MOLECULAR SIMULATION OF FRAMEWORK MATERIALS

Potential theory for gate adsorption on soft porous crystals

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We demonstrate that an adsorption potential at the gate adsorption pressure of soft porous crystals (SPCs) based on the Polanyi’s potential theory of adsorption shows a constancy to temperature. This was done using grand canonical Monte Carlo simulations and free energy analysis, which were carried out with a simplified stacked-layer SPC model. This finding implies that the characteristic curve obtained from an experimental gate adsorption isotherm on SPCs can be used to predict the temperature dependence of the gate-opening pressure, even though the potential theory of adsorption does not take into account the deformation of porous solids during the adsorption. We develop a modified potential theory for gate adsorption and show that the derived relation has a form that the Gibbs free energy change due to the host framework deformation per guest molecule, \(-\Delta G_{\text{host}}/N\), and a correction term, \(C\), are added to the expression of the original potential theory of adsorption. The term \(C\) is not an empirical correction factor but is the difference of intermolecular interaction potential and entropy between the bulk liquid phase at the saturated state and the adsorbed phase, originating from spatial constraint of adsorbed guest molecules in the host. By evaluating the modified expression for gate adsorption using the simulation results, we demonstrate that the constancy of the adsorption potential to temperature results from a compensation effect between three terms: guest-host interaction potential per guest molecule, \(-\Delta G_{\text{host}}/N\) and \(C\), which have a temperature dependence.

Keywords: gate adsorption; potential theory; characteristic curve; free energy analysis

1. Introduction

Porous metal–organic frameworks, also known as porous coordination polymers (PCPs), are a new class of nanoporous materials which have a wide range of crystal structures and host–guest properties.\([1–6]\) In particular, soft porous crystals (SPCs),\([7]\) which were previously classified as the third-generation PCPs by Kitagawa and Kondo \([4]\) and Kitagawa et al. \([6]\), have attracted much attention because of their anomalous adsorption behaviour, called ‘gate adsorption’ \([8]\) and ‘breathing effect’.\([9]\) Under this behaviour, guest molecules are adsorbed abruptly at a certain gas pressure accompanied by the deformation of the host framework. SPCs have various structural motifs such as one-dimensional chains,\([10,11]\) two-dimensional (2D) interdigitated layers,\([12,13]\) 2D elastic layered structures,\([8,14]\) three-dimensional (3D) mutually interpenetrated frameworks,\([15,16]\) 3D frameworks with breathing channels \([9,17]\) and zeolitic frameworks.\([18–20]\) The high sensitivity of gate adsorption and the breathing effect to the gas pressure suggests potential applications such as gas storage,\([21]\) separation,\([22,23]\) adsorption heat pump \([24]\) and molecular sensor \([25]\); however, the rational design of SPCs for a specific application is still challenging because it requires insight into the mechanisms of gate adsorption and the breathing effect. Thus, to shed light on the nature of adsorption-induced structural transitions, molecular simulation studies have been performed for various SPCs,\([26–34]\) but these transitions have not been completely understood yet.

Coudert et al. \([35]\) first developed an osmotic thermodynamic model for gate adsorption and the breathing effect: they devised an analytical free energy analysis method to determine the change in the Helmholtz free energy of the host framework, \(\Delta F_{\text{host}}\), during the adsorption-induced structural transition. Their method is simple and useful because it only requires fitting of a Langmuir isotherm to a plateau region of the experimental isotherm after the structural transition and integrating it to obtain the change in the grand potential of the guest, \(\Delta \Omega_{\text{guest}}\). The \(\Delta F_{\text{host}}\) value can be estimated such that the free energy change of the system, which is the sum of \(\Delta F_{\text{host}}\), \(\Delta \Omega_{\text{guest}}\) and \(P\Delta V\) terms (\(P\), gas pressure; \(\Delta V\), volume change of the host), becomes zero at the experimental gate adsorption pressure. Using their method, the temperature-loading phase diagrams of MIL-53 for Xe was successfully predicted, providing a good agreement with the experiment.\([36]\) Neimark et al. \([37,38]\) incorporated adsorption-induced stress exerted on SPCs into the osmotic thermodynamic model. They showed that the model provided a good description of the...
hysteresis phenomena experimentally observed during the breathing transitions for Xe and CH₄ adsorption on MIL-53, and concluded that the structural transition occurred when the stress reached a certain value that the host cannot resist.

Kanoh et al. applied the Hill equation, which was developed for demonstrating the allosteric effect on the binding of O₂ to haemoglobin (not a first-order phase transition but reaction equilibria), to reproduce the experimental adsorption isotherm of CO₂ on Elastic transition but reaction equilibria), to reproduce the experimental adsorption isotherms on one of the SPCs \([\text{Cu} (\text{dihydroxybenzonic acid)}]_{2}(4,4’-\text{bipyridine}) \) \([\text{Cu}(\text{dhhbc})]_{2}(4,4’-\text{bpy})\) for various adsorbates. However, more than two experimental adsorption isotherms at different temperatures are needed to predict the temperature dependence of the adsorption-induced structural transition using the above-mentioned theorems.

