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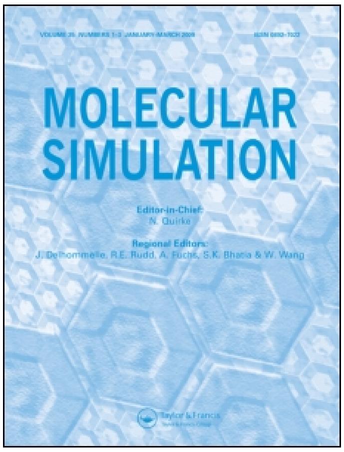

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INTERMOLECULAR POTENTIAL FUNCTIONS FOR ADSORPTION IN ZEOLITES: STATE OF THE ART AND EFFECTIVE MODELS

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In the simulation of physical adsorption, the adsorbate-adsorbent potential function plays a central role. Much labour is involved in obtaining a potential function which takes into account two-body and three-body dispersion terms in place of a more empirical effective potential, and it is important to enquire whether effective potentials can furnish an acceptable solution to the problem. Here we review the construction of a more elaborate potential function for the interaction of non-polar probes with silicalite and with $AlPO_4$-5, and analyze the contributions which arise from the different terms. The possibility of employing effective potentials based on the summation of 12-6 or 6-exp functions is examined, and it is concluded that no guarantee can be offered for the success of the simplified procedure.

Keywords: Potential functions; zeolites; silicalite; AlPO4-5

INTRODUCTION

Simulations of physical adsorption cover a wide range of conditions and systems. A feature common to all of them is that they require a potential model as their input, and that the potential involves at least two dissimilar species. A common solution to the problem is to use simple potential models, usually based on 12-6 Lennard-Jones functions and introduce com-

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bining rules - such as the well known Lorentz-Bertholet rule - to handle the cross interactions between adsorbate and adsorbent. At high temperature, where the potential energy is a relative small part of the total Hamiltonian, this solution can give quite satisfactory results, as judged by the criterion of agreement between experiment and simulation in well characterised systems [1]. However, adsorption studies are often made at low temperatures and more accurate modelling may be needed. Apart from this requirement, there remains the more general question of how accurately simple and/or approximate models can replicate the properties of real adsorption systems.

One way to approach this question is to attempt to construct an accurate potential function against which the performance of simpler models can be tested. Inside the confined spaces of real porous materials, such as zeolites or porous carbons, the potential surface will be a complex object which needs to be known at a large number of points on a three dimensional grid. Since long range van der Waals interactions make an important contribution, full scale quantum mechanical calculation would appear to be ruled out for the foreseeable future. An alternative approach is based on the *a priori* division of the potential into long range (dispersion, induction and electrostatic) terms, which can be handled with perturbation theory, and short range repulsion [2,3]. Of the long range terms, dispersion energy is often the most important contribution, and this subdivides into sums of two body and many body (in practice three body) terms each of which involves products of polarizabilities.

To make progress it is necessary in addition to model the adsorbent as an array of sites, usually centred on atoms in the solid. Because the sites are in an asymmetrical environment, they should, strictly speaking, be treated as having anisotropic polarizability [5]. In this respect graphite adsorbents present a special problem since the anisotropy of polarizability of graphite is quite large [6,7]. This leads to considerable complications in the evaluation of high order terms in the perturbation expansion [8]. For oxide adsorbents it would appear, from the little information available, that this is a less serious problem and that major error would not be incurred by ignoring this factor.

In earlier work [2,3] we have constructed an adsorbate-absorbent potential function, which for convenience of reference we designate the PN potential. The starting point was the argon silicalite-1 system. This choice offers a number of advantages: (i) The polarizability can be assumed to be isotropic. (ii) The adsorbent is well characterised and its crystal structure is known.

(iii) A number of low coverage data are available. The method developed in this work produces a fully transferable potential that, in principle, can be used for polyatomic as well as monatomic adsorbates, and can be extended to other adsorbents.

In this paper we first briefly review the content of the PN potential model and its applicability to zeolitic systems. We then discuss the relative importance of the various contributing terms to the total potential energy, and evaluate the possibility of using a model based on a 12-6 effective potential as a substitute for the full scale potential function.

