Additionally, all real materials must exhibit some degree of flexibility (however small), as a perfectly rigid material would have an infinite elastic modulus. Hence, insights into material flexibility for compliant adsorbent materials may also improve our understanding of materials with little adsorbent-induced deformation.

In the work that follows, we discuss the relationship between the pore-size distribution (PSD) of a deformable adsorbent material and the constraints on such a material during an adsorption process. These constraints include certain intrinsic mechanical properties (e.g., stiffness and compressibility) as well as the adsorbate properties and thermodynamic conditions. For this work, we also take an expansive definition of adsorbent deformation that encompasses any structural changes to an adsorbent, which may be generalized into two classes for simplicity. Firstly, we allow for macroscopic deformations accompanied by a change in the adsorbent's volume (like those for the aforementioned MIL-53 and DUT-49). Second, we also allow for structural/conformational deformations in which the adsorbent volume does not change, but in which there is an alteration to the pore structure (e.g., at some surface, an aperture, etc.) that leads to different adsorption behavior. An example of this second type of deformation is "gating" reported elsewhere (Espinal et al. 2012; Coudert et al. 2013). Consequently, our definition of "pore-size" is also expansive in that it may be a pore dimension, a pore conformation, or both; for simplicity we will retain the "pore-size" terminology.

Computation of PSDs for rigid adsorbent materials using commercial instruments coupled with various adsorption "kernels" is now a common technique for characterizing porous adsorbent materials (Rouquerol et al. 1999; Lowell et al. 2004), and the computed PSDs provide significant insight into the effect of adsorbent structure on

observed adsorption behavior. Relationships between an adsorbent's PSD and its structural deformation have been considered previously for carbonaceous materials (Ustinov and Do 2006; Balzer et al. 2016), but the alteration of a PSD due to structural deformation was not explicitly taken into account. Although it should be clear that the PSD of a deformable material depends on both the material's properties and the imposed thermodynamic conditions, we are unaware of any rigorous statistical mechanical description of the PSD of a flexible adsorbent material. We derive that PSD here and then discuss how those statistical mechanical expressions provide the rudiments of new characterization tools tailored to flexible porous materials. Of particular importance is the relationship between the PSD and the intrinsic flexibility of the material, suggesting that physical measurement of the PSD may allow for indirect determination of a more fundamental physical property of the adsorbent.

This work is based on our recent manuscript in which we presented a simulation method for studying adsorption of a single-component gas in flexible adsorbent materials (Shen and Siderius 2014). In short, our method uses flat-histogram Monte Carlo methods (Errington 2003; Shell et al. 2004; Rane et al. 2013) in the osmotic ensemble to compute the molecule number-volume joint probability distribution for a given set of ensemble constraints, e.g., $\Pi(N_1, V; \mu_1, N_2, p, T)$, where N_1 is the number of adsorbate molecules, V is the system volume, and (μ_1, N_2, p, T) are the adsorbate chemical potential, adsorbent quantity, pressure, and temperature constraints. This probability distribution is then used to obtain the adsorption isotherm, identify thermodynamic limits of stability, and determine phase coexistence conditions (Siderius and Shen 2013). Furthermore, our method strictly separates the potential energy of a particular state into contributions from (1) deformation of the material (a property of the bare adsorbent) and (2) interactions between the adsorbent material and adsorbate fluid. Hence, it is particularly suited to in-depth examination of the connections between adsorbent flexibility and other properties exhibited by the adsorption system. As we show here, it is straightforward to derive a PSD using the osmotic ensemble description of adsorption in a flexible material.

This paper is organized as follows. In Sect. 2, we review the essential background for our present work, including the adsorption kernel method for computing PSDs, the semigrand canonical ensemble description of adsorption isotherms for rigid adsorbents, and the osmotic ensemble formulation of adsorption isotherms for flexible adsorbents. Section 3 derives a mathematical description for the PSD of a deformable adsorbent material via a route that allows for analogy to the PSD of a rigid porous material. Following, Sect. 4 discusses the relationship between the PSD and

physical properties of an adsorbent material, along with possible applications of this mathematical relationship. Finally, we briefly conclude the paper in Sect. 5.

2 Background

Before presenting our statistical mechanical description of the PSD of a flexible adsorbent material, we must first provide essential background. We first present the conventional description of heterogeneous porous materials in terms of the PSD and associated adsorption kernels. Following, we present a statistical mechanical description of adsorption in rigid and flexible adsorbents.

2.1 Pore-size distribution and adsorption kernels

The kernel method of computing PSDs dates to work by Seaton et al. in 1989 in which the adsorption isotherm for a material with a nonuniform PSD is approximated by a weighted sum of isotherms for the various pore sizes in which the weights represent the PSD. The set of adsorption isotherms of the individual pore sizes (and, if desired, pore geometry) is termed the “adsorption kernel.” Kernels have been obtained by both statistical mechanical density functional theory (Seaton et al. 1989; Lastoskie et al. 1993) and molecular simulation (Ravikovitch et al. 2000).