Recently, Yamazaki et al. \([43]\) reported that, based on Polanyi’s \([44]\) potential theory of adsorption, a temperature-invariant ‘characteristic curve’ was obtained from the experimental adsorption isotherms on one of the SPCs \([\text{Cu} (\text{dihydroxybenzonic acid})]_{2}(4,4’-\text{bipyridine}) \) \([\text{Cu}(\text{dhhbc})]_{2}(4,4’-\text{bpy})\) for various adsorbates. However, more than two experimental adsorption isotherms at different temperatures are needed to predict the temperature dependence of the adsorption-induced structural transition using the above-mentioned theorems.

2. Simulation models and theory

Figure 1 shows a simplified model of a stacked-layer SPC, which was used in our previous studies \([30,32]\); this consists of smeared-atom layers, which have uniform 2D solid density, and pillaring atoms located on one side of the layers. The interlayer width of the host framework is \(h\), and it is assumed that the \(h\) value for all the neighbouring layers is the same.

The guest–guest interaction potential, \(\phi_{gg}\), was modelled with the 12-6 LJ potential; the potential parameters used were those of argon \((\sigma_{gg} = 0.341 \text{ nm} \text{ and } e_{gg}/k_{B} = 119.8 \text{ K})\). The interaction potential between a guest molecule and each host layer, \(\phi_{gh}\), was calculated using the 10-4 LJ potential:

\[
\phi_{gh}(z_{ik}) = 2 \pi \rho_{h} \sigma_{gh}^{2} \left( \frac{\sigma_{gh}^{2} - 4}{z_{ik}^{5}} - \frac{\sigma_{gh}^{4}}{z_{ik}^{5}} \right), \tag{1}
\]

where \(\rho_{h}\) is the atomic number density of the host layer (which was set to be \(\rho_{h} = \rho_{0} \sigma_{gg}^{2} = 2.2\)), and \(z_{ik}\) is the distance between the \(i\)th guest molecule and the \(k\)th layer. The LJ parameters for the guest–host layer interaction potential, \(\sigma_{gh}\) and \(e_{gh}\), were calculated according to the Lorentz–Berthelot mixing rules \([\sigma_{gg} + \sigma_{hh}] / 2 = \sigma_{gh}\) and \((e_{gg} e_{hh})^{1/2} = e_{gh}\), where the interaction parameters for the host layer were set to be \(\sigma_{hh} = 0.34 \text{ nm} \text{ and } e_{hh}/k_{B} = 28 \text{ K}\). The guest–host interaction potential, \(\phi_{gh}\), was modelled with the 12-6 LJ potential; the potential parameters used were those of argon \((\sigma_{gg} = 0.341 \text{ nm} \text{ and } e_{gg}/k_{B} = 119.8 \text{ K})\). The interaction potential between a guest molecule and each host layer, \(\phi_{gh}\), was calculated using the 10-4 LJ potential:

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The host layer–layer interaction potential per unit area of one layer, $\phi_{hh}$, was derived from an area integral of the 10-4 LJ potential as

$$
\phi_{hh}(h_{kl}) = 2\pi\rho^2_{*} h_{kl} \left\{ \frac{2}{5} \left( \frac{\sigma_{hh}}{h_{kl}} \right)^{10} - \left( \frac{\sigma_{hh}}{h_{kl}} \right)^{14} \right\},
$$

where $h_{kl}$ is the distance between the $k$th and $l$th layers, which can be expressed as $(l-k)h$. The host layer–pillar interaction, $\phi_{hp}$, and host pillar–pillar interaction, $\phi_{pp}$, were calculated by the 10-4 LJ and the 12-6 LJ potentials, respectively. The LJ parameters of the pillar were the same as those of the guest molecule. The number density of the pillar was set to be $1/(100 \sigma_{gg}^2)$. The guest–pillar interaction was neglected because of the low density of the pillars. Thus, total inter-framework potential of the host, $\Phi_{hh}$, is expressed as

$$
\Phi_{hh} = L_x L_y \sum_{k=1}^{N_1-1} \sum_{l=k+1}^{N_1} \phi_{hh}(h_{kl}) + \sum_{k=1}^{N_1} \sum_{l=k+1}^{N_1} \phi_{pp}(r_{kl}),
$$

where $N_1$ is the total number of the host layers, $L_x$ and $L_y$ are lengths of the layer in the $x$–$y$ directions and $d_p$ is the length of the pillar (distance from a layer to an attached pillar) and $r_{kl}$ is the distance between the pillars located at different layers. The interlayer width, $h_0$, at the degassed state was set to be $1.75\sigma_{gg}$ such that $\Phi_{hh}$ can be minimised by tuning the pillar length $d_p$. It is also worth noting that the work required to expand the interlayer spacing against the interlayer attractive force is increased as the pillar length is decreased, and finally for the system with $h_0 = 1.3\sigma_{gg}$, the gate adsorption is definitely not observed because the global minimum of the free energy of the system does not switch from the closed state to the open state below the saturated vapour pressure [32] (see also Section 3.1 for details).