THE PN POTENTIAL

Our model is based on the elementary assumption that the physical interaction between a non polar adsorbate and the adsorbent can be represented as a sum of attractive and repulsive terms. The repulsive term is expressed as an atom-atom Born-Mayer interaction which is a sum of exponentials of the form:

$$u_{\mathrm{rep}} = \sum_{i \neq j} A \exp(-br_{ij}) \tag{1}$$

where A and b are repulsive parameters. There is a pair of repulsive parameters for each different pair of interacting species. These parameters were determined from low coverage data for argon. A full description has been given elsewhere [2] and the procedure is briefly summarised below.

The attractive contributions are calculated within the framework of standard perturbation theory [9,10], including two body and three body interactions. The part of the dispersion energy due to pair interactions between spherically symmetric atoms A and B, separated by a distance R, can be expressed by a damped dispersion expansion as:

$$u_{\mathrm{disp}}^{AB}(R) = -\left[f_6 \frac{C_6^{AB}}{R^6} + f_8 \frac{C_8^{AB}}{R^8} + f_{10} \frac{C_{10}^{AB}}{R^{10}} + \cdots\right] \tag{2}$$

where the damping terms $f_{2n}(R)(n=3,4,5)$ depend on the repulsive parameter b in Equation (1), and are given by:

$$f_{2n} = 1 - \left(\sum_{k=0}^{2n} \frac{(bR)^k}{k!}\right) \exp(-bR) \tag{3}$$

The damping functions f_{2n} have a sigmoid variation with R and range from zero at distances where wavefunction overlap is large, to unity when R is sufficiently large for overlap between wavefunctions to be negligible.

In Equation (2) the dispersion coefficients C_6^{AB} describe the interaction between two instantaneous dipoles, C_8^{AB} the interaction between a quadrupole and a dipole and C_{10}^{AB} includes the interaction between an octopole and a dipole and between two quadrupoles.

Exact expressions for these coefficients can be written as integrals over the frequency dependent ℓth order polarizabilities $\alpha_\ell(i\omega)$ [9]. In practice it is difficult to obtain the necessary information, and an alternative route is to express the frequency dependence as a Padé approximant involving the average ℓth pole transition energy η_l and the static ℓth pole polarizability $\alpha_\ell(0)$:

$$\alpha_\ell(\omega) = \frac{\alpha_\ell(0)}{1 + (i\omega/\eta_\ell)^2} \tag{4}$$

Using this approach the dispersion coefficients can be rewritten:

$$C_6^{AB} = \frac{3}{2}\frac{\eta_1^A \eta_1^B}{\eta_1^A + \eta_1^B}\alpha_1^A \alpha_1^B \tag{5}$$

$$C_8^{AB} = \frac{15}{4}\left[\frac{\eta_1^A \eta_2^B \alpha_1^A \alpha_2^B}{\eta_1^A + \eta_2^B} + \frac{\eta_2^A \eta_1^B \alpha_2^A \alpha_1^B}{\eta_2^A + \eta_1^B}\right] \tag{6}$$

$$C_{10}^{AB} = 7\left[\frac{\eta_1^A \eta_3^B \alpha_1^A \alpha_3^B}{\eta_1^A + \eta_3^B} + \frac{\eta_3^A \eta_1^B \alpha_3^A \alpha_1^B}{\eta_3^A + \eta_1^B} + \frac{5}{2}\frac{\eta_2^A \eta_2^B \alpha_2^A \alpha_2^B}{\eta_2^A + \eta_2^B}\right] \tag{7}$$

Thus the C_n coefficients can be obtained if the set $\{\alpha_1^i, \alpha_2^i, \alpha_3^i, \eta_1^i, \eta_2^i, \eta_3^i\}$ is known for each interacting species.

Induced interactions due to the partial charges on the framework species are calculated for the dipole polarizability of the absorbate using the expression:

$$u_{\text{ind}} = -\frac{1}{2}\alpha_1\left(\sum_{i,j}^{n_j}\mathbf{E}_{i,j} + \sum_{i,k}^{n_k}\mathbf{E}_{i,k}\right)^2 \tag{8}$$

where $\mathbf{E}_{i,j}$ is the electrostatic field due to the framework j^{th} oxygen atom with the argon at the position i and $\mathbf{E}_{i,k}$ is the same quantity for silicon atoms. The framework atoms carry partial charges of $-1e$ and $+2e$ for oxygen atoms and the silicon atoms respectively. As shown below induction is not a significant contribution to the total interaction, and higher order and many body induced effects can be neglected.

