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Exact matrix treatment of statistical mechanical lattice model of adsorption induced gate opening in metal-organic frameworks

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Abstract. Here we present a statistical mechanical lattice model which is exactly solvable using a matrix method and allows treatment of adsorption induced gate opening structural transformations of metal-organic frameworks which are nanoporous materials with exceptional adsorption properties. Modelling of these structural changes presents a serious theoretical challenge when the solid and gas species are treated in an even handed way. This exactly solvable model complements other simulation based approaches. The methodology presented here highlights the competition between the potential for adsorption and the energy required for structural transition as a driving force for the features in the adsorption isotherms.

Keywords: rigorous results in statistical mechanics, solvable lattice models, adsorbates and surfactants (theory)

Contents

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1. Introduction

Exactly solvable lattice models such as the Ising model have played an important role in the theory of condensed systems, even when somewhat physically unrealistic. In this paper we present an exactly solvable one-dimensional statistical mechanical lattice model which mimics adsorption followed by gate opening [1] in metal-organic framework (MOF) type structures.

Novel materials for energy storage and carbon dioxide capture are the focus of many active research programmes [2, 3]. Accelerated depletion of non-renewable natural resources in combination with concerns over the damaging effects of greenhouse gases makes the search for sustainable innovative energy materials urgent [4]. MOFs [5] are intensely studied examples of nanoporous materials with exceptional adsorption properties. Many MOFs undergo structural transitions with adsorption resulting in isotherms with remarkable features which have been intensively investigated both experimentally and theoretically [6–9]. Structural transitions induced by adsorption of guest molecules occur because the organic entities linking the metal centres provide framework flexibility. The possibility to vary both metals and organic ligands in MOFs widens the application range from gas storage [10, 11] to drug delivery [12, 13], adsorption [14–16] heterogeneous catalysis [17, 18] and separation [19, 20].

Furthermore, the model may find applications in other related phenomena such as swelling of polymers and biopolymers induced by solvent adsorption. Structural transitions accompanied by reversible volume changes present a difficult challenge at the fundamental theoretical level [6–8]. The lattice model inherently embodies the gate opening structural changes following adsorption which we solve exactly by a matrix method. This work allows us to see very clearly the types of adsorption isotherms which may arise from the interplay of adsorption and gate opening.

Lattice models of fluids have been widely discussed [21–23] and successfully applied to a range of adsorption problems [24–27]. A lattice model of breathing in MOFs based on a Hamiltonian for the elastic deformations and host–guest interactions has been discussed by Triguero *et al* [28] where a Grand Canonical Monte-Carlo simulation is performed to

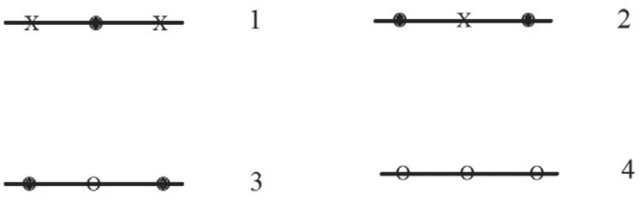

Figure 1. Clusters 1, 2, 3, 4 on the lattice of sites.

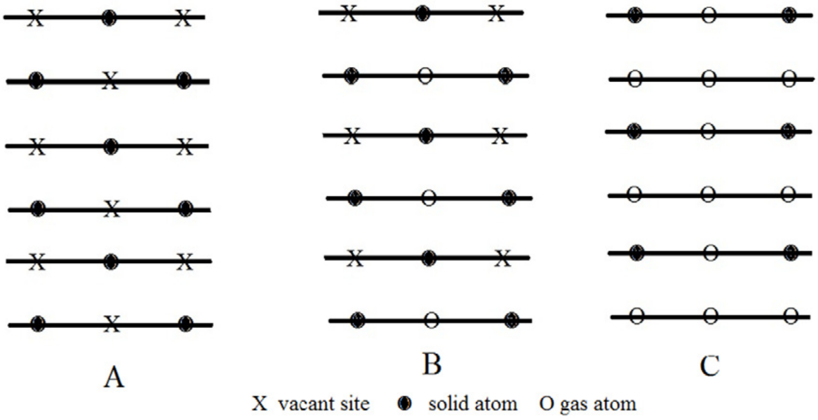

Figure 2. One-dimensional model showing the lattice and gas induced structural change.

