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Adsorbate-adsorbate interactions on microporous materials

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Abstract

Simple isotherm models can fit microporous adsorption yet the molecular interactions underlying the successful fitting have often remained obscure. Here we demonstrate how semi-empirical isotherm model data can be mined to reveal the reality of adsorbate-adsorbate molecular interactions. This was made possible by the fluctuation adsorption theory, a rigorous theory based only on the principles of statistical thermodynamics. For microporous carbons, adsorbate-adsorbate interactions quantified from the Dubinin-Radishkevich (DR) and Dubinin-Astakhov (DA) models successfully capture the primary micropore filling mechanism and the subsequent layer adsorption, leading to a liquid-like behaviour of the adsorbates. The microscopic meanings of the DR and DA parameters and the adsorption potential have also been clarified via statistical thermodynamics.

Keywords

Adsorption; Microporous carbon; Statistical thermodynamics; Fluctuation theory; Dubinin-Radishkevich model; Dubinin-Astakhov model; Adsorption potential

1. Introduction

Microporous materials, such as activated carbons and porous silica, are powerful adsorbents with many industrial applications [1–5]. The characteristics of such adsorbents have been quantified by adsorption isotherms. Hence, to understand the mechanism of adsorption we need to interpret adsorption isotherms, namely, to elucidate the molecular interactions that give rise to the shape of the isotherm [6,7]. However, the difficulty of this approach is at least twofold: (1) isotherm shapes are diverse and (2) the isotherm shapes for porous materials are often very complex [1–5,8].

The Dubinin-Astakhov (DA) model [9] (including its special case, the Dubinin-Radushkevich (DR) model) [9–13] has been used widely to fit the isotherms for microporous materials [1–5,8,14–16]. It was proposed as a semi-empirical relationship between the adsorbed quantity and the adsorption potential. The adsorption potential was originally proposed by Polanyi [17,18] founded on a thermodynamic argument. This approach fell into disuse [19,20] because it does not satisfy Henry's Law at the low adsorbate activity limit. However, because of its effectiveness for porous materials and the adoption by Dubinin and coworkers in their semi-empirical adsorption models [9–13], adsorption potential became a much-used concept for microporous adsorbents [1,2,4,21].

What is the foundation of the DA model? Even though the model claims to be based on micropore filling [9–13], much of its original foundation was on scaling and functional forms of the isotherm [12]. Indeed, "it became more and more obvious that the initial principles of the potential theory have no physical meaning for adsorption in micropores" [12] and the DA adsorption model function is semi-empirical [11–13]. Despite some attempts to give it a clearer molecular or statistical mechanical interpretation [4,22], revealing the molecular interactions underlying an isotherm of a microporous material is still an open question.

To clarify what molecular mechanism the DA model captures, our recent statistical thermodynamic approach to interpreting adsorption isotherms [7] will be helpful. The fluctuation adsorption theory [7], an extension of the fluctuation solution (or solvation) theory [23–28] to surfaces, is a rigorous and model-free theory applicable to any surface geometry. Its only postulate is that the deviation from the bulk solution structure due to the presence of the interface is confined within a finite distance [7]. The fluctuation adsorption theory can quantify adsorbate-adsorbate interactions directly from an isotherm [7].

Taking full advantage of rigorous statistical thermodynamics, this paper will clarify the microscopic mechanism of microporous adsorption based on a rigorous statistical thermodynamic approach. Adsorption models such as the DA model will be used as a fitting model, and the underlying physical meaning of the fitting parameters will be clarified. Our foundation is the rigorous fluctuation adsorption theory [7] which can evaluate adsorbate-adsorbate interactions directly from isotherms and adsorption models used for data fitting.

2. Quantifying adsorbate-adsorbate interactions via excess numbers

Consider a phase consisting of adsorbent and adsorbate (phase I) facing in equilibrium with the adsorbate vapour phase (phase II). We neglect absorption into the surface interior, and the adsorbent and adsorbate molecules are referred to as species 1 and 2, respectively. We summarize our statistical thermodynamic foundation [7] using our current notations of phases I and II. Firstly, the fluctuation adsorption theory can deal with any surface shape and porosity [7]. This was made possible through a rigorous statistical thermodynamic generalization of the Gibbs adsorption isotherm and the Gibbs dividing surface [7,27,29,30] to non-planar surfaces with any surface geometry [7]. Secondly, we have postulated that the effect of the interface is confined within an interfacial subsystem (with volume v) within a finite distance from the surface. Consequently, the Gibbs surface excess, $\langle n_2^I \rangle - \langle n_2^{II} \rangle$, is the difference in the number of adsorbates between the interfacial subsystem $\langle n_2^I \rangle$ and a small part of the adsorbate vapour phase $\langle n_2^{II} \rangle$ with the same volume v as the interfacial subsystem [7]. Note that $\langle \; \rangle$ denotes an ensemble average. Thirdly, how the surface excess depends on adsorbate activity a_2 leads to the difference in number fluctuations between the interface and the vapour phases [7],