In Seaton’s original work, which was adopted by subsequent work, the relationship between the adsorption isotherm for a heterogeneous porous material and the PSD is given by the integral adsorption equation (Seaton et al. 1989):

$$\langle N_1 \rangle(p) = \int_{w_{min}}^{w_{max}} f(w) \rho_1(p, w) dw \quad (1)$$

The terms in Eq. 1 are as follows: $\langle N_1 \rangle(p)$ is the adsorbed number of moles of gas (per unit of adsorbent, see comment below) at pressure p , w represents the pore size and geometry, w_{min} and w_{max} are the minimum and maximum pore sizes, respectively, $\rho_1(p, w)$ is the average molar density of adsorbate gas in a pore of size w at pressure p , and $f(w)$ is the pore size distribution. From Eq. 1, it becomes clear that $f(w)$ is the volume probability distribution of pores of size w (per unit of adsorbent). The set of $\rho_1(p, w)$ comprise the adsorption kernel. While both N_1 and $f(w)$ are given per unit adsorbent, the actual quantity of adsorbent is unimportant as $f(w)$ is normalized to yield a dimensionless probability distribution in actual application. The definition of f is more clear if the integral equation is converted to a discrete summation:

$$N_1(p) = \sum_w F(w) \rho_1(p, w). \quad (2)$$

In this form, the PSD is given by $F(w)$, which is the volume fraction of pore space with size w (per unit adsorbent). Note that we have not clearly defined the size w and, as a consequence, the pore geometry is left ambiguous here. In actual application, the pores are assumed to be slits, cylinders, spheres, or some mix of the three; the pore size is then either a width or a diameter. We leave w undefined in this discussion to retain generality. Lastly, we reiterate here that the PSD in Eq. 2 is assumed to be a static, unchanging property of the sorbent, despite any (presumably, small) adsorption-induced deformation.

2.2 Statistical mechanics—semigrand canonical ensemble

In a rigid adsorbent, the natural ensemble for studying gas adsorption is a semigrand canonical ensemble (Shen and Siderius 2014; Mahynski and Shen 2016). Adsorption is typically presented using a grand canonical ensemble but, strictly speaking, adsorption by a rigid material is better represented by a semigrand canonical ensemble in which the amount of adsorbate (species 1) fluctuates and the amount adsorbent (species 2) is fixed. There is no qualitative difference between the two approaches when the adsorbent is rigid. We choose to begin our derivations using the semigrand version to simplify discussion in the following section. The constraints on this ensemble are the chemical potential of the adsorbate species μ_1 , the number of adsorbent molecules N_2 , the system volume V_w where the subscript w defines the pore size and/or conformation (w and V_w are essentially interchangeable), and the temperature T . We note that the amount and conformation of the adsorbent are defined through N_2 and w , respectively.

Another consideration with more importance when we fully address deformation in the following subsection is the nature of the macroscopic porous adsorbent. Specifically, we must choose whether its constituent pores are (1) assembled into a monolith in which the pores deform collectively, (2) an ensemble of pores that deform independently, or (3) variable-size clusters of pores in which each cluster deforms collectively, but independently of other clusters. For simplicity, our discussion is for a single, isolated pore, but the mathematics are identical to the first option (since the extensive variables N_2 and V_w would scale linearly with the number of pores). Conversion of our statistical mechanics to the second option is also straightforward, via geometric scaling with the number of pores. The third option, while more realistic, adds complexity involving the cluster size probability that detracts from the more fundamental discussion we intend here.

The probability of a particular microstate, i.e., a particular fluid configuration of N_1 adsorbate molecules \mathbf{r}^{N_1} , in the semigrand ensemble is

$$\pi_{sg}(\mathbf{r}^{N_1}; \mu_1, N_2, V_w, T) = c_{sg} \exp(\beta \mu_1 N_1) \frac{\exp[-\beta U(\mathbf{r}^{N_1}, w)]}{\Lambda_1^{3N_1} N_1! \Lambda_2^{3N_2} N_2!}, \tag{3}$$

in which U is the intermolecular potential energy, Λ_1 is the thermal de Broglie wavelength of species 1, $\beta = 1/k_B T$ where k_B is the Boltzmann constant, and c_{sg} is a normalization constant. After assuming pairwise additivity for the potential energy, the N_1 -macrostate probability may be written as

$$\Pi_{sg}(N_1; \mu_1, N_2, V_w, T) = c_{sg} \exp(\beta \mu_1 N_1) \times \exp[-\beta F_2(N_2, V_w, T)] Q_1(N_1, N_2, V_w, T) \tag{4}$$

where F_2 is the Helmholtz free energy of the bare adsorbent material (i.e., devoid of adsorbate) of pore size w and Q_1 is a canonical partition function that includes the contributions to the potential energy involving the fluid. Both terms are introduced in the appendix, which includes a full derivation of the canonical ensemble partition function appropriate to our model system. In this semigrand canonical ensemble where the pore volume is fixed, F_2 is a constant (for a particular T) and could be ignored. We include F_2 here because it allows us to use the same canonical partition function (cf., the appendix) throughout the present work. Finally, the normalization constant c_{sg} is related to the semigrand partition function via

$$\frac{1}{c_{sg}} = \Xi(\mu_1, N_2, V_w, T) = \exp[-\beta F_2(N_2, V_w, T)] \sum_{N_1 \geq 0} \exp(\beta \mu_1 N_1) Q_1(N_1, N_2, V_w, T) \tag{5}$$

$$= \exp[-\beta F_2(N_2, V_w, T)] \Xi_1(\mu_1, N_2, V_w, T),$$

where we have introduced Ξ_1 to represent the portion of the semigrand partition function that does not include the adsorbent material's free energy. Using Eq. 5, the N_1 -macrostate probability distribution is

$$\Pi_{sg}(N_1; \mu_1, N_2, V_w, T) = \frac{\exp(\beta \mu_1 N_1) Q_1(N_1, N_2, V_w, T)}{\Xi_1(\mu_1, N_2, V_w, T)} \tag{6}$$

We note that the macrostate distribution does not depend on F_2 , since w is fixed in this ensemble and the free energy associated with the adsorbent conformation should not affect the probability of any macrostate. Finally, the molar density of adsorbate molecules in the system at pore size w , e.g., the adsorption isotherm is

$$\rho_1(\mu_1, N_2, V_w, T) = \frac{1}{V_w} \frac{\sum_{N_1 \geq 0} N_1 \exp(\beta \mu_1 N_1) Q_1(N_1, N_2, V_w, T)}{\Xi_1(\mu_1, N_2, V_w, T)} \tag{7}$$

For the present discussion, we consider only the simpler case of an isotherm with a single branch, such as adsorption at supercritical temperature or adsorbent materials with exclusively Type I isotherms (Sing et al. 1985; Thommes et al. 2015). This is reflected in Eq. 7 where the summation is over all N_1 states, i.e., all macrostates belong to a single adsorbed phase and Π_{sg} has a single maximum with respect to N_1 (Siderius and Shen 2013). Modifications to Eq. 7 (specifically, the bounds of the summation over N_1 -states) are necessary to account for coexisting phases at subcritical conditions (Siderius and Shen 2013; Shen et al. 2017), such as in an isotherm that displays adsorption-desorption hysteresis. Lastly, we note that the adsorption isotherm in Eq. 7 is given for a particular μ_1 ; the associated p is simply the pressure of the bulk gas at the same μ_1 and T .