All the potentials ($\phi_{gg}$, $\phi_{gh}$, $\phi_{hh}$, $\phi_{hp}$ and $\phi_{pp}$) were cut and shifted at the distance of $5 \sigma_{gg}$. As shown in Figure 1, the simulation cell has seven unit cells, which contain one layer and an interlayer space. The size of the unit cell was set to be $L_x \times L_y = 10\sigma_{gg} \times 10\sigma_{gg}$ in the $x$–$y$ layer directions and $1.60\sigma_{gg} - 2.05\sigma_{gg}$ in the $z$-direction normal to the layers. Periodic boundary conditions were applied for all the directions.

Grand canonical Monte Carlo (GCMC) simulations were conducted to obtain the adsorption isotherms for various interlayer widths ($1.60\sigma_{gg} - 2.05\sigma_{gg}$) with a step of 0.01$\sigma_{gg}$. The reduced temperature, $T^* = k_B T/\epsilon_{gg}$, was changed from 0.8 to 1.2. The length of the simulation run was at least $2.5 \times 10^7$ steps and $2 \times 10^8$ steps for the equilibration and sampling, respectively. The relation between the bulk gas pressure and the chemical potential was obtained from the Johnson–Zollweg–Gubbins [55] equation of state for the LJ fluid (LJ-EOS).

The thermodynamic states of the simplified stacked-layer SPC model at each gas pressure and interlayer width $h$ were determined by calculating the osmotic free energy, $\Omega^{OS}$, as [35]:

$$
\Omega^{OS}(\mu, h) = F_{host}(h) + PV(h) + \Omega_{guest}(\mu, h),
$$

where $\mu$ is the chemical potential of the adsorbed guest molecules, $F_{host}$ is the Helmholtz free energy of the host, $P$ is the bulk gas pressure at $\mu$, $V$ is the volume of the host with the interlayer width $h$ and $\Omega_{guest}$ is the grand thermodynamic potential of the adsorbed guest molecules. The grand thermodynamic potential can be calculated by integrating the GCMC adsorption isotherm, $N(\mu, h)$, with respect to the chemical potential under constant $T$ and $V(h)$ as

$$
\Omega_{guest}(\mu, h) = -\int_{-\infty}^{\mu} N(\mu, h) \, d\mu.
$$

The osmotic free energy change, $\Delta \Omega^{OS}$, with the change of the interlayer distance from $h_0$ to $h$ at constant $\mu$ is given by

$$
\Delta \Omega^{OS}(\mu, h) = \Omega^{OS}(\mu, h) - \Omega^{OS}(\mu, h_0) = \Delta F_{host} + P \Delta V(h) + \Delta \Omega_{guest}(\mu, h),
$$

where $\Delta F_{host}$, $\Delta V$ and $\Delta \Omega_{guest}$ are the changes in the Helmholtz free energy of the host, the volume of the host and the grand thermodynamic potential, respectively. The Helmholtz free energy change of the host, $\Delta F_{host}(h) = F_{host}(h) - F_{host}(h_0)$, was approximated to the change in the total inter-framework potential, $\Delta \Phi_{hh}(h) = \Phi_{hh}(h) - \Phi_{hh}(h_0)$, by assuming that the entropy change of the host is negligible.

3. Results and discussion

3.1 Theoretical gate adsorption isotherms

Figure 2 shows the typical osmotic free energy changes per unit cell, $\Delta \Omega^{OS} = \Delta \Omega^{OS}/\sigma_{gg}$, as a function of the interlayer width and gas pressure at $T^* = 1.0$. The osmotic free energy profiles were obtained from Equation (6) using the GCMC adsorption isotherms. At zero pressure, the global minimum is located at $h = h_0$ (closed state), and the system becomes unstable with opening the interlayer width from $h_0$ against the interlayer attractive force. The secondary minimum appears at $h^* = h_0/\sigma_{gg}$ as the gas pressure increases, because the adsorbed guests stabilise the system. The closed state ($h_0 = h_0/\sigma_{gg} = 1.75$) and the open state ($h^* = 1.99$) become bistable at the reduced pressure of $P^{*} = P\sigma_{gg}^2/\epsilon_{gg} = 6.8 \times 10^{-4}$. According to the theory of equilibrium, the adsorption-induced structural transition
occurs at this pressure (hereafter, equilibrium gate adsorption pressure: \( P^*_{\text{gate}} = P_{\text{gate}}^{\text{gg}} e_{\text{gg}} / e_{\text{gg}} \)). However, if the energy fluctuation of the system is smaller than the energy barrier, \( E^\text{cl} \), located at \( h^* = 1.87 \) between the two stable states, the equilibrium structural transition should not be observed, i.e., a further increase in the bulk gas pressure is required to reduce the energy barrier, to switch the global minimum from the closed state to the open state, and, finally, to cause a spontaneous structural transition (see \( \Delta \Omega^{\text{OS}} \) at \( P^* = 1.25 \times 10^{-3} \) in Figure 2; the energy barrier is designated as \( E^\text{op} \)). Then, in the desorption process, the system stays at the open state until the energy barrier, \( E^\text{cl} \), becomes smaller than the energy fluctuation of the system (see \( \Delta \Omega^{\text{OS}} \) at \( P^* = 5.4 \times 10^{-4} \) in Figure 2). This should be the reason why a hysteresis is experimentally observed during the adsorption-induced structural transition in SPCs; however, it is worth noting that the gate-closing pressure is much closer to the equilibrium gate adsorption pressure than the gate-opening pressure; a detailed mechanism of the structural transition has been reported in our previous studies.[30,32] Therefore, for the sake of simplicity, in this study, we only provide a discussion based on the theory of equilibrium.