$$\left(\frac{\partial(\langle n_2^I \rangle - \langle n_2^{II} \rangle)}{\partial \ln a_2}\right)_T = \left(\langle {n_2^I}^2 \rangle - \langle n_2^I \rangle^2\right) - \left(\langle {n_2^{II}}^2 \rangle - \langle n_2^{II} \rangle^2\right) \tag{2.1}$$

Since the adsorbate number and the adsorbate fluctuation in the adsorbate vapour (phase II) are negligibly small compared to those in the interfacial subsystem (phase I), we obtain [7]

$$\left(\frac{\partial \langle n_2 \rangle}{\partial \ln a_2}\right)_T = \langle n_2^2 \rangle - \langle n_2 \rangle^2 \tag{2.2}$$

where we have omitted the superscript I in Eq. (2.2), as we will do from now onwards.

Eq. (2.2) will serve as the foundation for quantifying adsorbate-adsorbate interaction from an experimental isotherm data or an isotherm fitted to a model (such as DA and DR). To translate the language of statistics into that of intermolecular interactions, it is useful to rewrite Eq. (2.2) into the following form:

$$\left(\frac{\partial \ln\langle n_2\rangle}{\partial \ln a_2}\right)_T = N_{22} + 1 \tag{2.3}$$

$$N_{22} = \frac{\langle n_2(n_2-1)\rangle - \langle n_2\rangle^2}{\langle n_2\rangle} \tag{2.4}$$

where N_{22} is the excess number of adsorbates around an adsorbate [7]; here, "excess" is defined with respect to $\frac{\langle n_2\rangle^2}{\langle n_2\rangle} = \langle n_2\rangle$, i.e., the number of adsorbates around an adsorbate in the absence of adsorbate-adsorbate correlation [7].

N_{22} is a quantitative measure of adsorbate-adsorbate interaction. A stronger adsorbate-adsorbate interaction makes N_{22} more positive. The concept of the excess number, which comes from the solvation theory [26,27], was demonstrated to be powerful in clarifying the mechanisms of solubilization and in controlling macromolecular conformation and aggregation [28,31]. We have extended this concept to adsorption [7]. Its significance in adsorption can be appreciated intuitively by rewriting Eq. (2.3) as

$$\left(\frac{\partial \ln a_2}{\partial \ln\langle n_2\rangle}\right)_T = \frac{1}{N_{22} + 1} \tag{2.5}$$

Based on Eq. (2.5), let us consider a surface with $\langle n_2\rangle$ adsorbates and measure its vapour pressure, instead of adsorption measurements. A strong adsorbate-adsorbate interaction, N_{22}, suppresses the increase of activity (hence vapour pressure) that accompanies the increase of adsorbates $\langle n_2\rangle$.

3. A microscopic interpretation of the Dubinin-Astakhov (DA) model

Our next goal is to clarify the molecular interactions underlying adsorption to microporous materials. To this end, we employ the potential theory, especially the DA model and its subset, the DR model [11–13], due to their successful fitting. This means that they somehow have captured the underlying molecular interactions. However, DA and DR models are semi-empirical, which means that there is no clear connection between molecular interactions and isotherms. These models are founded on the adsorption potential, whose physical basis has been ambiguous [12] and controversial [19,20]. Thus, we use the DA model solely as a fitting equation of experimental data necessary for the calculation of the excess number, N_{22}, as a measure of sorbate-sorbate interaction at the surface. In Appendix A, we have presented a statistical thermodynamic clarification of this concept. More importantly, the fluctuation adsorption theory, through differentiating an isotherm model, can quantify the adsorbate-adsorbate interactions underlying the isotherm [7].

Let us first write down the DA model in a way consistent with our notation. The adsorbed quantity, $\langle n_2 \rangle$ is the function of the adsorption potential ϵ (Appendix A), as

$$\frac{\langle n_2 \rangle}{n_2^0} = \exp\left[-\frac{\epsilon^m}{E}\right] \tag{3.1}$$

$$\epsilon = -RT \ln a_2 \tag{3.2}$$

where n_2^0, the maximum adsorption capacity, is a constant. The parameter E has often been decomposed into various contributions with some physical interpretation [21]. In addition, m is another fitting parameter; when $m = 2$, the DA model is reduced to the DR model. Note that Eq. (3.1) can be expressed as

$$\ln\langle n_2 \rangle = -\frac{\epsilon^m}{E} + \ln n_2^0 \tag{3.3}$$

which inspires the application of Eq. (2.3).