2.3 Statistical mechanics—osmotic ensemble

For a flexible adsorbent, the natural ensemble is the osmotic ensemble, which in this case is a system at fixed μ_1 , p , and T , i.e., an isobaric semigrand canonical ensemble. The fourth constraint is the fixed amount of adsorbent itself, indicated here by N_2 . The osmotic ensemble is a canonical ensemble (fixed N_1 , N_2 , V , and T) that has undergone Legendre transforms with respect to N_1 and V . As in the previous section, we consider a single isolated pore, but the statistical mechanics that follow can easily be converted to analyze an adsorbent composed of a network of collectively deforming pores or an ensemble of independently deforming pores. The probability of a microstate of N_1 adsorbate molecules in configuration \mathbf{r}^{N_1} at pore size w subject to the ensemble constraints (μ_1, N_2, p, T) is:

$$\pi_{os}(\mathbf{r}^{N_1}, V_w; \mu_1, N_2, p, T) = c_{os} \exp[-\beta p V_w] \times \exp(\beta \mu_1 N_1) \frac{\exp[-\beta U(\mathbf{r}^{N_1}, w)]}{\Lambda_1^{3N_1} N_1! \Lambda_2^{3N_2} N_2!} \tag{8}$$

in which U is the potential energy of the microstate, composed of the adsorbate-adsorbate, adsorbate-adsorbent, and adsorbent-adsorbent interactions, and c_{os} is a normalization constant. Then, following the previous section, we may integrate over the adsorbate and adsorbent degrees of freedom to obtain the probability of a macrostate defined by N_1 and w ,

$$\Pi_{os}(N_1, V_w; \mu_1, N_2, p, T) = c_{os} \exp[-\beta p V_w] \exp(\beta \mu_1 N_1) \times \exp[-\beta F_2(N_2, V_w, T)] Q_1(N_1, N_2, V_w, T) \tag{9}$$

Again, the appendix provides details explaining the necessary relations to transform Eq. 8 to Eq. 9. We note that F_2 appears in Eq. 9 but that it cannot be ignored as was the case in Eq. 4. In Shen and Siderius (2014) F_2 was

introduced as the “bonding potential” of the adsorbent and it accounts for the flexibility of the adsorbent material. For example, in Shen and Siderius (2014) where the flexible adsorbent was composed of slit pores, F_2 was the free energy potential that governs the distance between the walls of the pores. Here, where we have left the pore geometry ambiguous, F_2 is interpreted as the Helmholtz free energy of the bare adsorbent in conformation w . F_2 may be related to material properties such as the isothermal bulk modulus or elastic constants [cf. Section II.A. of Mahynski and Shen (2016), Eqs. 3–5 in particular], as these descriptors are reflective of the underlying adsorbent-adsorbent interactions in U .

The normalization constant, c_{os} , is simply the inverse of the partition function (Shen and Siderius 2014),

$$\frac{1}{c_{os}} = \Gamma_{os}(\mu_1, N_2, p, T) = \sum_w \sum_{N_1 \geq 0} \exp[-\beta p V_w] \exp(\beta \mu_1 N_1) \times \exp[-\beta F_2(N_2, V_w, T)] Q_1(N_1, N_2, V_w, T) \tag{10}$$

Continuing, the (N_1, V_w) macrostate probability distribution is

$$\Pi_{os}(N_1, V_w; \mu_1, N_2, p, T) = \exp[-\beta F_2(N_2, V_w, T)] \times \frac{\exp[-\beta p V_w] \exp(\beta \mu_1 N_1) Q_1(N_1, N_2, V_w, T)}{\Gamma_{os}(\mu_1, N_2, p, T)} \tag{11}$$

Lastly, the adsorption isotherm for the flexible adsorbent material is, then,

$$\langle N_1 \rangle(\mu_1, N_2, p, T) = \sum_w \exp[-\beta F_2(N_2, V_w, T)] \exp[-\beta p V_w] \times \frac{\sum_{N_1 \geq 0} N_1 \exp(\beta \mu_1 N_1) Q_1(N_1, N_2, V_w, T)}{\Gamma_{os}(\mu_1, N_2, p, T)}, \tag{12}$$

in which the $\langle \rangle$ angle brackets indicate an ensemble average.

3 Pore-size distribution for a flexible material

In this section, we combine the kernel method with the statistical mechanics of adsorption in flexible adsorbents to obtain a relationship between the PSD of an adsorbent and its flexibility. In the first subsection, we derive the PSD using statistical mechanics. Following, we make substitutions for the partition functions that allow us to present the PSD using macroscopic thermodynamics.