study the adsorption process. The matrix method used in this paper evaluates the Grand Canonical partition function for a mixture of solid and adsorbed phase components and empty sites on a background rigid ladder-like framework to be shown in figures 1 and 2. These sites constitute an underlying rigid framework which may be occupied by any one of three types of constituents on this lattice namely solid, gas, and vacant sites or holes. In our analysis we make a choice as to the statistically significant contributions to the Grand partition function discussed below. In this way a non-trivial exactly solvable statistical mechanical lattice model is obtained.

2. Model

We consider a strip of N groups of three lattice sites so that there are $3N$ sites in total. We have chosen to focus on four types of energetically significant clusters, 1, 2, 3, 4 shown in figure 1.

The solid spheres represent parts of the solid MOF structure while the open circles represent spherical adsorbed gas molecules. The species shown in figure 1 may be configured one-dimensionally to represent the stages of adsorption induced structural changes in a MOF type structure as shown in figure 2.

Structure A is the pure solid in its original state, B contains solid and some adsorbed gas species while C has undergone a structural transition induced by the adsorption of more spherical gas molecules. This structural transition is represented by the change of shape of arrangement of solids, from diamond to square. The steps in the calculated isotherms to be shown below correspond to the transitions between A, B and C structures and are similar to those found experimentally. In this model, the gate opening is represented by a diamond arrangement of atoms (figure 2A) which expands to a square at higher loading (figure 2C).

The solid species occupying the sites of the background framework are assumed to be in equilibrium with a reservoir of solid atoms representing the original framework, at chemical potential μ_{s}, assumed to be independent of the external gas pressure. An expression for μ_{s} is given in the Debye model of a crystalline solid [29] although the explicit form is not utilized here.

Similarly, adsorbed gas species are at equilibrium with an ideal gas reservoir at a chemical potential μ_i for component i given by [30]

$$\mu_i{=}\mu_i^0{+}kT\ln P, \tag{1}$$

where the standard chemical potential μ_i^0 is given by

$$\mu_i^0{=}-kT\ln\left[\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2}kT\right] \tag{2}$$

and where modification for non-ideal behaviour is straightforwardly achieved by replacing pressure by fugacity.

Matrix methods for statistical mechanical treatment of one-dimensional lattice fluid problems have been reviewed by us previously [31]. The Grand Canonical partition function Ξ for the mixture of solid and gas molecules on the lattice framework with N groups of three lattice sites may be written as the sum of the products of N factors given by

$$\Xi=\sum_{\alpha=1}^{n}\sum_{\beta=1}^{n}\sum_{\gamma=1}^{n}\ldots\sum_{\omega=1}^{n}A_{\alpha\beta}A_{\beta\gamma}A_{\gamma\delta}\ldots A_{\omega\alpha}, \tag{3}$$

where $n=4$ is the number of possible clusters which can occupy a row of three sites. Cyclic boundary conditions have been assumed where the lattice is folded on to a ring. For N strips there are at most $3N$ species on the lattice as higher numbers than this are energetically prohibited and do not contribute to the Grand partition function. As is usual in the matrix method [31] we define the terms in (3) as the product of an internal partition function for the cluster and an interspecies interaction term given by