Our interest here is to attribute a rigorous molecular interpretation for E. This can be achieved by substituting Eqs. (3.2) and (3.3) into Eq. (2.3), which yields

$$N_{22} + 1 = \frac{mRT}{E}\epsilon^{m-1} \tag{3.4}$$

Eq. (3.4) shows that excess number increases with the adsorption potential. Moreover, it clarifies the meaning of the parameter E in the DA model; the larger the parameter E the smaller the excess adsorbate number at a given adsorption potential. This is the underlying molecular picture underlying the DA model. Rewriting Eq. (3.4) shows the driving force of the adsorption potential in the framework of the DA model

$$\epsilon = \left[\frac{E}{mRT}(N_{22} + 1)\right]^{\frac{1}{m-1}} \tag{3.5}$$

The adsorption potential is determined by the excess adsorbate number N_{22} around an adsorbate. The larger N_{22} the higher the adsorption potential, because the stronger the adsorbate-adsorbate interaction the lower the vapour pressure (hence higher ϵ). The DA parameter E governs how adsorbate-adsorbate interaction N_{22} is related to the vapour pressure and the adsorbate potential. (The microscopic meaning of the parameter E itself can be attributed as the adsorbate-adsorbate-adsorbate interaction for the DR model. See Appendix B).

Now we calculate the adsorbate-adsorbate interactions from isotherms, by using the DA model purely as a fitting equation. From Wood's extensive collection [14,15], we have chosen alkanols (methanol, ethanol, 1-propanol, 1-butanol, 1-hexanol and 2-hexanol) as adsorbates and BPL activated carbon for adsorbent [15], whose adsorption isotherms at 298 K are shown in Figure 1. Note that Wood's DR parameters (DA model with $m = 2$) were compiled in terms of $\tilde{\epsilon} = \frac{\epsilon}{RT} = -\ln a_2$ and $\tilde{E} = \frac{E}{RT}$ [15], with which Eq. (3.4) is expressed as

$$N_{22} = \frac{2RT}{\tilde{E}}\tilde{\epsilon} - 1 \tag{3.6}$$

Figure 2 shows N_{22} against adsorbate activity, a_2. As is well-known, the DA model exhibits an anomaly at the $a_2 \to 0$ limit. In principle, at this limit, n_2 must be proportional to a_2, or $\ln n_2 = \ln a_2 + \text{const}$. This leads via Eq. (2.3) to $N_{22} \to 0$. However, as is seen in Figure 2, N_{22} deviates from 0, which means that this limiting condition is not satisfied by the DR model. Attempts were made to rectify the behaviour at this limit [32–34].

Indeed, according to Eq. (3.6), since $\tilde{\epsilon} \to \infty$ as $a_2 \to 0$, $N_{22} \to \infty$ at this limit, which is unphysical. The physically correct limit, i.e., $N_{22} \to 0$, shows that there is no correlation between adsorbate molecules. From a molecular perspective, the lack of adsorbate-adsorbate correlation suggests that the adsorbate-adsorbent interaction is a dominant factor for adsorption at this limit, such as around the oxygen residues or the smaller necks within the pore.

4. Liquid-like adsorbate-adsorbate interactions towards the maximum adsorption capacity

With the help of the DA/DR model as a fitting equation, we have calculated the adsorbate-adsorbate interaction characterized by the excess number from adsorption isotherms. Now we turn to the behaviour towards $a_2 \rightarrow 1$. According to DA, $N_{22} = -1$, as can be seen in Figure 2 and from Eq. (3.4).

Here we show that the limiting behaviour of the DA model, $N_{22} = -1$, is consistent with the previously proposed liquid-like behaviour of the condensed adsorbate molecules in a pore [4]. This can be seen from the Kirkwood-Buff theory for a pure solvent, i.e.,

$$N_{22}^0 + 1 = RTc_2^0\kappa_T^0 \tag{4.1}$$

where c_2^0 is the molar concentration of adsorbate in its pure liquid phase and κ_T^0 is its isothermal compressibility [23]; here we use the superscript 0 to emphasize that it refers to a pure liquid. Table 1 shows, based on experimental data [35], that $RTc_2^0\kappa_T^0$ for liquids is negligibly small compared to 1, which is well known for liquid and solutions in general [36].