The three body dispersion terms involving triplets of species A, B and C can be obtained from the perturbation theory at the third and fourth order. For a triplet, the total dispersion energy is non additive:

$$u_{\text{disp}} = u_{\text{disp}}^{AB} + u_{\text{disp}}^{BC} + u_{\text{disp}}^{CA} + u_{\text{disp}}^{ABC} \tag{9}$$

where u_{disp}^{ABC} represents a sum of several terms describing the three-body interaction. These can be expressed in a general form by the equation [10,11]:

$$u^{ABC}(l_1,l_2,l_3) = \sum_{l_1}\sum_{l_2}\sum_{l_3} Z^{ABC}(l_1,l_2,l_3)\, W^{ABC}(l_1,l_2,l_3) \tag{10}$$

where W^{ABC} is a geometrical factor and Z^{ABC} is an electronic function. The latter, like the two body dispersion coefficients, can be written as an integral over the product of frequency dependent polarizabilities which can be reduced to the following expression involving static polarizabilities using a Padé approximant [11]:

$$Z^{ABC}(l_1,l_2,l_3) = \frac{1}{2}\alpha_{l_1}{}^{A}(0)\alpha_{l_2}{}^{B}(0)\alpha_{l_3}{}^{C}(0)\eta_{l_1}{}^{A}\eta_{l_2}{}^{B}\eta_{l_3}{}^{C}$$

$$\times \frac{\eta_{l_1}{}^{A} + \eta_{l_2}{}^{B} + \eta_{l_3}{}^{C}}{(\eta_{l_1}{}^{A} + \eta_{l_2}{}^{B})(\eta_{l_2}{}^{B} + \eta_{l_3}{}^{C})(\eta_{l_3}{}^{C} + \eta_{l_1}{}^{A})} \tag{11}$$

The calculation of the three body dispersion terms requires the same set of parameters as the two body terms. The geometrical factor $W^{ABC}(l_1,l_2,l_3)$, for orders of multipole up the quadrupole terms, depends on the side lengths of the triangle, R_{12}, R_{23}, R_{31}, for which the triplet of atoms are vertices and the interior angles, ϕ_1, ϕ_2, ϕ_3,

$$W(DDD) = 3R_{12}^{-3}R_{23}^{-3}R_{31}^{-3}(1 + 3\cos\phi_1\cos\phi_2\cos\phi_3) \tag{12}$$

$$W(DDQ) = \frac{3}{16}R_{12}^{-3}R_{23}^{-4}R_{31}^{-4}[(9\cos\phi_3 - 25\cos 3\phi_3)$$

$$+ 6[\cos(\phi_1 - \phi_2)][3 + 5\cos 2\phi_3]] \tag{13}$$

$$W(QQD)=\frac{15}{64}R_{12}^{-5}R_{23}^{-4}R_{31}^{-4}[3(\cos\phi_3-5\cos3\phi_3)$$

$$+20\cos(\phi_1-\phi_2)(1-3\cos(2\phi_3))+70\cos2(\phi_1-\phi_2)\cos\phi_3] \quad (14)$$

$$W(QQQ)=\frac{15}{128}R_{12}^{-5}R_{23}^{-5}R_{31}^{-5}[-27+220\cos\phi_1\cos\phi_2\cos\phi_3)$$

$$+490\cos2\phi_1\cos2\phi_2\cos2\phi_3$$

$$+175(\cos2(\phi_1-\phi_2)+\cos2(\phi_2-\phi_3)+\cos2(\phi_3-\phi_1))] \quad (15)$$

A triple dipole interaction also occurs in the fourth-order perturbation term for which the expression is:

$$W^{(4)}(DDD)=Z_2^{(4)}R_{12}^{-6}R_{23}^{-6}[1+\cos^2\phi_2]+Z_3^{(4)}R_{23}^{-6}R_{31}^{-6}[1+\cos^2\phi_3]$$

$$+Z_1^{(4)}R_{31}^{-6}R_{12}^{-6}[1+\cos^2\phi_1] \quad (16)$$

The conjugate electronic factors are given by:

$$Z_i^{(4)}=-\frac{45}{32}[\alpha_1^{(i)}]^2\alpha_1^{(j)}\alpha_1^{(k)}\eta_1^{(i)}\eta_1^{(j)}\eta_1^{(k)}$$

$$\frac{2(\eta_1^{(i)})^2+(\eta_1^{(j)}+\eta_1^{(k)})(\eta_1^{(j)}\eta_1^{(k)})+2\eta_1^{(i)}(\eta_1^{(j)}+\eta_1^{(k)})(2\eta_1^{(i)}+\eta_1^{(j)}+\eta_1^{(k)})}{(\eta_1^{(i)}+\eta_1^{(j)})^2(\eta_1^{(i)}+\eta_1^{(k)})^2(\eta_1^{(j)}+\eta_1^{(k)})^2} \quad (17)$$

where $\alpha^{(i)}$ is the dipole polarizability of the atom at the vertex i. Although the three body terms should also be damped, no suitable expression is available.