The resulting gate adsorption isotherm at \( T^* = 1.0 \) obtained from the free energy analysis using the GCMC data is plotted in Figure 3. The adsorption isotherm remains zero at less than \( P^*_{\text{gate}} = 6.8 \times 10^{-4} \), because the interlayer width of the closed state is smaller than the size of the guest molecule and the \( \Delta \Omega^{\text{OS}} \) value is always positive (see Figure 2). Then, at \( P^*_{\text{gate}} \), the adsorption isotherm shows a steep rise, because the global minimum of the system shifts from the closed state to the open state (see Figure 2) and the gate-opening is induced. Namely, the gate adsorption isotherms at different temperatures in the range between \( T^* = 0.80 \) and 1.2 were also obtained in the same manner and are plotted in Figure 3. It is clear that the gate adsorption pressure increases, and the adsorption amount decreases after the gate-opening as the temperature increases. The interlayer width \( h^* \) at the gate adsorption pressure \( P^*_{\text{gate}} \) was increased from 1.75 (\( = h_0^* \)) to 1.99 at \( T^* = 0.80 \) to 1.1, and to 1.98 at \( T^* = 1.2 \).

### 3.2 Potential theory for gate adsorption

The characteristic curves based on the Polanyi’s [44] potential theory of adsorption were obtained from the theoretical gate adsorption isotherms obtained as above. The adsorption volume, \( V_{\text{guest}} \), was calculated from the number of adsorbed guest molecules, \( N \), and the number density of the saturated bulk liquid LJ argon, \( \rho_{\text{liq}} \), at the adsorption temperature

\[
V_{\text{guest}} = \frac{N}{\rho_{\text{liq}}},
\]

where the bulk liquid density was taken from Lotfi et al. [54]. The adsorption potential \( A(P) \), which corresponds to the compression work to transform the gas phase at pressure \( P \) to the adsorbed phase, was calculated according to Polanyi [44] as

\[
A(P) = \mu_{\text{liq}}(P_0) - \mu_{\text{gas}}(P),
\]

where \( \mu_{\text{liq}}(P_0) \) is the chemical potential of the bulk liquid.
at saturated vapour pressure $P_0$,[54] and $\mu_{\text{gas}}(P)$ is that of the gas phase at pressure $P$ that can be obtained from LJ-EOS.[55]

The characteristic curves ($V^*_{\text{guest}} = V_{\text{guest}}/\sigma_{gg}^3$ vs. $A^* = A/\sigma_{gg}$) obtained from the simulated gate adsorption isotherms using Equations (7) and (8) are shown in Figure 4.

The characteristic curves over the range of temperatures from $T^* = 0.8$ to $1.0$ show good agreement with each other: the deviations of $V^*_{\text{guest}}$ at $A^*(P_0) = 0$ are less than $\pm 2.4\%$ from the centre value and those of the $A^*(P_{\text{gate}})$ value are less than $\pm 0.64\%$. However, the characteristic curves at $T^* = 1.1$ and $1.2$ have large deviations of $V^*_{\text{guest}}$ from these four characteristic curves, which should be because the compressibility of the adsorbate rapidly increases upon approaching the critical temperature $T^* = 1.3$ and the adsorbed phase is in a highly compressed state compared with that of the saturated bulk liquid at the adsorption temperature. We therefore re-evaluated the adsorption volume $V_{\text{guest}}$ according to Ozawa et al. [46] as

$$V^*_{\text{guest}} = \frac{N}{\rho_{\text{liq}}(T_b) \exp[\alpha(T_b - T)]},$$

where $T_b$ is the boiling temperature, $\rho_{\text{liq}}(T_b)$ is the number density of the saturated bulk liquid at $T_b$ (the data were taken from Lotfi et al. [54] in this study) and $\alpha = 0.0025$ is the thermal expansion coefficient of the superheated liquid. The re-calculated characteristic curves using Equations (8) and (9) are shown in Figure 5. The convergence of $V^*_{\text{guest}}$ at $A^*(P_0) = 0$ was considerably improved and the deviations were decreased to less than $\pm 1.3\%$ over the whole range of temperatures $T^* = 0.8–1.2$; however, the convergence just after the gate adsorption becomes worse, which suggests that the compressibility of the adsorbed phase depends on the gas pressure.

