

One-dimensional Xenon Gas in the Pores of Mordenite

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Xenon atoms in the pores of mordenite have been approximated by the hard-rod model, with an effective diameter. To investigate the adsorption isotherm and the density profile of xenon gas in the mordenite pores, the exact statistical results obtained from the hard-rod system have been used. The results have been compared with the available experimental data. For the adsorption isotherms of xenon gas, the calculated results are in good agreement with these experimental data. The temperature dependence for the density profiles of xenon atoms in the mordenite pores have also been investigated. The calculated results show an immobile adsorption at lower temperatures, in contrast to a mobile adsorption at higher temperatures, and suggest a deviation from a strict one-dimensionality of xenon gas in the mordenite pores at low temperature and high coverage.

The aluminosilicate framework of mordenite $[\text{Na}_{4.8}(\text{AlO}_2)_{4.8}(\text{SiO}_2)_{43.4}]$ with a free aperture of $0.67 \text{ nm} \times 0.75 \text{ nm}$ comprises a bundle of elliptical straight channels which run parallel to the c -axis.¹ Each channel has a wall side-pocket, which can be entered through an eight-membered oxygen ring, with a free aperture of $0.29 \text{ nm} \times 0.57 \text{ nm}$. Ohgushi and Yokoyama² have recently studied the adsorption isotherms of rare gases in the pores of mordenite. They have shown that (i) the rare gases in mordenite behave as one-dimensional rare gases (as they do in ferrierite^{2–5}), even though some deviations from the strict one-dimensionality occurred with respect to collision diameters, σ , owing to a difference between the size of the molecules and channel pores, and (ii) the observed virial coefficients are well described by a repulsive-interaction potential between the rare gas atoms. However, it is expected that the deviation from strict one-dimensionality can be reduced if a rare gas with a large molecular (collision) diameter is chosen, *e.g.* xenon gas in the pores of mordenite is relatively well described by a one-dimensional model, compared with argon and krypton gas, because of the larger molecular diameter ($\sigma = 0.457 \text{ nm}$).^{2–6} On the other hand, unlike the adsorption isotherms of rare gases, it is very difficult to measure directly the density profiles (distributions) of rare gases in the pores of zeolites such as mordenite and ferrierite. Some theoretical methods^{7–9} can provide detailed information about the density behaviour of a molecule adsorbed in zeolite pores, such as the density profiles: rare gases in the pores of mordenite, which have dimensions on the order of nanometres, have very different properties than bulk rare gases. Two approaches to predict the thermodynamic properties of confined rare gases are computer simulations, or the exactly solvable fluid (or gas) model. An example of the latter is the hard-rod model, which is simply a hard-sphere model confined to one dimension. It is known that in the liquid theory, a repulsive potential with a large repulsive parameter can be approximated to the hard-rod model (with an effective diameter).¹⁰ Thus, xenon gas in the pores of mordenite can be well approximated to a hard-rod gas with an effective diameter, and the density behaviour of xenon gas can also be predicted from the exact statistical result of this hard-rod model.

We will first summarize the results of Ohgushi and Yokoyama for the one-dimensional rare gases in the pores of mordenite (see Theory). As a first approximation, the repulsive interaction potential is assumed to be that of the hard-rod model. We compute the equation of state and density profile

equation of the hard-rod gases, in order to calculate the adsorption isotherms (the temperature dependence for the density profiles of xenon gas adsorbed in mordenite). Later we explain how to calculate the xenon–zeolite potential in mordenite due to xenon–mordenite rather than xenon–xenon interactions (see Results and Discussion). We compare our results with the available experimental data. Finally, we will briefly discuss future applications of the equation of state, and the density profile equation of the hard-rod model, to one-dimensional rare gases adsorbed in zeolite pores.

Theory

Ohgushi and Yokoyama² have recently used the modified Lennard-Jones potential, which was introduced by Takaishi *et al.*,^{3–5} to analyse the adsorption isotherms of rare gases in the mordenite pores as follows:

$$U(z) = U_0 \left[\left\{ \frac{z_0}{z} \right\}^{12} - \eta \left\{ \frac{z_0}{z} \right\}^6 \right]; \quad \eta \leq 2 \quad (1)$$

where z_0 and U_0 are the length and energy parameters, respectively, z is a separation distance measured along the pore channel and η is an adjustable parameter for attractive potentials.