3.1 Statistical mechanics

First, we acknowledge that the PSD of a flexible adsorbent is not a fixed characteristic of the material; for a particular temperature, it varies with the imposed pressure (or other mechanical stresses) and chemical potential of the adsorbate. Thus, a discretized integral adsorption equation for a flexible adsorbent accounting for these dependencies in the osmotic ensemble is

$$\langle N_1 \rangle(\mu_1, p, T) = \sum_w \mathcal{F}(w; \mu_1, p, T) \rho_1(\mu_1, N_2, V_w, T) \tag{13}$$

We include the dependence on both μ_1 and p in \mathcal{F} , even though the constraints are equivalent for a pure adsorbate. Second, substitution of the *rigid* pore isotherm in Eq. 7 into Eq. 12 yields

$$\langle N_1 \rangle(\mu_1, N_2, p, T) = \sum_w V_w \exp[-\beta F_2(N_2, V_w, T)] \times \exp[-\beta p V_w] \frac{\Xi_1(\mu_1, N_2, V_w, T)}{\Gamma_{os}(\mu_1, N_2, p, T)} \rho_1(\mu_1, N_2, V_w, T) \tag{14}$$

Equation 14 is closely related to the integral adsorption equations in Eqs. 2 and 13 as it is the weighted sum of an adsorption kernel, $\rho_1(\mu_1, N_2, V_w, T)$, where the weight is a group of terms that contain the size characteristics of the flexible adsorbent (along with other thermodynamic terms, see below). This group of terms is, effectively, the pore-size distribution:

$$\mathcal{F}(w; \mu_1, p, T) = V_w \exp[-\beta F_2(N_2, V_w, T)] \times \exp[-\beta p V_w] \frac{\Xi_1(\mu_1, N_2, V_w, T)}{\Gamma_{os}(\mu_1, N_2, p, T)} \tag{15}$$

Equation 15 is the mathematical relationship between (1) the adsorbent flexibility and (2) the probability distribution of the pore size.

The relationship between Eq. 15 and the traditional PSD may be clarified by derivation of an additional term. Consider, for example, the probability of observing a particular volume state w , which may be obtained by summing Eq. 11 over all N_1 states,

$$\Pi_{os}(V_w; \mu_1, N_2, p, T) = \sum_{N_1 \geq 0} \Pi_{os}(N_1, V_w; \mu_1, N_2, p, T) = \exp[-\beta F_2(N_2, V_w, T)] \times \exp[-\beta p V_w] \frac{\Xi_1(\mu_1, N_2, V_w, T)}{\Gamma_{os}(\mu_1, N_2, p, T)}. \tag{16}$$

Finally, substitution of the above in Eq. 15 yields

$$\mathcal{F}(w; \mu_1, p, T) = V_w \Pi_{os}(V_w; \mu_1, N_2, p, T) \tag{17}$$

Using Eq. 17, the PSD of a flexible adsorbent at a particular pressure, chemical potential, and temperature is the product

of the pore volume and the probability of observing a particular pore size. This is perfectly intuitive and could have been derived directly from the macrostate distribution and some basic arguments. We derived Eq. 15 first to obtain a relationship for the PSD of the flexible adsorbent that was mathematically akin to the traditional integral adsorption equation. Ultimately, the longer derivation beginning with the introduction of an isotherm kernel (Eq. 13) and finally arriving at the PSD (Eq. 15) demonstrates that the adsorption isotherm for a flexible material may be written as a weighted sum of the isotherms of individual (rigid) pores, where the weighting function is the PSD itself (assuming, as done in the Appendix, that the canonical partition function is separable). Furthermore, the resultant PSD follows naturally from the statistical mechanics of adsorption in the osmotic ensemble.

3.2 Macroscopic thermodynamics

Thus far, we have written the PSD of a flexible adsorbent using statistical mechanical partition functions, which may be difficult to interpret for real applications. We can, however, further rewrite the PSD using concepts from macroscopic thermodynamics. We resume our discussion at Eq. 16 and then use three bridge functions that relate the semigrand and osmotic partition functions to their associated free energy potentials (Shen and Siderius 2014; Mahynski and Shen 2016):

$$-k_B T \ln \Xi(\mu_1, N_2, V_w, T) = F(V_w) - \mu_1 \langle N_1 \rangle_{sg}(V_w) \quad (18)$$

$$-k_B T \ln \Xi_1(\mu_1, N_2, V_w, T) = F_2(N_2, V_w, T) - k_B T \ln \Xi(\mu_1, N_2, V_w, T) \quad (19)$$

$$-k_B T \ln \Gamma_{os}(\mu_1, N_2, p, T) = \langle \mu_2 N_2 \rangle_{os}(p) \quad (20)$$

In the above, F is the Helmholtz free energy and, as noted in the appendix, may be decomposed as $F = F_1 + F_2$, where F_1 contains all contributions to that free energy involving the fluid-fluid and fluid-solid interactions. To simplify the above and following expressions, we drop the dependencies on μ_1 , N_2 , and T and use subscripts “sg” and “os” to identify averages in the semigrand and osmotic ensembles, respectively. For example, $\langle \mu_2 N_2 \rangle_{sg}(V_w)$ in Eq. 18 is properly $\langle \mu_2 N_2 \rangle(\mu_1, N_2, V_w, T)$. Additionally, we lump μ_2 and N_2 together as a single term since N_2 generically represents the adsorbent, as noted previously. With Eqs. 18–20, Eq. 16 may be written as:

$$\Pi_{os}(V_w; \mu_1, N_2, p, T) = \exp[-\beta F_2(V_w)] \exp[-\beta p V_w] \times \frac{\exp[-\beta F_1(V_w) + \beta \mu_1 \langle N_1 \rangle_{sg}(V_w)]}{\exp[-\beta \langle \mu_2 N_2 \rangle_{os}(p)]}, \quad (21)$$

Lastly, we introduce the substitutions $F_1 = U_1 - TS_1$, where U_1 and S_1 are the fluid potential energy and entropy, respectively, and $\langle N_1 \rangle = \rho_1 V_w$ and note that $\langle \mu_2 N_2 \rangle_{os}(p)$ is independent of w and is effectively a normalization constant. Consequently,

$$\Pi_{os}(V_w; \mu_1, N_2, p, T) \propto \exp[-\beta F_2(V_w)] \exp[-\beta p V_w] \times \exp[-\beta U_1(V_w) + S_1(V_w)/k_B + \beta \mu_1 \rho_1(V_w) V_w] \quad (22)$$