$$A_{\mu v}=(f_\mu f_v)^{1/2}\,\exp\left(\frac{-J_{\mu v}}{kT}\right), \tag{4}$$

where subscripts μ, v run over the species 1 to 4 and the parameter $J_{\mu v}$ is the interaction energy of nearest neighbour pairs of species μ, v. For example, $J_{12}\approx 2j_{\mathrm{ss}}$, $J_{13}\approx 2j_{\mathrm{ss}}+3j_{\mathrm{sg}}$, $J_{34}\approx 6j_{\mathrm{sg}}+3j_{\mathrm{gg}}$ here j_{gg}, j_{ss} and j_{sg} are effective interaction energies of pairs of solid (s) and gas (g) species. Since other clusterings are forbidden in this model as they are not represented in structures A, B, C in figure 2 an energy penalty function is imposed which reduces their statistical weight to zero in the Grand partition function. The internal partition function for clusters 1 to 4 are given by

$$f_1 = \exp\left(\frac{-u_{\mathrm{s}}+\mu_{\mathrm{s}}}{kT}\right), \tag{5}$$

$$f_2 = (f_1)^2, \tag{6}$$

$$f_3 = (f_1)^2 \exp\left(\frac{-u_{\mathrm{g}}+\mu_{\mathrm{g}}}{kT}\right), \tag{7}$$

$$f_4 = \exp\left(\frac{3(-u_{\mathrm{g}}+\mu_{\mathrm{g}})}{kT}\right), \tag{8}$$

where μ_{g} and μ_{s} are the gas and solid species chemical potentials respectively while u_{g} and u_{s} are the interaction energies of these species with the background framework which mimics their interaction with the other atoms in a three-dimensional bulk crystal which we do not explicitly include in this model. The chemical potential and energy of a vacant site or 'hole' on the background framework is evidently zero.

Using the inner product rule $D_{ij} = \sum_k B_{ik}C_{kj}$ for matrix multiplication of a pair of conformable matrices $\mathbf{B}$ and $\mathbf{C}$ the Grand Canonical partition function given in (3) can be expressed as

$$\Xi = \sum_{\alpha=1}^{n} (\boldsymbol{A}^N)_{\alpha\alpha} = \mathrm{Tr}(\boldsymbol{A}^N) = \sum_{i=1}^{n} (\lambda_i)^N, \tag{9}$$

where λ_1, λ_2, λ_3, λ_4 are the eigenvalues of the matrix $\mathbf{A}$ which is given below as

$$\boldsymbol{A} = \begin{pmatrix} 0 & (f_1f_2)^{\frac{1}{2}} \exp\left(\frac{-J_{12}}{kT}\right) & (f_1f_3)^{\frac{1}{2}} \exp\left(\frac{-J_{13}}{kT}\right) & 0 \\ (f_1f_2)^{\frac{1}{2}} \exp\left(\frac{-J_{12}}{kT}\right) & 0 & 0 & 0 \\ (f_1f_3)^{\frac{1}{2}} \exp\left(\frac{-J_{13}}{kT}\right) & 0 & 0 & (f_3f_4)^{\frac{1}{2}} \exp\left(\frac{-J_{34}}{kT}\right) \\ 0 & 0 & (f_3f_4)^{\frac{1}{2}} \exp\left(\frac{-J_{34}}{kT}\right) & 0 \end{pmatrix}. \tag{10}$$

The zero values for some matrix elements A_{ij} arises because the interaction energy between those clusters i,j is infinitely repulsive due to the penalty function discussed above. For example, species 1 is not allowed to be next to another species 1 in figure 2 etc. Fortuitously, this feature renders the solution of the characteristic polynomial of the matrix $\mathbf{A}$ to be obtained analytically.