The excitation energies η_ℓ that appear in the expressions for the dipole dispersion coefficients can be expressed [9] in terms of the sum rules S_ℓ, and the polarizabilities α_ℓ by

$$\eta_\ell=\sqrt{S_\ell/\alpha_\ell(0)} \quad (18)$$

The sum rules S_2 and S_3 can be re-expressed in terms of the polarizabilities and the lower order rules by

$$S_2=3(S_1\alpha_1)^{1/2} \quad (19)$$

$$S_3=\frac{15}{2}(S_2\alpha_2)^{1/2} \tag{20}$$

and the first sum rule is the effective number of electrons $N_{\rm eff}$. A method for finding the higher order static polarizabilities in terms of these quantities has been described in earlier work [2]. This is based on expressions for C_8 and C_{10} written in terms of η_1 and α_1 and requires two coefficients, K_8 and K_{10}, which can be found with the aid of results from accurate calculations. The equations for α_2 and α_3 may be expressed as follows:

$$\alpha_2=\frac{K_8^2\alpha_1}{144}[1+X]^2 \tag{21}$$

where

$$X=\left[1+\frac{24\sqrt{3}}{K_8}\left(\frac{\alpha_1}{N_{\rm eff}}\right)^{1/4}\right]^{1/2} \tag{22}$$

$$\alpha_3=\frac{K^2\alpha_1^2}{4S_3}[1+Y]^2 \tag{23}$$

where

$$Y=\left[1+\frac{4\alpha_1 S_3}{KN_{\rm eff}}\right]^{1/2} \tag{24}$$

and

$$K=\frac{1.6406K_{10}}{\eta_1}-\frac{0.625}{\eta_2}\left(\frac{\alpha_2}{\alpha_1}\right)^2 \tag{25}$$

The determination of all the parameters necessary to evaluate the long range two-body and three-body terms is thus reduced to the determination of $N_{\rm eff}$ and α_1, K_8 and K_{10}.

For neutral first and second row atoms it was found that $N_{\rm eff}$ could be expressed as a quadratic function of the total number of electrons $(s+p)$ in the outer shells. In zeolites, the atomic species generally carry partial charges. We therefore assume that the effective number of electrons in the more negative species is increased by the partial charge and that in the more positive species it is reduced by the deficit of charge, so that $N_{\rm eff}$ is found from

$$N^{A}_{\text{eff}} = N^{A_0}_{\text{eff}} \pm |q| \tag{26}$$

where $N^{A_0}_{\text{eff}}$ is the effective number of electrons of the species A in the isolated and neutral (ground) state and $|q|$ is the magnitude of the partial charge of A. The static polarizabilities for the charged lattice species were estimated from Auger data using a method given in previous work [12].

The four repulsive parameters $\{A^{\text{Ar,O}}, b^{\text{Ar,O}}, A^{\text{Ar,Si}}, b^{\text{Ar,Si}}\}$ required to evaluate the Ar silicalite interaction were obtained by fitting to experimental Henry law constants [2]. SCF calculations for the adsorption of He on NaCl and LiF surfaces [13] provided a basis for imposing preliminary constraints on $\{A, b\}$ pairs such as the magnitude of the cationic repulsive parameters with respect to the anionic ones. A trial and error method controlled by four Henry law constants at four different temperatures was then used to obtain better repulsive parameters. For calculations at temperatures less than 340 K the monoclinic silicalite structure was used and the orthorhombic structure was used for higher temperatures. The total energy is very sensitive to small variations of the b parameters which can be considered as coarse parameters. The A parameters were therefore adjusted in order to fine tune the repulsive energy.