The end result is that $\Pi_{os}(w)$ is a function of F_2 , pV_w , U_1 , S_1 , and ρ_1 , and F_2 . Since, as shown in the Appendix, the fluid-fluid potential energy, U_1 , was decoupled from the adsorbent-adsorbent potential energy (U_2 , see Eqs. 29–33), the adsorbent free energy, F_2 , is the sole remaining term related to the pore flexibility. Ultimately, the full PSD \mathcal{F} can be expressed in terms of the pore flexibility encoded in $F_2(V_w)$, pV_w , and three kernels: the individual rigid-pore isotherms $\{\rho_1(V_w)\}$, the potential energy kernel $\{U_1(V_w)\}$ and the entropy kernel $\{S_1(V_w)\}$.

Lastly, one final form of $\Pi_{os}(V_w; \mu_1, N_2, p, T)$ can be written with an alternate form of the bridge function for Ξ :

$$-k_B T \ln \Xi(\mu_1, N_2, V_w, T) = -\langle p \rangle_{sg} V_w + \langle \mu_2 N_2 \rangle_{sg}(V_w) \quad (23)$$

Substitution of the above along with Eqs. 19 and 20 into Eq. 16 yields

$$\Pi_{os}(V_w; \mu_1, N_2, p, T) = \exp[-\beta(p - \langle p \rangle_{sg}) V_w] \times \frac{\exp[-\beta \langle \mu_2 N_2 \rangle_{sg}(V_w)]}{\exp[-\beta \langle \mu_2 N_2 \rangle_{os}(p)]} \quad (24)$$

For $p = \langle p \rangle_{sg}$, one finds the interesting result:

$$\Pi_{os}(V_w; \mu_1, N_2, p, T) = \frac{\exp[-\beta \langle \mu_2 N_2 \rangle_{sg}(V_w)]}{\exp[-\beta \langle \mu_2 N_2 \rangle_{os}(p)]} \quad (25)$$

Since $\mu_2 N_2$ is a Gibbs free energy for the empty adsorbent, one finds that the probability for a pore of size w is equal to the ratio of the free energy of the adsorbent at that pore width to the free energy of the adsorbent when it is allowed to deform against the adsorbate fluid.

4 Discussion

In the previous sections, the two main results are the statistical mechanical expression for the PSD and the integral adsorption equation for a flexible material. To aid further discussion, the PSD given in the previous section can be reorganized as:

$$\begin{aligned}
\mathcal{F}(w; \mu_1, p, T) &= \exp[-\beta F_2(N_2, V_w, T)] \\
&\times V_w \exp[-\beta p V_w] \frac{\Xi_1(\mu_1, N_2, V_w, T)}{\Gamma_{os}(\mu_1, N_2, p, T)} \\
&= \exp[-\beta F_2(N_2, V_w, T)] V_w \exp[-\beta p V_w] \\
&\times \frac{\exp[-\beta U_1(V_w) + S_1(V_w)/k_B + \beta \mu_1 \rho_1(V_w) V_w]}{\Gamma_{os}(\mu_1, N_2, p, T)} \quad (26)
\end{aligned}$$

Thus, the PSD of a flexible material contains information describing the material's deformation physics, though it is multiplied by other terms. The terms in Eq. 26 are, of course, related to all of the factors that affect the pore size. First, the βF_2 term accounts for the intrinsic flexibility of the adsorbent. Second, the volume term is a necessary scaling factor. Third, the $\beta p V_w$ term accounts for the thermodynamic pressure of the fluid reservoir. Finally, the confined fluid effects are contained in the last term, though it also includes effects of the reservoir pressure, chemical potential, and adsorbent constraints. The important point is that the description of the interaction of the adsorbate fluid with both itself and the adsorbent material is contained in this term. It is the balance of the terms listed here that determines the PSD.

Despite the elegant similarity of the integral adsorption equations in Eqs. 13 and 14, there is a major difference between the two. In the conventional usage of the PSD in combination with an adsorption kernel, a core assumption is that the PSD is invariant with respect to the thermodynamic state of the system (i.e., μ_1 , p , or T); it is a static property of the adsorbent. For a flexible material, however, the PSD contains a direct dependence on the thermodynamic constraints (μ_1 and p). As noted in the introduction and elsewhere, this is entirely expected, as the PSD must necessarily vary as the adsorbent material deforms in response to the adsorbate gas and its surrounding environment (for instance, an applied external stress).

The key result shown in Eq. 26 is that there is a mathematical relationship between the flexibility of an adsorbent and the pore size distribution exhibited by that material. Since the PSD is, at least conceptually, an observable property of an adsorbent material, measurements of the PSD could be used to indirectly describe the deformation characteristics of the material. The important distinction from contemporary interest in the PSDs of adsorbent materials is that the PSD itself is not the quantity of interest; instead the PSD provides the (theoretically) determinable deformation free energy of the adsorbent. This distinction from contemporary kernel-based characterization of adsorbent materials is critical, despite the deep similarity of the two methods. Furthermore, one may question the importance of the flexibility-related terms throughout our analysis (Eqs. 21 and 22 in particular) of the PSD of a flexible adsorbent material. The importance lies largely in the scale of any adsorbent deformation. For a material

that deforms only a small amount, e.g., an adsorbent whose pores do not undergo structural transitions, the flexibility-related terms might very well be neglected. However, for an adsorbent material that does undergo a structural transition, these flexibility-related terms should prove essential. For example, when MIL-53 transforms from its large-pore configuration to its narrow-pore, its pore volume is reduced by approximately 30% (Serre et al. 2002; Neimark et al. 2011). Clearly, adsorbent deformations such as this could not be described by a static, pressure-independent PSD; the flexibility-related terms are necessary for a proper description of the adsorption isotherm.