Furthermore, the bulk solvent-like behaviour of N_{22} at $a_2 \rightarrow 1$ is consistent with the Gurvitsch rule, i.e., the maximum adsorption capacity measured in volume and measured in molar concentration can be interconverted using the liquid phase molar volume of the adsorbate [15,37,38], V_2^0. Let us translate this to our theoretical framework. The excess number N_{22}, by definition, is related to the Kirkwood-Buff integral, G_{22}, as [23,36]

$$N_{22} = c_2 G_{22} \tag{4.2}$$

and the Kirkwood-Buff integral is defined in terms of the adsorbate-adsorbate distribution function $g_{22}(\vec{r})$, as [23,36]

$$G_{22} = \int d\vec{r}[g_{22}(\vec{r}) - 1] \tag{4.3}$$

where $\vec{r}$ is the position from an adsorbate molecule. Eqs. (4.2) and (4.3) hold true for pure liquids [23] and, following our statistical thermodynamic theory of interface [7], is applicable for adsorbates as well. For an incompressible pure liquid, it has been well known that the Kirkwood-Buff integral is related to the molar volume V_2^0 [36], by

$$G_{22}^0 = -V_2^0 \tag{4.4}$$

with the isothermal compressibility contribution neglected. Hence, $N_{22}^0 = -1$ comes from the inverse relationship between c_2^0 and V_2^0. Thus, the conclusion from the DA model, $N_{22} = -1$, is consistent with the Gurvitsch rule.

Here, the negative sign of the N_{22}^{0}, the excess number of adsorbates around an adsorbate, can be rationalized from its microscopic definition, Eq. (4.3). When the distance between adsorbates, $|\vec{r}|$, is small, $g_{22} - 1 = -1$, contributing negatively to G_{22}. Thus, the fluctuation adsorption theory, through the calculation of adsorbate-adsorbate interaction using the DA model as a fitting equation, clarified the liquid-like nature of condensed adsorbates at higher a_2.

However, when comparing adsorbates to a solution, we must bear in mind, according to the Gibbs phase rule, that the pure bulk solvent has 2 degrees of freedom whereas the adsorbates have 1 degree of freedom [27,30]. In the case of adsorbates, N_{22} comes from the vapour pressure derivative rather than the pressure itself; pressure is no longer an independent thermodynamic variable, and the concept of the isothermal compressibility does not exist for adsorbates. However, the liquid-like behaviour of adsorbates at the maximum capacity was captured by the fluctuation adsorption theory [7].

5. Adsorbate-adsorbate interactions in micropore filling and layering

Let us examine adsorbate-adsorbate interaction at lower a_2. Figure 2 shows that the reduction of a_2 leads to a drastic increase in the excess number, N_{22}. The smaller the adsorbate the larger the excess number. This observation is not limited to n-alcohols. With an extensive collection of DA parameters, Wood [15] reported a positive correlation between $\tilde{E}$ (in Eq. (3.6)) and molar volume (in pure solvent); the larger the molar volume the larger the parameter $\tilde{E}$ hence (via Eq. (3.6)) the smaller the excess number becomes.

That the excess number is larger for smaller adsorbates seems paradoxical at first sight. Because of a good positive correlation between polarizability and molar volume [15], the parameter $\tilde{E}$ also exhibits a good correlation with polarizability. We expect that the higher the polarizability the more dimerization. This expectation is supported by the second virial coefficient B_{22}, a measure of dimerization, in the gas phase [39], which is related to the Kirkwood-Buff integral as $B_{22} = -\frac{1}{2}G_{22}$ [40]. Consequently, the decreasing (i.e., more negative) B_{22} for larger alcohols [39] means the increasing (i.e., more positive) G_{22}. However, in Figure 2, N_{22} of adsorbates decrease with the molecular size, which is contradictory to the expectation from the gas phase dimerization data [39]. The decrease of N_{22} with molecular size is a conclusion based only on the principles of statistical thermodynamics [7] and the accuracy of isotherm fitting by the DA model.

This apparent paradox reflects the balance between the adsorbate-adsorbent and adsorbate-adsorbate interactions. In the gas phase, the adsorbate-adsorbate interaction is strong enough to override the excluded volume effect and G_{22} is positive. In the pore, on the other hand, G_{22} turns into negative, which must be due to the presence of the adsorbent. Indeed, adsorbate-adsorbent interaction, relative to full coverage, is strengthened with the size of alcohol, according to Figure 1. Consequently, the adsorbate-adsorbate interaction for smaller alcohols remains stronger while the one between the larger alcohols is made weaker in the presence of the adsorbent, leading to the observation in Figure 2. Therefore, the balance between the adsorbate-adsorbent and adsorbate-adsorbate interaction is the key to understand Figures 1 and 2 in combination. Thus, the adsorption-induced change of adsorbate-adsorbate interaction is important in understanding isotherms. To reveal the precise molecular details underlying this balance, all-atom molecular simulations are required.