Having established the basic parameters for Ar in silicalite-1, further calculations were made for Ar, Kr and Xe rare gas species [2] in this adsorbent, and for Ar in AlPO$_4$-5 [14, 15]. The repulsive parameters for the silicalite adsorbent were found from the following combination rule, based on an SCF study [16,21] of repulsive interactions between non bonded species A and B,

$$u^{A,B}_{\text{rep}}(R) = (A^A A^B)^{1/2} \exp[-2b^A b^B R/(b^A + b^B)] \tag{27}$$

No other parameter adjustment was made for the silicalite calculations. For AlPO$_4$-5 the repulsive parameter b for the lattice oxygen was altered so as to optimise agreement with experimental zero coverage isosteric heat data. The change in b from $4.138\,\text{Å}^{-1}$ to $4.350\,\text{Å}^{-1}$ is consistent with the lower partial charge of -0.9 on the oxygen in AlPO$_4$, compared to -1.0 in silicalite. The parameters used for the adsorbent species and for the adsorbate species studied in this work are summarised in Table I. Extensive calculations of low coverage properties and simulations of adsorption at higher loading [17] in silicalite and AlPO$_4$-5 [14,15] have confirmed that the potential model is superior to the widely used model developed by

TABLE I Parameters for the calculation of intermolecular interactions

	q/e	N_{eff}	$\alpha_1(0)/\mathrm{\AA}^3$	$A/e\mathrm{V}$	$b/\mathrm{\AA}^{-1}$	K_8	K_{10}
O silicalite	−1.0	4.656	1.20	4.20×10^4	4.138	2.89	7.00
O AlPO4	−0.9	4.556	1.12	4.20×10^4	4.350	2.87	6.85
Si	+2.0	1.52	0.38	1.67×10^5	4.526	2.00	–
Al	+1.6	1.13	0.31	1.84×10^5	18.3	1.72	2.86
P	+2.0	2.26	0.551	5.87×10^4	43.55	2.33	4.55
Ar	0	6.106	1.641	8.94×10^3	3.624	1.602	9.511
Xe	0	7.901	4.048	2.79×10^4	3.265	3.602	11.55

Kiselev and co-workers [18] based on a 12-6 model and interactions with only the oxygens in the adsorbent.

Nevertheless the considerable expenditure of time and effort involved in developing a potential model of this type prompts a number of questions: (i) Can effective potentials be developed based on simpler models which have the same degree of transferability? (ii) Which, if any, terms in the present model can be neglected without impairing the performance of the potential model? (iii) Do additional terms need to be considered and where should attention be focused in future attempts at further development of the model? In the following section we attempt to provide some answers to these questions by analysing calculations for argon and xenon in silicalite.

RESULTS AND DISCUSSION

Calculations were performed over a unit cell embedded at the centre of $3 \times 3 \times 3$ unit cells containing 5184 O and 2592 Si atoms. The summations were cut off after 16.5 Å. The monoclinic form of silicalite was used in the calculations reported, since this is the most stable structure at the common adsorption temperature of 77 K. Results are displayed as (potential energy)/k at this temperature although, of course the potential energy itself does not depend on temperature.

Figure 1 shows the total potential energy for argon and xenon probes in a cross section through the centre of the straight pore of silicalite. Since there is only a single minimum, it is clear that there is a strong overlap of the zeolite wall potential for both probes. This is also the case for the widest pore space available to the adsorbate which is to be found in a cross section through the intersection shown in Figure 2. The variation of the potential