Using PSD measurements to determine adsorbent deformation characteristics is, at present, complicated by the fact that several terms in Eq. 26 are not directly measurable, specifically the partition functions, the potential energy, the entropy, and the (hypothetical, fixed volume) adsorption isotherm, the latter three of which depend on w . In the spirit of contemporary adsorption kernels used to obtain a PSD, this method might be made feasible by introducing new kernels for the potential energy and entropy of a confined fluid via computational models like density functional theory or molecular simulations alongside adsorption isotherm kernels. If, for example, one assumes ideal gas-like behavior for adsorbate in a dilute state, U_1 would be approximately the fluid-solid interaction energy and $S_1 \approx N_1 k_B \ln V_w$. An additional challenge is that the measurement of the PSD $\mathcal{F}(w, \mu_1, p, T)$ would necessitate measurements of the PSD at single pressures, which is not possible with existing adsorbent characterization techniques. Recent work (Gor 2014; Gor et al. 2015; Gor et al. 2016) discusses relationships between pore size and the compressibility of a liquid-like confined fluid, measured at a single pressure, which might be further developed to compute the PSD of a material using single-pressure measurements. Such a method could provide the single-pressure measurements essential to application of the statistical mechanics presented here. Alternatively, since F_2 is itself independent of pressure and characteristics of the adsorbate fluid, one could envision estimating F_2 via an optimization procedure that utilizes measurements at several pressures. Elimination of the remaining terms in Eq. 26 is still necessary, possibly through clever ratios or scalings of $\mathcal{F}(w; \mu_1, p, T)$ at different pressure conditions.

Lastly, the integral adsorption equation in Eq. 13 demonstrates that a kernel-based approach to adsorption in a flexible adsorbent material is consistent with a statistical mechanical description of the adsorption isotherm, under the assumption that the canonical partition function is separable. The major difference with the existing kernel-based approach to determining PSDs is that, at least in principle, the adsorption isotherm of a flexible adsorbent may be described via kernels of isotherms, energies, and entropies

for a rigid adsorbent. The aforementioned complicating factor is that the PSD is dependent on pressure and (or) chemical potential. Thus, solution for the PSD using a rigid-material kernel is an ill-formed problem and would require some layer of assumptions or constraints on the PSD. Future work is necessary to develop a solution technique that could measure the pressure-dependent PSD.

5 Conclusion

In this work, we derived a statistical mechanical description of adsorption in a flexible adsorbent material, which yielded both the PSD of a flexible adsorbent material (Eq. 26) and an associated integral adsorption equation (Eq. 13). Of key importance is the appearance of the adsorbent deformation potential, $F_2(N_2, V_w, T)$, in the mathematical description of the PSD. The important implication is that a measurement of the temperature- and pressure-dependent PSD of a deformable adsorbent contains information that might be used to indirectly describe certain material properties related to flexibility and deformation, through a kernel-based approach. We stress that experimental measurements necessary to support calculation of F_2 , specifically measurement of the PSD at fixed pressure, must be developed first. With such tools, Eq. 26 might then be the basis of a new tool for characterizing adsorbent materials and, thus, aid future development of porous materials for various applications in chemical processing.

6 Appendix: Canonical Ensemble partition function

Here we derive a form of the canonical ensemble partition function specific to our model of a flexible adsorbent material, which simplifies and streamlines our discussion in Sect. 2.3. It is an essential characteristic of our model, as it allows us to separate the canonical partition function of the full system (adsorbate and adsorbent) into one part describing the adsorbent degrees of freedom and another containing all other degrees of freedom. First, we write the partition function for a canonical ensemble for a classical bicomponent system as

$$Q(N_1, N_2, V_w, T) = \frac{1}{\Lambda_1^{3N_1} N_1! \Lambda_2^{3N_2} N_2!} \times \int_{V_w} \mathbf{dr}^{N_1} \mathbf{dr}^{N_2} \exp[-\beta U(\mathbf{r}^{N_1}, \mathbf{r}^{N_2})] \quad (27)$$

in which $U(\mathbf{r}^{N_1}, \mathbf{r}^{N_2})$ is the intermolecular potential energy of the particular configuration. The system is contained in a volume V_w and is in thermal equilibrium with a reservoir

at temperature T . It contains N_1 molecules of the adsorbate (species 1) and N_2 is an extensive constraint identifying the amount of adsorbent (species 2). As in the main paper, we do not necessarily specify a “number” of molecules of the adsorbent but, importantly, it establishes extensivity with respect to the adsorbent material. For completeness, we include the kinetic degrees of freedom of the adsorbent material (contained in $\Lambda_2^{3N_2}$) in the partition function.

In our model of a flexible adsorbent system, we assume that the potential energy may be separated into fluid-fluid, solid-solid, and fluid-solid contributions. The solid-solid potential energy in our model is solely a function of the adsorbent pore size or conformation (i.e., w). Furthermore, the fluid-fluid contribution is only a function of the fluid configuration, but the fluid-solid contribution depends on both \mathbf{r}^{N_1} and w . Thus, we may write the total potential energy for a particular state ($\mathbf{r}^{N_1}; w$) as

$$U(\mathbf{r}^{N_1}; w) = U_{11}(\mathbf{r}^{N_1}) + U_{12}(\mathbf{r}^{N_1}; w) + U_{22}(w) \quad (28)$$

where U_{11} , U_{12} , and U_{22} are the fluid-fluid, fluid-solid, and solid-solid contributions to the potential energy, respectively. Equation 27 may be rewritten as

$$Q(N_1, N_2, V_w, T) = \frac{1}{\Lambda_2^{3N_2} N_2!} \int_{V_w} \mathbf{dr}^{N_2} \exp[-\beta U_{22}(w)] \times \frac{1}{\Lambda_1^{3N_1} N_1!} \int_{V_w} \mathbf{dr}^{N_1} \exp[-\beta(U_{11}(\mathbf{r}^{N_1}) + U_{12}(\mathbf{r}^{N_1}; w))] \quad (29)$$