As is usual in matrix evaluations of partition functions only the largest eigenvalue of $\mathbf{A}$ concerns us here since for large N equation (9) reduces to

$$\Xi = (\lambda_{\max})^N, \tag{11}$$

where $\lambda_{\max}$ is the largest eigenvalue of the matrix $\mathbf{A}$ whose square is calculated exactly as

$$(\lambda_{\max})^2 = \frac{\sqrt{\Psi}}{2} + \frac{f_1f_2 \exp\left(\frac{-2J_{12}}{kT}\right)}{2} + \frac{f_1f_3 \exp\left(\frac{-2J_{13}}{kT}\right)}{2} + \frac{f_3f_4 \exp\left(\frac{-2\mathrm{J}_{34}}{\mathrm{kT}}\right)}{2},$$

where

$$\begin{aligned} \Psi = {} & \exp\left(\frac{-4J_{12}}{kT}\right) f_1^2 f_2^2 + 2\exp\left(\frac{-2(J_{12}+J_{13})}{kT}\right) f_1^2 f_2 f_3 + \exp\left(\frac{-4J_{13}}{kT}\right) f_1^2 f_3^2 \\ & -2\exp\left(\frac{-2(J_{12}+J_{34})}{kT}\right) f_1 f_2 f_3 f_4 + 2\exp\left(\frac{-2(J_{13}+J_{34})}{kT}\right) f_1 f_3^2 f_4 \\ & +\exp\left(\frac{-4J_{34}}{kT}\right) f_3^2 f_4^2. \end{aligned} \tag{12}$$

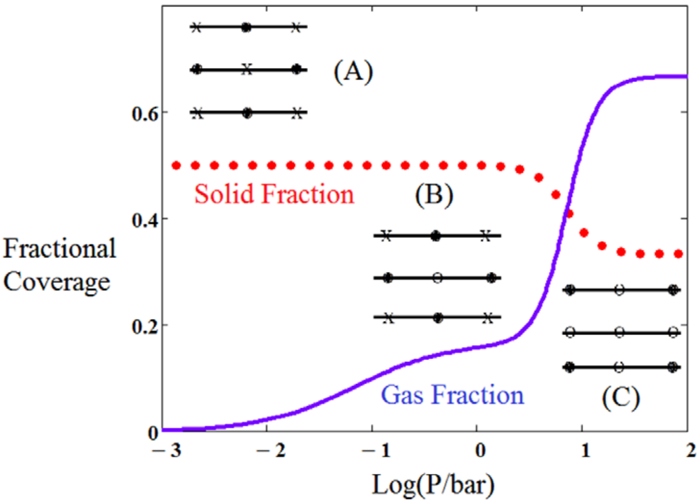

Figure 3. Theoretical isotherm calculated using exact matrix method. Both the coverage of the empty lattice by solid and gas species are shown. The inflections in the isotherm reflect the structural transitions A to B and B to C, as shown above. The parameters are $J_{12} = -3.0kT$, $J_{13} = -8.0kT$, $J_{34} = -13.5kT$, $\mu_{\mathrm{s}} = -10.0kT$, $u_{\mathrm{s}} = -5.0kT$, $u_{\mathrm{g}} = -9.0kT$. All other parameters are infinitely repulsive.

The mean density of solid or adsorbed molecules expressed as 3 times the fractional coverage of lattice site is given by the standard relationship [30]

$$\rho_i = kT\frac{\partial}{\partial\mu_i}\ln(\lambda_{\max}), \tag{13}$$

where i refers to solid or gas as required. The required differentiations were performed analytically in a straightforward manner using mathematical software. Thus for a given gas phase pressure adsorption isotherms can be constructed for this exact one-dimensional model.

3. Results and discussion

The model displays three types of isotherm discussed below.

The isotherm in figure 3 shows adsorption (A → B) followed by gate opening (B → C) as shown in the pictures on the graph. The shape of the adsorption isotherm follows the general pattern seen in the results of Coudert and co-workers [1]. The density of the solid phase falls due to the gas take-up and the accompanying solid expansion due to gate opening. The shape of the adsorption isotherms reflects the competition between the potential for adsorption and the energy required for structural transformations as a driving force for the features in the adsorption isotherms. The gate opening does not occur until the chemical potential of the gas phase is sufficiently high. Some further types of adsorption isotherm reproduced by the model with different parameter values are given (only gas fractional coverage is shown) in figure 4.