From the measurement of the adsorption isotherms of xenon gas, they have shown that at low coverage, the adsorption isotherm of xenon can be expressed by the virial form of one-dimensional xenon gas. In this case, an attractive part of the Lennard-Jones potential can be neglected, and only a repulsive-interaction potential is needed to represent such one-dimensional systems, *i.e.*,

$$U(z) = U_0 \left[\frac{z_0}{z} \right]^{12} \quad (2)$$

This type of repulsive-model potential was applied for the system of one-dimensional gases adsorbed in ferrierite, with a cross-section of $0.43 \text{ nm} \times 0.55 \text{ nm}$.⁵

The length parameter, z_0 , defined in eqn. (2) is somewhat different from the usual collision diameter of xenon, σ . In this case, z_0 is given by

$$z_0 = \sigma \cos \theta \quad (3)$$

where the angle θ depends on the configurational arrangement of xenon atoms trapped in the pore channel. Furthermore, they have also shown that, at temperatures greater than 200 K, the temperature dependence of z_0 was very weak,

and, consequently, z_0 could be approximated as a constant. For the xenon/mordenite system considered here, we have chosen the potential depth U_0/k_B to be 225.0 K and the length parameter z_0 to be 0.233 Å using eqn. (3) (i.e., $z_0 = 0.51\sigma$).

To investigate the adsorption isotherms and density profiles of xenon gas we approximate the repulsive interaction potential to the hard-rod potential, with an effective diameter d , since little is known about the equation of state (i.e. pressure equation) and the density profile equation of xenon gas for such model systems. It is known that the repulsive-interaction potential with parameter $n = 12$ is well approximated to the hard-rod model. The advantage of the hard-rod model is that the exact solutions of the equation of state, and the density profile equation in the presence of an arbitrary external potential, are known.⁹ In this case, the hard-rod potential, with an effective diameter, d , is defined as

$$\beta U_{hr}(z) = \infty; \quad z < d \\ = 0; \quad z > d \quad (4)$$

where $\beta = 1/k_B T$ and the subscript hr denotes the hard-rod model. In eqn. (4), d is generally determined by the Barker-Henderson criterion,¹⁰

$$d = \int_0^\infty \{1 - \exp[-\beta U(z)]\} dz \quad (5)$$

where d depends on the temperature only, and decreases with increasing temperature. However, note that, in general, d is a function of the repulsive potential, density and temperature.

In the hard-rod model, the adsorption isotherm of xenon gas is simply given by the equation of state for hard-rod gases with an effective diameter, d ;

$$\beta P_{hr} = \frac{\rho}{(1 - \rho d)} \quad (6)$$

since the adsorption isotherm (equation of state) of xenon gas adsorbed in the mordenite pores does not depend on the xenon-zeolite potential. In eqn. (6), ρ and P_{hr} represent the density and the pressure for the hard-rod gases, respectively. From the expansion of eqn. (6),

$$\frac{\beta P_{hr}}{\rho} = 1 + d\rho + d^2\rho^2 + d^3\rho^3 + \dots \quad (7)$$

where the virial coefficients are

$$B = d, \quad C = d^2, \quad D = d^3, \dots \quad (8)$$

From the adsorption isotherms of xenon gases [eqn. (8)],²

$$P = \frac{\rho}{K_H} \exp[2B\rho + \frac{3}{2}C\rho^2 + \frac{4}{3}D\rho^3 + \dots] \quad (9)$$

we have

$$P = \frac{\rho}{K_H} \exp[2d\rho + \frac{3}{2}(d\rho)^2 + \frac{4}{3}(d\rho)^3 + \dots] \quad (10)$$

where K_H is Henry's constant. In eqn. (10), Henry's constant is given by

$$\ln K_H = -a + \frac{b}{T} \quad (11)$$

where $a = 6.93$ and $b = 3.80 \times 10^{-3}$ K for xenon gas.²

Unlike the adsorption isotherm of xenon gas, the density profile of xenon atoms in the mordenite pores depends strongly on the external potential, such as the xenon-zeolite potential in mordenite. Percus⁹ treated an exact expression

for the density profiles of confined hard-rod gases with the hard-rod potential, in the presence of an arbitrary external potential $U^{ext}(z)$ (which describes confined gases in equilibrium with an external bath). In this case, the density profile equation for the hard-rod gases is given by

$$\beta\mu - \beta U^{ext}(z) = \ln \rho(z) - \ln[1 - A(z)] + \int_{z-d}^z \frac{\rho(y) dy}{1 - A(y)} \quad (12)$$

where μ is the chemical potential and $A(z)$ is defined as

$$A(z) = \int_z^{z+d} \rho(y) dy \quad (13)$$

In eqn. (12), the external potential $U^{ext}(z)$, which is the xenon-zeolite potential in mordenite, is determined by the interaction between the number of molecules composed of mordenite and xenon atoms adsorbed in the mordenite pores.^{11,12} Since $U^{ext}(z) = 0$ and $\rho(z) = \rho$ in the uniform systems, eqn. (12) can be written as

$$\beta\mu = \ln \rho - \ln(1 - \rho d) + \frac{\rho d}{(1 - \rho d)} \quad (14)$$