We now make the following definitions (following Mahynski and Shen 2016):

$$Q_1(N_1, N_2, V_w, T) = \frac{1}{\Lambda_1^{3N_1} N_1!} \times \int_{V_w} \mathbf{dr}^{N_1} \exp[-\beta(U_{11}(\mathbf{r}^{N_1}) + U_{12}(\mathbf{r}^{N_1}; w))] \quad (30)$$

$$Q_2(N_2, V_w, T) = \frac{1}{\Lambda_2^{3N_2} N_2!} \int_{V_w} \mathbf{dr}^{N_2} \exp[-\beta U_{22}(w)] \quad (31)$$

Q_2 in Eq. 31 is, effectively, the canonical partition function of the solid in conformation w and may be separated from the full Q because the adsorbent-adsorbent potential energy is entirely decoupled from the fluid degrees of freedom. The Helmholtz free energy of the adsorbent material is given by

$$F_2(N_2, V_w, T) = -k_B T \ln Q_2(N_2, V_w, T) \quad (32)$$

Using Eqs. 30 and 32, we may rewrite the full canonical partition function in Eq. 29 as

$$Q(N_1, N_2, V_w, T) = \exp[-\beta F_2(N_2, V_w, T)] Q_1(N_1, N_2, V_w, T) \quad (33)$$

In the form of Eq. 33, the partition function is compactly written as a product of the Boltzmann factor of the free energy of the adsorbent and Q_1 . We find this expression for the canonical partition function useful as it is a reminder that the energy associated with the adsorbent conformation may be decoupled from the fluid-fluid and fluid-solid contributions to the energy.

References

- Balzer, C., Brameier, S., Neimark, A.V., Reichenauer, G.: Deformation of microporous carbon during adsorption of nitrogen, argon, carbon dioxide, and water studied by in situ dilatometry. *Langmuir* **31**, 12512–12519 (2015)
- Balzer, C., Cimino, R.T., Gor, G.Y., Neimark, A.V., Reichenauer, G.: Deformation of microporous carbons during N₂, Ar, and CO₂ adsorption: Insight from the density functional theory. *Langmuir* **32**, 8265–8274 (2016)
- Bousquet, D., Coudert, F.X., Boutin, A.: Free energy landscapes for the thermodynamic understanding of adsorption-induced deformations and structural transitions in porous materials. *J. Chem. Phys.* **137**, 044,118 (2012)
- Coudert, F.X., Boutin, A., Fuchs, A.H., Neimark, A.V.: Adsorption deformation and structural transitions in metal-organic frameworks: From the unit cell to the crystal. *J. Phys. Chem. Lett.* **4**, 3198–3205 (2013)
- Coudert, F.X., Boutin, A., Jeffroy, M., Mellot-Draznieks, C., Fuchs, A.H.: Thermodynamic methods and models to study flexible metal-organic frameworks. *ChemPhysChem* **12**, 247–258 (2011)
- Coudert, F.X., Fuchs, A.H., Neimark, A.V.: Adsorption deformation of microporous composites. *Dalton Trans.* **45**, 4136–4140 (2015)
- Errington, J.R.: Direct calculation of liquid-vapor phase equilibria from transition matrix Monte Carlo simulation. *J. Chem. Phys.* **118**, 9915–9925 (2003)
- Espinal, L., Wong-Ng, W., Kaduk, J.A., Allen, A.J., Snyder, C.R., Chiu, C., Siderius, D.W., Li, L., Cockayne, E., Espinal, A.E., Suib, S.L.: Time-dependent CO₂ sorption hysteresis in a one-dimensional microporous octahedral molecular sieve. *J. Am. Chem. Soc.* **134**, 7944–7951 (2012)
- Evans, J.D., Bocquet, L., Coudert, F.X.: Origins of negative gas adsorption. *Chem* **1**, 873–886 (2016)
- Farha, O.K., Eryazici, I., Jeong, N.C., Hauser, B.G., Wilmer, C.E., Sarjeant, A.A., Snurr, R.Q., Nguyen, S.T., Yazaydin, A., Hupp, J.T.: Metal-organic framework materials with ultrahigh surface areas: Is the sky the limit? *J. Am. Chem. Soc.* **134**, 15016–15021 (2012)
- Ferey, G.: Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **37**, 191–214 (2008)
- Furukawa, H., Ko, N., Go, Y.B., Aratani, N., Choi, S.B., Choi, E., Yazaydin, A., Snurr, R.Q., O’Keeffe, M., Kim, J., Yaghi, O.M.: Ultrahigh porosity in metal-organic frameworks. *Science* **329**, 424–428 (2010)
- Ghysels, A., Vanduyfhuys, L., Vandichel, M., Waroquier, M., Van Speybroeck, V., Smit, B.: On the thermodynamics of framework breathing: A free energy model for gas adsorption in MIL-53. *J. Phys. Chem. C* **117**, 11540–11554 (2013)
- Gor, G.Y.: Adsorption stress changes the elasticity of liquid argon confined in a nanopore. *Langmuir* **30**, 13564–13569 (2014)
- Gor, G.Y., Siderius, D.W., Rasmussen, C.J., Krekelberg, W.P., Shen, V.K., Bernstein, N.: Relation between pore size and the compressibility of a confined fluid. *J. Chem. Phys.* **143**, 194,506 (2015)
- Gor, G.Y., Siderius, D.W., Shen, V.K., Bernstein, N.: Modulus–pressure equation for confined fluids. *J. Chem. Phys.* **145**, 164,505 (2016)
- Kowalczyk, P., Balzer, C., Reichenauer, G., Terzyk, A.P., Gauden, P.A., Neimark, A.V.: Using in-situ adsorption dilatometry for assessment of micropore size distribution in monolithic carbons. *Carbon* **103**, 263–272 (2016)
- Krause, S., Bon, V., Senkovska, I., Stoeck, U., Wallacher, D., Tobbens, D.M., Zander, S., Pillai, R.S., Maurin, G., Coudert, F.X., Kaskel, S.: A pressure-amplifying framework material with negative gas adsorption transitions. *Nature* **532**, 348–352 (2016)
- Lastoskie, C., Gubbins, K.E., Quirke, N.: Pore size distribution analysis of microporous carbons: a density functional theory approach. *J. Phys. Chem.* **97**, 4786–4796 (1993)
- Li, H., Eddaoudi, M., O’Keeffe, M., Yaghi, O.M.: Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **402**(6759), 276–279 (1999)
- Li, J.R., Sculley, J., Zhou, H.C.: Metal-organic frameworks for separations. *Chem. Rev.* **112**, 869–932 (2012)
- Liu, Y., Her, J.H., Dailly, A., Ramirez-Cuesta, A.J., Neumann, D.A., Brown, C.M.: Reversible structural transition in MIL-53 with large temperature hysteresis. *J. Am. Chem. Soc.* **130**, 11813–11818 (2008)
- Lowell, S., Shields, J.E., Thomas, M.A., Thommes, M.: *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*. Kluwer, Boston (2004)
- Mahynski, N.A., Shen, V.K.: Multicomponent adsorption in mesoporous flexible materials with flat-histogram monte carlo methods. *J. Chem. Phys.* **145**, 174709 (2016)
- Millange, F., Serre, C., Ferey, G.: Synthesis, structure determination and properties of MIL-53as and MIL-53ht: The first Cr^{III} hybrid inorganic-organic microporous solids: Cr^{III}(OH)·(O₂C-C₆H₄-CO₂)_x{HO₂C-C₆H₄-CO₂H}_x. *Chem. Commun.* 822–823 (2002)
- Neimark, A.V., Coudert, F.X., Boutin, A., Fuchs, A.H.: Stress-based model for the breathing of metal-organic frameworks. *J. Phys. Chem. L* **1**, 445–449 (2010)
- Neimark, A.V., Coudert, F.X., Triguero, C., Boutin, A., Fuchs, A.H., Beurroies, I., Denoyel, R.: Structural transitions in MIL-53 (Cr): View from outside and inside. *Langmuir* **27**, 4734–4741 (2011)
- Rane, K.S., Murali, S., Errington, J.R.: Monte Carlo simulation methods for computing liquid-vapor saturation properties of model systems. *J. Chem. Theory Comput.* **9**, 2552–2566 (2013)
- Ravikovitch, P.I., Vishnyakov, A., Russo, R., Neimark, A.V.: Unified approach to pore size characterization of microporous carbonaceous materials from N₂, Ar, and CO₂ adsorption isotherms. *Langmuir* **16**(5), 2311–2320 (2000)
- Rouquerol, F., Rouquerol, J., Sing, K.: *Adsorption by Powders and Porous Solids*. Academic Press, London (1999)
- Sarkisov, L., Martin, R.L., Haranczyk, M., Smit, B.: On the flexibility of metal-organic frameworks. *J. Am. Chem. Soc.* **136**, 2228–2231 (2014)
- Seaton, N.A., Walton, J.P.R.B., Quirke, N.: A new analysis method for the determination of the pore size distribution of porous carbons from nitrogen adsorption measurements. *Carbon* **27**, 853–861 (1989)
- Serre, C., Millange, F., Thouvenot, C., Nogues, M., Marsolier, G., Louer, D., Ferey, G.: Very large breathing effect in the first nanoporous chromium(III)-based solids: MIL-53 or Cr^{III}(OH)·