While the adsorption potential at the gate adsorption pressure $A^*(P_{\text{gate}})$ is almost invariant to temperature in the whole temperature range without any modifications (the deviations are less than $\pm 2.0\%$ from the centre value), which can well explain the experimental results reported by Yamazaki et al. [43]: the characteristic curves for methane adsorption on Cu(dhbc)$_2$(4,4'-bpy) at $T^* = 1.1$ and $1.2$ ($\sigma_{gg}/k_B = 148.1$ K) are in good agreement. This is curious because the original potential theory of adsorption does not take into account the deformation of porous solids during the adsorption. We therefore constructed a model to derive a thermodynamic theory for the gate adsorption behaviour based on the Polanyi's potential theory. Figure 6 shows two isobaric-isothermal systems including an SPC crystal and a bulk gas phase. In one system (Figure 6(a), hereafter pre-transition state), the SPC crystal is closed, and in the other system (Figure 6(b), hereafter post-transition state), it is opened. The two systems have the same number of fluid molecules, $N_f$. Adsorption of the fluid molecules on the outer surface of the SPC crystal was neglected for both the systems. In the pre-transition state, $N_f$ fluid molecules are all in the gas phase; in the post-transition state, $N$ molecules are

![Figure 4](image1.png)

Figure 4. (Colour online) Characteristic curves obtained from the theoretical gate adsorption isotherms shown in Figure 3, where $V^*_{\text{guest}} = V_{\text{guest}}/\sigma_{gg}^3$ is the adsorption volume from Equation (7) and $A^* = A/\sigma_{gg}$ is the adsorption potential from Equation (8).

![Figure 5](image2.png)

Figure 5. (Colour online) Characteristic curves obtained from the theoretical gate adsorption isotherms shown in Figure 3, where $V^*_{\text{guest}} = V_{\text{guest}}/\sigma_{gg}^3$ is the adsorption volume from Equation (9) and $A^* = A/\sigma_{gg}$ is the adsorption potential from Equation (8).

![Figure 6](image3.png)

Figure 6. (Colour online) Schematic illustration of isobaric-isothermal systems including an SPC crystal and a bulk gas phase: (a) pre-transition state with the closed SPC crystal and $N_f$ gas molecules and (b) post-transition state with the opened SPC crystal encapsulating $N$ guest molecules and $N_f - N$ gas molecules. The two systems are in equilibrium at pressure $P_{\text{gate}}$. 
adsorbed in the SPC crystal, and therefore \( N_i - N \) molecules are in the gas phase. The two systems are in equilibrium at pressure \( P_{gate} \), and thus the Gibbs free energies of the two systems are equal:

\[
G_{pre} = G_{post}.
\]

This equation gives the following relation:

\[
G_{host}^{pre} + N_i \mu_{gas}(P_{gate}) = G_{host}^{post} + (N_i - N) \mu_{gas}(P_{gate}) + G_{guest},
\]

where \( G_{host}^{pre} \) and \( G_{host}^{post} \) are the Gibbs free energy of the SPC crystals at the pre- and post-transition states, respectively; \( \mu_{gas}(P_{gate}) \) is the chemical potential of the bulk gas phase at pressure \( P_{gate} \), and \( G_{guest} \) is the Gibbs free energy of the adsorbed guest molecules. By defining the changes in the Gibbs free energy of the SPC crystal as \( \Delta G_{host} = G_{host}^{post} - G_{host}^{pre} \), Equation (11) can be rewritten as

\[
\Delta G_{host} = G_{host}^{post} - G_{host}^{pre} = -N_i \mu_{gas}(P_{gate}) - G_{guest},\]

where \( \Delta G_{host} \) is the chemical potential of the guest molecule excluding the contribution of the guest–host interaction.

It should be noted that the first and second terms in the left-hand side of Equation (12) are not equal because we are considering the equilibrium relation between the pre- and post-transition states, not that between gas and guest in the post-transition state. If we assume that the adsorbed phase is similar to the bulk liquid phase as is the case of the original potential theory of adsorption, \( G_{guest} \) can be expressed as

\[
G_{guest} = N [ \mu_{liq}(P_0) + \mu_{gh} ],
\]

where \( \mu_{gh} \) is the guest–host interaction for one guest molecule. By substituting Equation (13) into Equation (12) and using Equation (8), we obtain

\[
A(P_{gate}) = \mu_{liq}(P_0) - \mu_{gas}(P_{gate}) = -u_{gh} - \frac{\Delta G_{host}}{N}. \tag{14}
\]

Equation (14) indicates that, in the case of gate adsorption, the work for the host deformation per guest molecule, \( -\Delta G_{host}/N \), should be added to the expression of the original potential theory of adsorption: \( A(P) = \mu_{liq}(P_0) - \mu_{gas}(P) = -u_{gh} \).