Eliminating μ from eqn. (12) and (14), the density $\rho(z)$ of xenon atoms in the mordenite pores is given by

$$\rho(z) = \rho \exp[-\beta U^{ext}(z)] \exp\{f[\rho(z)]\} \quad (15)$$

where $f[\rho(z)]$ is given by

$$f[\rho(z)] = -\ln(1 - \rho d) + \frac{\rho d}{(1 - \rho d)} \\ + \ln[1 - A(z)] - \int_{z-d}^z \frac{\rho(y) dy}{1 - A(y)} \quad (16)$$

The resulting equation for the density profile is the highly non-linear equation about the density $\rho(z)$, and strongly depends on the xenon-zeolite potential in mordenite. The pore density profile was obtained by the numerical iteration between the old density profiles on the right-hand side and the new ones on the left-hand side in eqn. (15).

Results and Discussion

We have calculated the adsorption isotherms of xenon gas in the pores of mordenite, and compared our results with the available experimental data^{2,13} (Fig. 1). As mentioned in the previous section, the length parameter along the pore channel, z_0 , is taken to be a constant because the temperature dependence of the second virial coefficient was measured to be very weak at temperatures greater than 200 K.² Note that Spriguel-Huet and Fraissard¹³ have used larger pore mordenites (such as $\text{Na}_7\text{Al}_{17}\text{Si}_{41}\text{O}_{96}$) and measured the amount of xenon gas adsorbed in the channel and side-pockets. As can be seen from Fig. 1, the results obtained from the hard-rod model are in good agreement with the experimental data. These results confirm that the hard-rod model, with an appropriate effective diameter, can be used to describe the adsorption isotherms of one-dimensional xenon gas in the mordenite pore, particularly for systems at high temperature.

In Fig. 2, the external potential $U^{ext}(z)$ for a single xenon atom moving through the main channel in the mordenite is plotted as a function of z . The xenon-zeolite potential is symmetric around $z = 3.76$ Å, with a maximum at $z = 0$ Å and a minimum at $z = 1.88$ Å. The main pore channel is along the c -direction of the unit cell and the path is along that of minimum energy, which is not necessarily along the centre

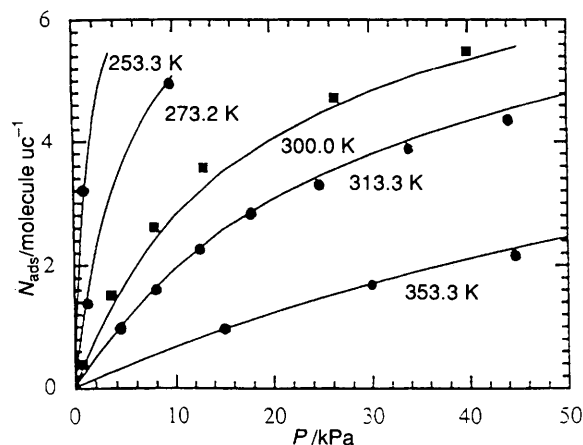


Fig. 1 Adsorption isotherms of xenon gas in the pores of mordenite. Solid lines correspond to the calculated results; (●) and (■), experimental data from Ohgushi and Yokoyama and Springuel-Huet and Fraissard, respectively.

line of the pore. This was done by simply calculating the potential at the grid points (100×100) to determine the minimum energy. Monte Carlo simulations using this external potential for Lennard-Jones fluid systems in the zeolite mordenite are currently employed to investigate the thermodynamic and equilibrium properties of such systems.¹²

Fig. 3 shows the density profiles of xenon atoms adsorbed in the mordenite pores at $T = 300$ K. Here, the number of xenon atoms adsorbed per unit cell, N_{ads} , is given by

$$N_{\text{ads}} = 2 \int_0^{7.52} \rho(z) dz \quad (17)$$

where the factor 2 comes from the number of channels in the unit cell.¹ As can be seen from Fig. 3, the pore density increases with the number of xenon atoms adsorbed in the mordenite pores. The peak minima appear at $z = 0$ Å and the maxima at $z = 1.88$ Å. We expect these results from eqn. (15); at low coverage the density profile depends strongly on the xenon-zeolite potential in mordenite.