Note that the above discussion may not apply to some adsorbates. For example, water, which forms a specific interaction with the oxygenated species and with each other may exhibit a different isotherm type [15,41]. For formic and acetic acids, due to its tendency for self-association [42], Wood's correlations with polarizability and molar volume involve adjustments [15].

Let us relate our interpretation of the DR model via the fluctuation adsorption theory [7] with the "primary micropore filling" model [37,43]. At low a_2 chiefly the micropore filling [37,43] takes place. Here, the adsorbate excess number N_{22} cannot become positive because adsorbate-adsorbate interaction is not strong enough to overcome the excluded volume effect. Yet N_{22} is larger (less negative) than the pure solvent phase, because the portioning of adsorbates into pores enhance their positional correlation and the values of $g_{22} - 1$ in Eq. (4.3). However, when the micropores are filled and the layer adsorption follows [37,43], the correlation between adsorbates decrease because they are no longer spatially confined. Thus, the DA and DR models do indeed capture the micropore filling and the subsequent layer adsorption via adsorbate-adsorbate correlation, N_{22}. The fluctuation adsorption theory [7] has clarified the underlying molecular mechanism of the DA and DR models.

We have chosen the adsorption of alcohols on activated carbon as examples. However, since our theory is general, without any assumptions made on the nature of adsorbates and adsorbents, it can be applied readily to more porous materials (such as zeolites) and polar and non-polar adsorbates alike.

6. Comparison to the model-based approaches to adsorption

Here we compare our rigorous statistical thermodynamic approach to the commonly adopted theoretical counterparts that can be classified chiefly into the following two categories: simple isotherm models [1–3,5,29,44] and computer simulation [45–48]. An isotherm model is built upon assumptions regarding the energetic and geometrical structure of the surface, such as microporous size and shape, including their distribution, as well as the interactions that take place therein [1–3,5,29,44]. Based on these model assumptions, the functional shape of an isotherm can be derived statistical thermodynamically, and the parameters are determined via fitting [7]. Likewise, molecular dynamics and Monte Carlo simulations are a numerical implementation of statistical thermodynamics, based on a set of model assumptions regarding the atomistic and molecular interactions that take place at the interface [45–48].

Our approach, however, is distinct and different from the model-based approaches [7,49]. Our theory is rigorous with a minimum number of assumptions involved, such as the finite-ranged nature of the interface, but without any assumptions introduced on the geometry of the interface and the energetics of interactions. Such a foundation guarantees certainty, credibility, and clarity in the interpretation of experimental data [7,49].

The two approaches are complementary in strengths and scopes. When the model assumptions reflect the surface structure and the behaviour of adsorbates and the experimental adsorption isotherm can be successfully reproduced under these assumptions, the model-based approach is clearly advantageous [7,49]. However, it is well-known that being able to fit experimental data is not a guarantee for the accuracy of the underlying assumptions [49–51]. Often, multiple different models can fit an experimental isotherm [52–55], and successful fitting can be achieved by the models whose assumptions are different from the system [56] or by purely empirical models without clear a molecular basis [7,49]. This is when our approach can be useful in its ability to probe interactions underlying adsorption directly from the isotherm data alone [7,49].

We emphasize here that the DA (including DR) model has been used purely as a fitting equation of experimental sorption data. As we discussed in Section 1, the DA model is semi-empirical at best, founded upon an ambiguous (and hence, oft-debated) physical foundation of Polanyi's adsorption potential. Moreover, multiple DA equations in combination have often been employed to fit an isotherm [37,43]. For these reasons, we have redeployed the DA model simply as a standard fitting equation of experimental data, with the widely available compilations of fitting parameters in the literature, from which we have extracted the underlying interactions through our rigorous statistical thermodynamic theory. Thus, molecular driving forces can be extracted readily from decades-long compilations of isotherm fitting parameters. Such an approach has previously been demonstrated to be fruitful in clarifying, on a quantitative basis, the driving forces underlying solubilization into water [57,58] and supercritical CO_2 [59,60], headspace vapour pressure [61,62] and solution-phase self-aggregation [63] of flavour molecules, and high-performance affinity chromatography [64].