We tested Equation (14) using the GCMC data. The adsorption potentials for gate adsorption, \( A(P_{gate}) \), at each temperature were obtained from the results of the adsorption isotherms shown in Figure 3. On the other hand, the \( -u_{gh} - \Delta G_{host}/N \) term of the right-hand side of Equation (14) was estimated separately. In particular, \( u_{gh} \) and \( N \) were taken from the results of the GCMC simulations, and \( \Delta G_{host} \) was calculated by Equation (3) with the relation of \( \Delta G_{host} = \Delta P_{host} + P_{gate} \Delta V_{host} = \Delta G_{host} + P_{gas} \Delta V_{host} \) (\( \Delta V_{host} \) change in the volume of SPC between the pre- and post-transition states). A comparison between \( A(P_{gate}) \) and \( -u_{gh} - \Delta G_{host}/N \) is shown in Figure 7. The value of \( -u_{gh} - \Delta G_{host}/N \) is almost independent of the temperature along with \( A(P_{gate}) \); however, a marked difference can be observed between the two values at all temperatures, indicating that Equation (14) is not adequate. This error possibly originates from the assumption made in the derivation of Equation (14) (the adsorbed molecules are in the bulk liquid state). This suggests that, as shown in Figure 1, the adsorbed guest molecules form a 2D-like liquid and have smaller coordination number than the 3D bulk liquid; therefore, the intermolecular interaction between the guest molecules is overestimated. Moreover, the entropy of the guest molecules should also be different from those of the bulk liquid, i.e. \( \mu_{liq}(P_0) \) in Equation (14) should be replaced by \( \mu_{guest}(P_0) \). Therefore, the equation can be rewritten as

\[
\mu_{guest}(P_0) - \mu_{gas}(P_{gate}) = -u_{gh} - \frac{\Delta G_{host}}{N}, \tag{15}
\]

where \( \mu_{guest}(P_0) \) is the chemical potential of the guest molecule excluding the contribution of the guest–host interaction at pressure \( P_0 \), which is not the saturated vapour pressure but the pressure required for condensing the guest molecules between the host layers. Substituting \( \mu_{gas}(P_{gate}) = A(P_{gate}) - \mu_{liq}(P_0) \) from Equation (14) into Equation (15), we obtain

\[
A(P_{gate}) = -u_{gh} - \frac{\Delta G_{host}}{N} + \mu_{liq}(P_0) - \mu_{guest}(P_0). \tag{16}
\]

Using the thermodynamic state function, \( G = \mu N = U - TS + PV (U, \text{ internal energy}; S, \text{ entropy}) \) and \( U = 3k_B T N/2 + u\tilde{N} (u, \text{ intermolecular interaction potential per molecule}) \), \( \mu_{liq}(P_0) \) and \( \mu_{guest}(P_0) \) can be
represented as

\[
\mu_{\text{liq}}(P) = \frac{3k_B T}{2} + u_{\text{liq}} - T s_{\text{liq}} + P_0 v_{\text{liq}}
\]

and

\[
\mu_{\text{guest}}(P') = \frac{3k_B T}{2} + u_{\text{gg}} - T s_{\text{guest}} + P'_0 v_{\text{guest}}.
\]

where \(u_{\text{liq}}\) is the intermolecular interaction potential per molecule of the bulk liquid, \(u_{\text{gg}}\) is the guest–guest interaction potential per molecule of the adsorbed phase, \(s_{\text{liq}}\) and \(s_{\text{guest}}\) are entropies per molecule of the bulk liquid and adsorbed phase, \(v_{\text{liq}}\) and \(v_{\text{guest}}\) are the volumes per molecule of the bulk liquid and adsorbed phase, respectively. Finally, the difference between Equations (17) and (18) can be arranged as

\[
\mu_{\text{liq}}(P) - \mu_{\text{guest}}(P') = u_{\text{liq}} - u_{\text{gg}} - T(s_{\text{liq}} - s_{\text{guest}}) = C.
\]

where the \(P_0 v_{\text{liq}} - P'_0 v_{\text{guest}}\) term was neglected because of its small quantity. By substituting Equation (19) into Equation (16), we obtain

\[
A(P_{\text{gate}}) = -u_{\text{gg}} - \frac{\Delta G_{\text{host}}}{N} + C.
\]

We tested the modified expression in Equation (20) by using the simulation data. The \(u_{\text{liq}}\) and \(s_{\text{liq}}\) values were taken from Johnson et al. [55]; \(u_{\text{guest}}\) was obtained from the GCMC simulations. Then, the entropy of the guest molecule, \(s_{\text{guest}}\), was calculated using the following expression:

\[
s_{\text{guest}} = \frac{1}{T} \left[ \frac{U_{\text{guest}} - \Omega_{\text{guest}}}{N} - \mu_{\text{guest}}(P_{\text{gate}}) \right].
\]

All the terms in the right-hand side of Equation (21) were obtained from the GCMC simulations.