In Fig. 4, the pore density profiles of xenon atoms are presented to illustrate the variation with temperature. In this case, the resulting density profiles of xenon atoms at $z = 1.88$ Å decreases with increasing temperature, whereas the pore density at $z = 0$ Å increases. Such results explain the mobile adsorption at higher temperatures, in contrast to the immobile adsorption at lower temperatures,² *i.e.*, there is a shallow adsorption-potential valley at the entrance window to the side-pocket on the channel wall, and the xenon atoms may be

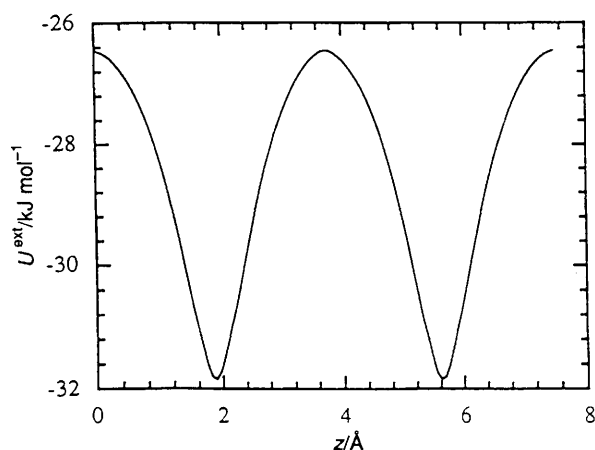


Fig. 2 Minimum potential energy, $U^{\text{ext}}(z)$, for a single xenon molecule in the mordenite pores

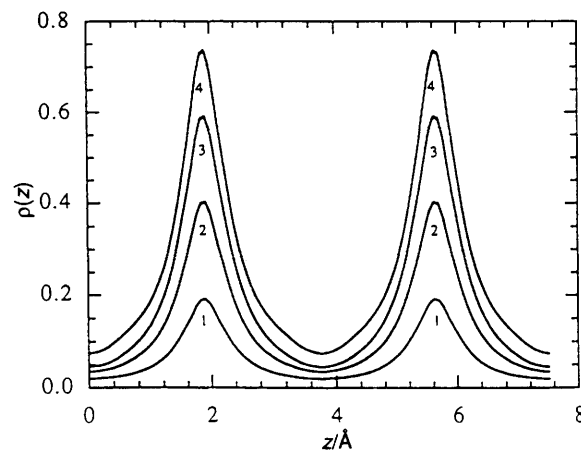


Fig. 3 Pore density profiles of xenon gas adsorbed in the mordenite pores for $T = 300$ K. 1, $N_{\text{ads}} = 1$; 2, $N_{\text{ads}} = 2$; 3, $N_{\text{ads}} = 3$; 4, $N_{\text{ads}} = 4$.

trapped in the valley at lower temperatures, as indicated by Ohgushi and Yokoyama.²

Fig. 5 and 6 show the local density profiles of xenon atoms at $z = 0$ Å and $z = 1.88$ Å, respectively. At low coverage, the pore density at $z = 0$ Å and $z = 1.88$ Å increases with

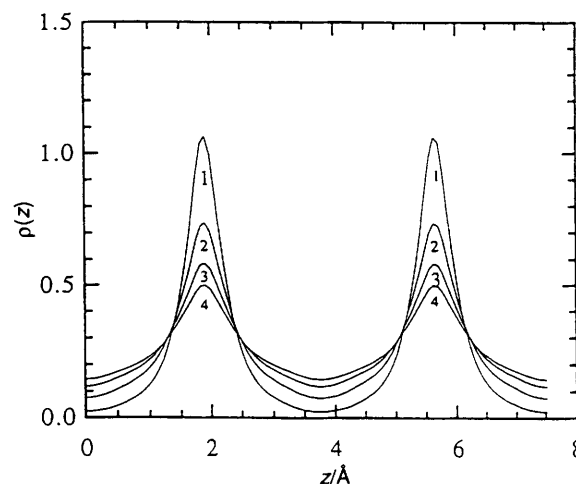


Fig. 4 Pore density profiles of xenon gas adsorbed in the mordenite pores for $N_{\text{ads}} = 4$. 1, $T = 200$ K; 2, $T = 300$ K; 3, $T = 400$ K; 4, $T = 500$ K.