- $O_2C-C_6H_4-CO_2\cdot HO_2C-C_6H_4-CO_2H_x\cdot H_2O_y$. *J. Am. Chem. Soc.* **124**, 13519–13526 (2002)
34. Shell, M.S., Debenedetti, P.G., Panagiotopoulos, A.Z.: Flat-histogram dynamics and optimization in density of states simulations of fluids. *J. Phys. Chem. B* **108**, 19748–19755 (2004)
 35. Shen, V.K., Siderius, D.W.: Elucidating the effects of adsorbent flexibility on fluid adsorption using simple models and flat-histogram sampling methods. *J. Chem. Phys.* **104**, 244106 (2014)
 36. Shen, V.K., Siderius, D.W., Mahynski, N.A.: Capillary phase transitions in flexible porous materials. *J. Chem. Phys.* (2017). (In Preparation)
 37. Siderius, D.W., Shen, V.K.: Use of the grand canonical transition-matrix Monte Carlo method to model gas adsorption in porous materials. *J. Phys. Chem. C* **117**, 5861–5872 (2013)
 38. Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniowska, T.: Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* **57**, 603–619 (1985)
 39. Thommes, M.: Physical Adsorption Characterization of MOFs (Metal Organic Framework) Materials. Webinar (2015)
 40. Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W.: Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution. *Pure Appl. Chem.* **87**, 1051–1069 (2015)
 41. Ustinov, E.A., Do, D.D.: Effect of adsorption deformation on thermodynamic characteristics of a fluid in slit pores at sub-critical conditions. *Carbon* **44**, 2652–2663 (2006)
 42. Wilmer, C.E., Leaf, M., Lee, C.Y., Farha, O.K., Hauser, B.G., Hupp, J.T., Snurr, R.Q.: Large-scale screening of hypothetical metal-organic frameworks. *Nat. Chem.* **4**, 83–89 (2012)
 43. Zaworotko, M.J.: Materials science: designer pores made easy. *Nature* **451**, 410–411 (2008)