Note that the "adsorbate-adsorbate interactions" evaluated in this paper are in principle influenced by the adsorbate-adsorbent interaction [7]. The linkage between adsorbate-adsorbate and adsorbate-adsorbent interactions is incorporated already in our rigorous statistical thermodynamic theory, firstly because the ensemble averaging in phase I (Eq. (2.1)) already involve the sorbate-sorbent interactions [7], secondly because adsorbate-adsorbate interaction is determined by the adsorption potential derivative of the adsorbed quantity (Eq. (2.2)), which is necessarily determined by the sorbate-sorbent interaction [7].

7. Conclusion

Adsorbate-adsorbate interaction underlying adsorption isotherm has been quantified from rigorous statistical thermodynamics [7]. This was made possible by combining the fluctuation adsorption theory with the semi-empirical models, such as the Dubinin-Astakhov (DA) model and its special case, the Dubinin-Radushkevitch (DR) model. The adsorbate-adsorbate correlation calculated in this paper is consistent with the primary micropore filling model [37,43] and the Gurvitsch rule. Partitioning of adsorbates into micropores enhances adsorbate-adsorbate correlation but is not strong enough to override the excluded volume effect between the pair. The subsequent layer adsorption [37,43] reduces the correlation eventually to the level of the bulk solvent, consistent with the hypothesized liquid-like behaviour of adsorbates[4] and the Gurvitsch rule. Thus, the fluctuation theory, fruitful in solvation and conformational equilibria of small and macromolecules alike [28,61,63,64], is demonstrated here to be capable of clarifying interfacial phenomena [7] as well.

From a perspective of the semi-empirical models, like DA and DR models, their physical interpretation and the microscopic meaning of their parameters have been established via the fluctuation adsorption theory [7]. The present approach is applicable to other adsorption models that contain more molecular details, such as the enthalpy of adsorption and the effect of pore size distribution [4–6,65–69]. Also, the fluctuation adsorption theory is applicable even when no known model can fit an isotherm.

Appendix A: The adsorption potential

What is confusing about the adsorption potential is the multiplicity of its definition. Firstly, we classify the definitions into the following two categories.

a) The adsorbate activity-based ϵ
b) The adsorbate transfer free energy-based ϵ'

Definition (a) was adopted in the DA and DR models. Consider an adsorbent phase in equilibrium with the vapour phase of adsorbates. Following the standard chemical thermodynamics, the activity of adsorbates, a_2, is defined using the vapour pressure of the adsorbate. The adsorption potential, ϵ, is defined as

$$\epsilon = -RT \ln a_2 \tag{A1}$$

Note also that there is a variant of Eq. (A1), $\epsilon'' = RT \ln\left(1 + \frac{1}{c_2^{II}}\right)$, used mainly in adsorption from a solution phase, which was already discussed in Ref [70] and will not be analyzed here.

Secondly, we aim here to clarify the molecular basis of definition (b), ϵ', as the work required to move an adsorbate molecule from the interface (phase I) to the vapour phase (II). If we simply used the adsorbate chemical potentials in phases I and II, μ_2^I and μ_2^{II}, the adsorption potential would be simply zero, because of the equilibrium condition, $\mu_2^I = \mu_2^{II}$, which leads to $\mu_2^{II} - \mu_2^I = 0$. This is different from Polanyi's conclusion, necessitating a careful, microscopic approach to defining the adsorption potential.

Let us start from the foundation of the fluctuation adsorption theory [7]. Following Gibbs, we have introduced the interface as the difference between the entire system (adsorbate and adsorbent phases in equilibrium) and the reference systems (adsorbate and adsorbent phases separately) [7,29]. Generalizing Gibbs' approach to arbitrary interfacial shapes and geometries, we then have postulated that the effect of the interface is confined within a finite distance and introduced the volume of the local interfacial subsystem, v [7]. Considering that the number of adsorbate molecules in the local interfacial subsystem $\langle n_2^I \rangle$ (denoted as $\langle n_2^* \rangle$ in Ref [7]) is much larger than that in the bulk vapour phase [7], we can introduce the density of adsorbates in the interfacial subsystem, $c_2^I = \langle n_2^I \rangle / v$. The adsorbate chemical potentials both phases ($\alpha = I, II$) can be expressed as

$$\mu_2^\alpha = \mu_2^{*\alpha} + kT \ln c_2^\alpha \Lambda_2^3 \tag{A2}$$

where $\mu_2^{*\alpha}$ is the chemical potential of adsorbate in phase α with its centre of mass position fixed [36]. Eq. (A2) is valid not only in canonical but also in grand canonical, isobaric, and partially open ensembles as well [40,71]. Since the momentum partition function, Λ_2, is common in both phases, the equilibrium condition, $\mu_2^I = \mu_2^{II}$, leads to the following relationship:

$$\mu_2^{*I} + kT \ln c_2^I = \mu_2^{*II} + kT \ln c_2^{II} \tag{A3}$$

Eq. (A3) leads to a statistical thermodynamic interpretation of the adsorption potential ϵ' as the work required to move an adsorbate molecule from a fixed centre-of-mass position in the vapour phase (phase II) to a fixed centre-of-mass position in the interphase phase (phase I). This definition, under the equilibrium condition (Eq. (A3)), yields

$$\epsilon' = \mu_2^{*I} - \mu_2^{*II} = kT \ln \frac{c_2^{II}}{c_2^I} \tag{A4}$$

which is just like the general statistical thermodynamic expression for the transfer free energy between two phases in equilibrium [36]. If we use the ideal gas equation of state to convert c_2^I in Eq. (A4) to the pressure for phase I, P^I, or what Polanyi called the "vapour tension" [18], we obtain

$$\epsilon' = \mu_2^{*I} - \mu_2^{*II} = kT \ln \frac{P}{P^I} \tag{A5}$$

where $P^{II} = P$ is the pressure of the vapour phase. Eq. (A5) is identical in form with the adsorption potential.

Thus, we have established a statistical thermodynamic foundation of the adsorption potential ϵ', which is the work of transferring a fixed adsorbate molecule from the vapour phase to the interface. Note that the two definitions (Eqs. (A1) and (A5)) have fundamentally different physical meanings. In both cases, the adsorption isotherm is the function of the adsorption potential would be obvious. For the definition ϵ', which is a function of c_2^I, is a function of the surface excess, $\langle n_2 \rangle = c_2^I v$ (because $c_2^I \gg c_2^{II}$), hence the surface excess $\langle n_2 \rangle$ is the function of the surface potential ϵ'. For the definition ϵ, the adsorption isotherm ($\langle n_2 \rangle$ as a function of a_2) means $\langle n_2 \rangle$ is a function of ϵ. Either way, the adsorption isotherm is a function of the adsorption potential. Plotting isotherms against the adsorption potential is beneficial because isotherms measured at different temperatures frequently fall onto a single characteristic curve [1,2,4,17–21]. The statistical thermodynamic mechanism underlying such common observation requires the extension of the fluctuation theory and will be discussed in a forthcoming paper.

Appendix B: Triplet correlation in the Dubinin-Radushkevich model

For simplicity, here we deal with the DR model, expressed in the logarithmic form (Eq. (3.3) with $m = 2$). Differentiating it twice, we obtain

$$\left(\frac{\partial^2 \ln\langle n_2 \rangle}{\partial(\ln a_2)^2}\right)_T = -\frac{2(RT)^2}{E} \tag{B1}$$

Based on Eq. (B1), can we give a clear physical interpretation of the parameter E? To do so, let us start from

$$\left(\frac{\partial^2 \ln\langle n_2 \rangle}{\partial(\ln a_2)^2}\right)_T = \frac{\partial}{\partial \ln a_2}\left[\frac{1}{\langle n_2 \rangle}\left(\frac{\partial \langle n_2 \rangle}{\partial \ln a_2}\right)_T\right] \tag{B2}$$

$$= \frac{1}{\langle n_2 \rangle}\left(\frac{\partial^2 \langle n_2 \rangle}{\partial(\ln a_2)^2}\right)_T - \frac{1}{\langle n_2 \rangle^2}\left[\left(\frac{\partial \langle n_2 \rangle}{\partial \ln a_2}\right)_T\right]^2$$

The first term can be evaluated by further differentiation of Eq. (2.2) as

$$\left(\frac{\partial^2 \langle n_2 \rangle}{\partial(\ln a_2)^2}\right)_T = \langle n_2^3 \rangle - \langle n_2^2 \rangle\langle n_2 \rangle - 2\langle n_2 \rangle(\langle n_2^2 \rangle - \langle n_2 \rangle^2) = \langle (n_2 - \langle n_2 \rangle)^3 \rangle \tag{B3}$$

Eq. (B3) signifies the triplet correlation minus doublet correlation. The second term is the square of Eq. (2.2). We finally obtain

$$-\frac{2(RT)^2}{E}=\frac{\langle(n_2-\langle n_2\rangle)^3\rangle}{\langle n_2\rangle}-\frac{\langle(n_2-\langle n_2\rangle)^2\rangle^2}{\langle n_2\rangle^2} \tag{B4}$$

Thus, the parameter E in the DR model can be expressed in terms of the triplet and doublet correlation functions between adsorbates.