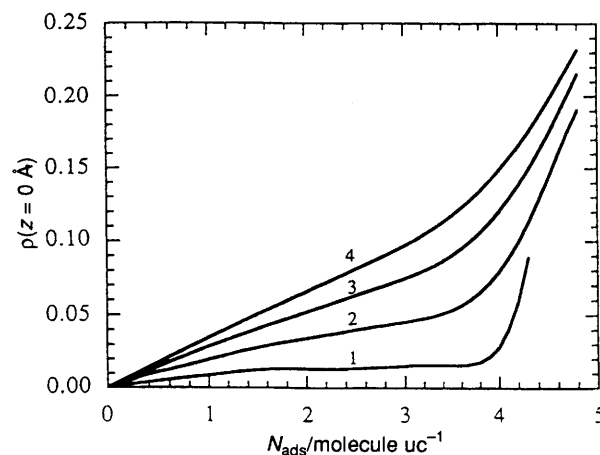


Fig. 5 Local density profiles of xenon gas adsorbed in the mordenite pores at $z = 0$ Å. 1, $T = 200$ K; 2, $T = 300$ K; 3, $T = 400$ K; 4, $T = 500$ K.

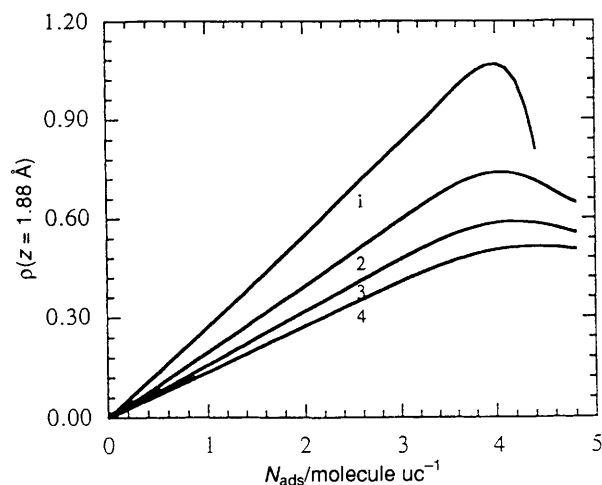


Fig. 6 Local density profiles of xenon gas adsorbed in the mordenite pores at $z = 1.88 \text{ \AA}$. 1, $T = 200 \text{ K}$; 2, $T = 300 \text{ K}$; 3, $T = 400 \text{ K}$; 4, $T = 500 \text{ K}$.

increasing N_{ads} . At high coverage, the local pore density at $z = 1.88 \text{ \AA}$ decreases rapidly with decreasing temperature, whereas the density at $z = 0 \text{ \AA}$ increases rapidly with decreasing temperature. These results are those expected from eqn. (15). The pore density, $\rho(z)$, at low coverage is largely determined by the external potential as we can see from Fig. 3–6. At high coverage, the contribution of $\exp[-\beta U^{\text{ext}}(z)]$ is reduced by the repulsive interaction between xenon atoms. On the other hand, Fig. 5 and 6 suggest the deviation from the strict one-dimensionality of xenon gas in the mordenite pores¹³ at low temperatures and high coverage, as can be seen from Fig. 4. The overall picture shows that the exact statistical theory of the one-dimensional hard-rod model not only predicts the thermodynamic behaviour of xenon gas adsorbed in the mordenite pores, but also gives detailed information about the inhomogeneous structural properties of adsorbed xenon atoms, which is very difficult, or impossible, to probe in experimental studies.

In summary, we have used the hard-rod model, with an effective diameter, to investigate the adsorption isotherms and the density profiles of xenon gas in mordenite pores. The results obtained indicate that the simple hard-rod model can

be used to determine the adsorption isotherm of xenon gas. For the investigation of the density profile, immobile adsorption at low temperatures was observed, at higher temperatures mobile adsorption was found. At low temperatures and high coverage, the calculated results suggest a deviation from the strict one-dimensionality of xenon gas owing to the effects of the side-pockets of the mordenite pores. The hard-rod-model results, as a first approximation, are an inexpensive by-product and this approach will yield insight into the interplay between the intermolecular and the external interaction potential.

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