The obtained value of the right-hand side of Equation (20) is plotted as a function of the temperature in Figure 7, and the typical terms in Equations (17)–(21) at each temperature are listed in Table 1. The good agreement between the terms \(A(P_{\text{gate}})\) and \(-u_{\text{gg}} - \Delta G_{\text{host}}/N + C\) (the error is < 4%) suggests the validity of Equation (20). Data in Table 1 clearly show that the \(C\) value mainly results from the large difference between \(u_{\text{liq}}\) and \(u_{\text{guest}}\) [because of the smaller coordination number of the guest molecules in the confined space (ca. 6) than that of the bulk liquid (ca. 12)] and not from the contribution of the entropy term, which is negligibly small. Thus, the inadequacy of Equation (14) can be attributed to the assumption that the adsorbed molecules are in the bulk liquid state, as stated above. Moreover, the constancy of the right-hand side of Equation (20) to temperature is due to a compensation effect between the three terms \(-u_{\text{gg}} - \Delta G_{\text{host}}/N + C\), which show a temperature dependence.

These findings confirm that the gate adsorption pressure at any temperature in the range of \(T^* = 0.8–1.2\) can be predicted by converting experimental gate adsorption data at one temperature into \(A(P_{\text{gate}})\) based on the original potential theory of adsorption, though the correct thermodynamic expression for the gate adsorption should be Equation (20). The conversion can be made by assuming the ideal gas law as \(A(P_{\text{gate}}) = k_B T \ln(P_f/P_{\text{gate}})\); however, it gives a worse convergence (the deviations are less than ± 6.5% from the centre value, see Table S1, Supplemental Data) than that (± 2.0%) using \(\mu_{\text{liq}}(P) - \mu_{\text{guest}}(P_{\text{gate}})\) (Equation (8)). Therefore, it is desirable to calculate the adsorption potential using \(k_B T \ln(f_{\text{liq}}/f_{\text{gate}})\), where \(f_0\) and \(f_{\text{gate}}\) are fugacities at the saturated vapour pressure and the gate adsorption pressure, according to the relation \(k_B T \ln(f_0/f_{\text{gate}}) = \mu_{\text{liq}}(P) - \mu_{\text{guest}}(P_{\text{gate}})\). Then, it is worth noting that the difference between the terms \(A(P_{\text{gate}})\) and \(-u_{\text{gg}} - \Delta G_{\text{host}}/N + C\) slightly increases with

| \(T^*\) | 0.8    | 0.85   | 0.9    | 0.95   | 1.0    | 1.1    | 1.2    |
|-------|--------|--------|--------|--------|--------|--------|--------|
| \(N\)  | 60.8   | 57.1   | 53.4   | 50.3   | 46.7   | 41.2   | 35.1   |
| \(u_{\text{gg}}\) | -7.75  | -7.73  | -7.71  | -7.69  | -7.66  | -7.62  | -7.59  |
| \(\Delta F_{\text{host}}\) | 42.1   | 42.1   | 42.1   | 42.1   | 42.1   | 42.1   | 40.2   |
| \(P_{\text{gate}}\) | 1.46 × 10^{-3} | 2.97 × 10^{-3} | 5.76 × 10^{-3} | 9.71 × 10^{-3} | 1.56 × 10^{-2} | 3.55 × 10^{-2} | 6.53 × 10^{-2} |
| \(\Delta G_{\text{host}}/N\) | 0.693  | 0.738  | 0.789  | 0.838  | 0.902  | 1.02   | 1.15   |
| \(u_{\text{liq}}\) | -5.72  | -5.52  | -5.30  | -5.09  | -4.89  | -4.46  | -3.90  |
| \(u_{\text{gg}}\) | -1.96  | -1.82  | -1.70  | -1.58  | -1.44  | -1.24  | -1.07  |
| \(u_{\text{liq}} - u_{\text{gg}}\) | -3.76  | -3.70  | -3.60  | -3.51  | -3.45  | -3.22  | -2.83  |
| \(T s_{\text{liq}}\) | 5.61   | 6.26   | 6.92   | 7.60   | 8.28   | 9.72   | 11.36  |
| \(T s_{\text{guest}}\) | 5.76   | 6.40   | 7.05   | 7.71   | 8.42   | 9.79   | 11.21  |
| \(T(s_{\text{liq}} - s_{\text{guest}})\) | -0.146 | -0.142 | -0.130 | -0.119 | -0.141 | -0.073 | 0.159  |
| \(A(P_{\text{gate}})\) | 3.46   | 3.45   | 3.46   | 3.47   | 3.50   | 3.55   | 3.59   |
| \(C\) | -3.62  | -3.55  | -3.46  | -3.39  | -3.31  | -3.15  | -2.99  |
| \(-u_{\text{gg}} - \Delta G_{\text{host}}/N\) | 7.06   | 6.99   | 6.92   | 6.85   | 6.76   | 6.61   | 6.44   |
| \(-u_{\text{gg}} - \Delta G_{\text{host}}/N + C\) | 3.44   | 3.44   | 3.45   | 3.46   | 3.45   | 3.45   | 3.45   |