In figure 4 the red curve is close in shape to that shown in figure 3. Configurations A, B, C can all have a significant statistical weight at some pressure which causes two steps

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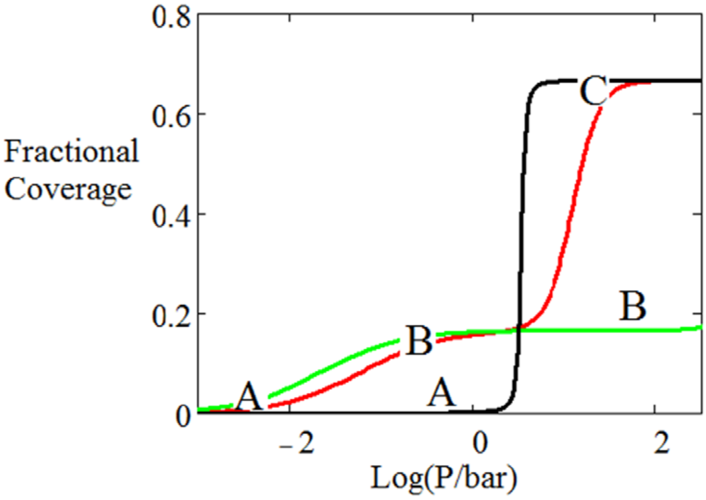

Figure 4. Further types of theoretical isotherm for gas adsorption by MOF calculated using exact matrix method for range of parameters. The parameters are as follows: red: $J_{12} = -3.0kT$, $J_{13} = -8.0kT$, $J_{34} = -12.5kT$, $u_s = -5.0kT$, $u_g = -9kT$; black: $J_{12} = -3.0kT$, $J_{13} = -4.5kT$, $J_{34} = -12.5kT$, $u_s = -5kT$, $u_g = -9kT$; green: $J_{12} = -3.0kT$, $J_{13} = -8.5kT$, $J_{34} = -6.0kT$, $u_s = -5.0kT$, $u_g = -9.0kT$; $\mu_s = -10kT$. All other parameters are infinitely repulsive.

in the isotherm. This may be compared with the green curve in which configurations A, B are preferred so that only one step is seen in the isotherm. Configuration C is unfavoured while configuration B is favoured. This is a simple adsorption isotherm. In the black curve configurations A, C are preferred while B is unfavoured. Hence only an abrupt step in the gas fractional coverage is observed corresponding to only gate opening without previous adsorption which is equivalent to gate opening in a non-porous solid as described by Coudert and co-workers [1]. The isotherm is practically discontinuous. The dominant configurations at any given gas pressure are marked on figure 4.

4. Conclusion

Exactly solvable models in statistical mechanics have the virtue of readily providing an insight into a range of physical and chemical phenomena, even if somewhat restricted in nature. MOFs are nanoporous materials with exceptional adsorption properties whose structural transitions with gas adsorption pose a challenge theoretically. We have devised an exactly solvable statistical mechanical lattice model using a matrix method. The approach treats the solid and gas component on an equal footing. The methodology presented here highlights the competition between the potential for adsorption and the energy required for structural transition as a driving force for the features in the adsorption isotherms.

Further work is underway to extend this exactly solvable model to a realistic MOF structure. Considerable progress towards more realistic models seem possible. For example, if an extended eigenvalue problem of the type described above is treated numerically then more realistic chemical and physical features can be incorporated in the future.

The model also has the possibility of investigating the mechanical pressure through the relation [30] $PV = kT \ln \Xi$ although this possibility has yet to be investigated. Similarly, the relationship with this model and the more realistic osmotic ensemble of Coudert *et al* [1] remains to be explored. Work on both of these points is being considered.

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