To generalize Eq. (B4) to the parameter E in the DA theory, we need to evaluate the mth derivative of Eq. (3.3). This will lead to the presence of correlations up to $(m+1)$-body, which is quite complicated.

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Table 1. The negligibility of $RTc_2^0\kappa_T^0$ in Eq. (4.1) compared to 1 in pure liquids. Experimental data at 298 K from Ref [35].

	Density kg dm^{-3}	c_2^0 mol m^{-3}	κ_T^0 (TPa)$^{-1}$	$RTc_2^0\kappa_T^0$
Methanol	0.78686	2455.86	1248	7.594×10^{-3}
Ethanol	0.76540	1661.39	1153	4.746×10^{-3}
1-Propanol	0.79991	1330.97	1006	3.317×10^{-3}
1-Butanol	0.80854	1090.85	942	2.546×10^{-3}
1-Hexanol	0.81565	798.092	836	1.653×10^{-3}

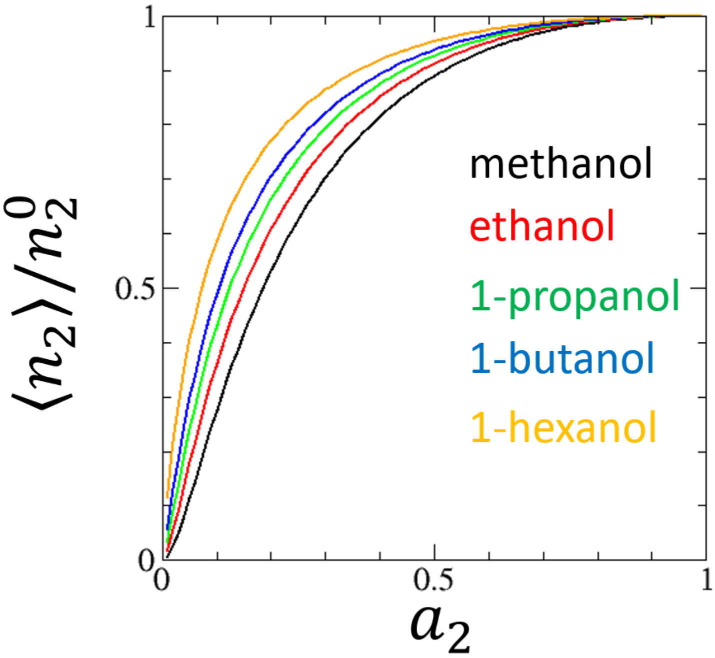

Figure 1. The adsorption isotherm of alcohols on microporous carbons. The fitting parameters for the DA model have been taken from Table 3 of Ref [15] (for BPL activated carbon).

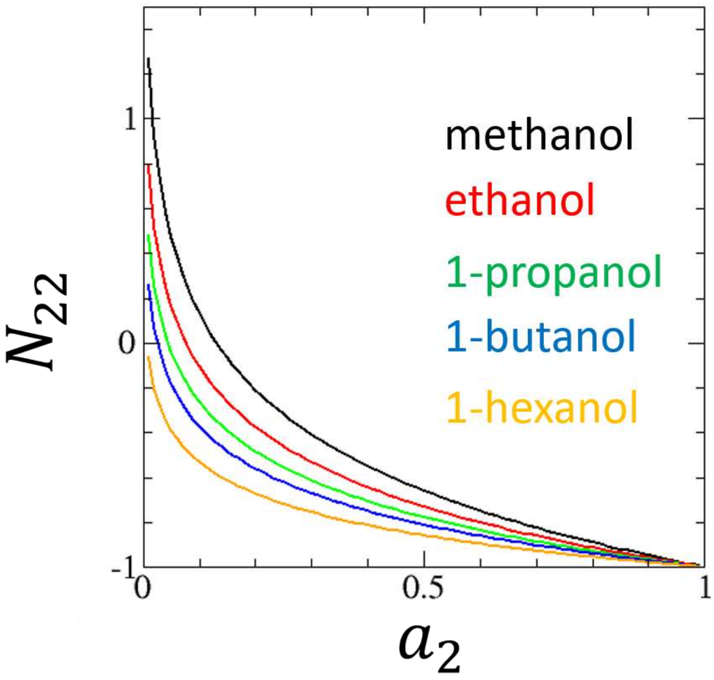

Figure 2. The excess adsorbate number around an adsorbate, N_{22}, calculated from the adsorption isotherm fitting in Figure 1 via Eq. (3.6).