Note: \(T^* = k_B T/\epsilon_{\text{gg}}\) and the other values are reduced by \(\epsilon_{\text{gg}}\).
increasing temperature above $T^* = 1.0$, which should be because of the neglect of the $P_{\text{v,liq}}^0 - P_\text{v, guest}^0$ term in the definition of $C$ (Equation (19)). We thus calculated $C_m = C + P_{\text{v,liq}}^0 - P_\text{v, guest}^0$ by assuming $P_\text{v}^0 = P_\text{gate}$, and confirmed that a perfect agreement between the terms $A(P_\text{gate})$ and $-u_{\text{gh}} - \Delta G_{\text{host}}/N + C_m$ was obtained (the errors are less than ±0.53%) over the whole range of temperatures $T^* = 0.8–1.2$ (see Table S2 and Figure S1, Supplemental Data). It should also be noted that, in our modified potential theory for gate adsorption, the temperature dependence of the internal energy of the host, $U_{\text{host}}$, and the entropy change, $\Delta S_{\text{host}}(T)$, due to the host deformation, are neglected by assuming $\Delta G_{\text{host}} = \Delta F_{\text{host}} + P_\text{gate} \Delta V_{\text{host}} = \Delta \Phi_{\text{hh}} + P_\text{gate} \Delta V_{\text{host}}$. If the $\Delta S_{\text{host}}$ value is too large for a real SPC, then $\Delta G_{\text{host}}$ should change with the temperature, according to the thermodynamic state function $\Delta F_{\text{host}}(T) = \Delta U_{\text{host}} - T \Delta S_{\text{host}}(T) + P_{\text{gate}} \Delta V_{\text{host}}$. Therefore, the constancy of $A(P_\text{gate})$ to temperature should not be observed experimentally. Moreover, if the guest molecules are highly confined in the host framework (e.g. only one guest molecule is isolated in a narrow cavity of the host), the $V_{\text{v, guest}}$ values after the gate opening at different temperatures would show some deviations because the $\rho_{\text{v, liq}}$ value changes with temperature.

4. Conclusions
In this work, we assessed the characteristic curves transformed from the theoretical gate adsorption isotherms at several temperatures, which were obtained from the GCMC simulations for the simplified stacked-layer SPC model and free energy analysis, based on the Polanyi’s potential theory of adsorption. The obtained theoretical characteristic curves showed a good agreement with each other; this can well demonstrate the experimental observations reported by Yamazaki et al. [43] and suggests that a characteristic curve obtained from an experimental gate adsorption isotherm can be used to predict the gate adsorption pressure at any temperature.

We also developed a modified thermodynamic theory for gate adsorption on the basis of Polanyi’s potential theory of adsorption (Equation (20)) and verified it using the simulation results for the simplified stacked-layer SPC model. The derived relation shows that the work for the host deformation per guest molecule $-\Delta G_{\text{host}}/N$ and the correction term $C$ originating from the spatial constraint of adsorbed guest molecules in the host framework are added to the expression of the original potential theory of adsorption. The thermodynamic formulation and extension of the potential theory of adsorption to the SPC system are unprecedented. Moreover, the introduction of the dimensionality effect on the adsorbed phase (the correction term $C$), which can also have an impact to raise controversial feature of the application of the original potential theory of adsorption for the rigid porous materials with narrow adsorption space, should give a new physical insight into the confinement of fluid in a low-dimensional pore.

By evaluating the modified expression for gate adsorption with the use of the simulation results, we confirmed that the constancy of the adsorption potential $A(P_\text{gate})$ to temperature results from a compensation effect between the three terms with a temperature dependence: guest–host interaction potential per molecule, $-\Delta G_{\text{host}}/N$ and $C$. However, if the entropy change due to the host deformation is significant in a real SPC, the $\Delta F_{\text{host}}$ value would change with the temperature, and thus the characteristic curves obtained from the experimental gate adsorption isotherms on the SPC at different temperatures would no longer coincide with each other.

The next challenge is to assess the applicability of the modified potential theory for gate adsorption to understand the process of adsorption-induced structural transitions in SPCs through meta-stabilised and activated states, which cause hysteresis phenomenon. Several related investigations using a real SPC are currently in progress.

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No potential conflict of interest was reported by the authors.

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Supplemental data
Supplemental data for this article can be accessed here.

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