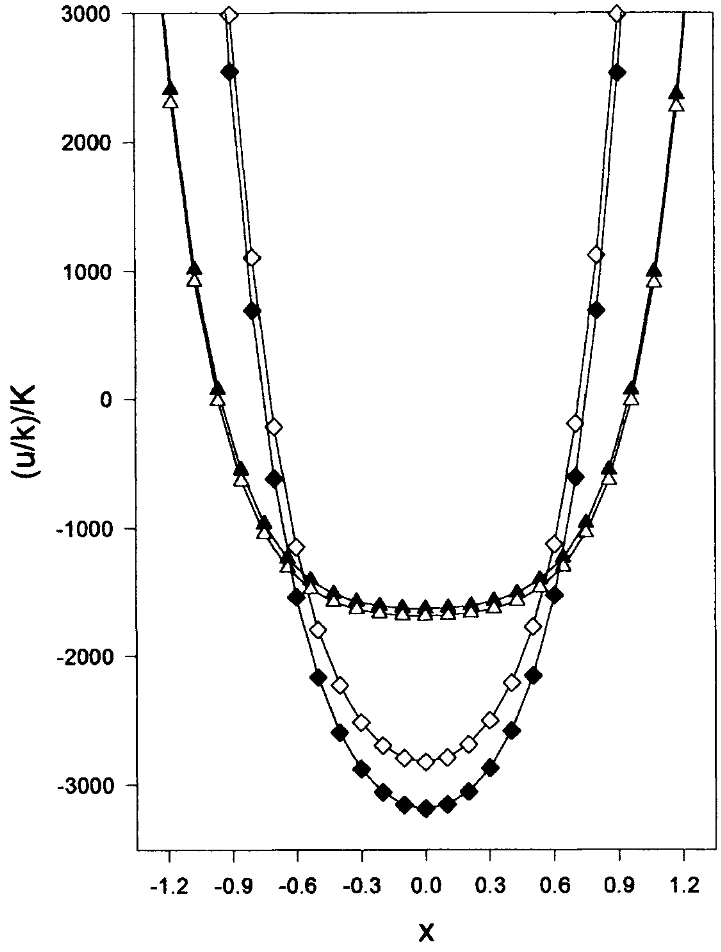

FIGURE 1 Potential energy through the central cross section of the straight pore of silicalite (along a line through $y=0$, $z=0$) according to the PN potential. The triangles are for Ar and the diamonds for Xe. Filled points are the total potential function, open points are two body attractive terms only + repulsive terms.

energy along the centre of the straight pore is shown in Figure 3. This is also the position of the minimum energy, as can be deduced from Figures 1 and 2. The asymmetry in this plot, which is particularly noticeable for Xe, is due to the asymmetry of the monoclinic structure and does not accur in the more symmetrical Pnma orthorhombic structure which is stable at high temperatures. Contour maps [2] showing the variation of potential energy over this cross section confirm that the PN1 function predicts very narrow pores, in contrasts to the Kiselev potential [18] which is based on the

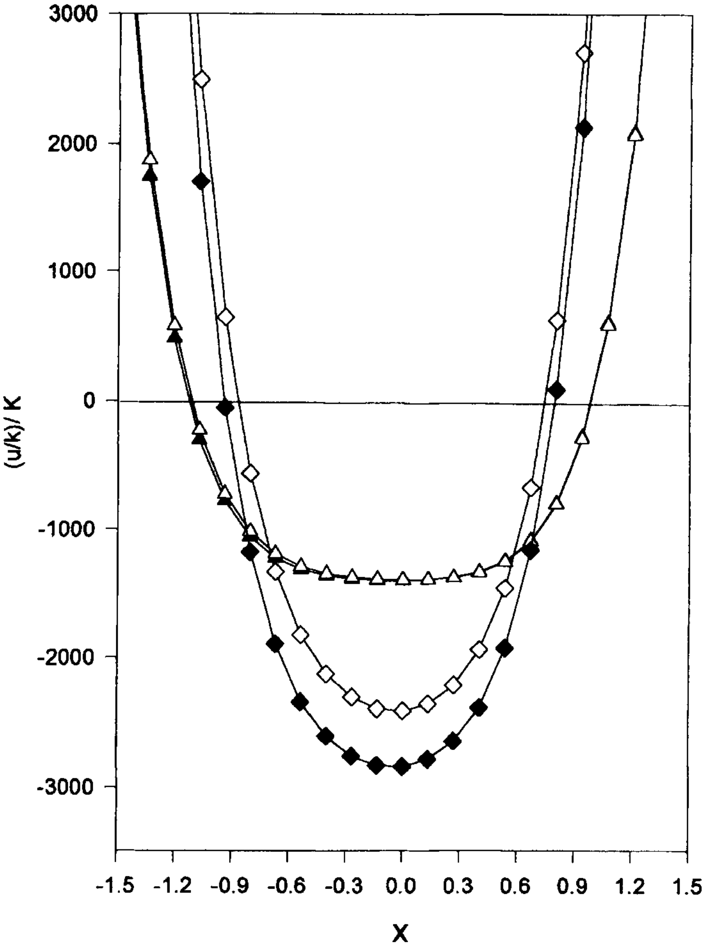

FIGURE 2 Potential energy through the intersection of the straight pore of silicalite with the sinusoidal pore (along a line through $y=0.33b$, $z=0$) according to the PN potential. The triangles are for Ar and the diamonds for Xe. Filled points are the total potential function, open points are two body attractive terms only + repulsive terms.

summation of 12-6 interactions with oxygen only, and which exhibits a shallow double minimum for Ar in the ($y=0, z=0$) cross section [2].

Also shown in Figures 1–3 are the potential energy functions obtained by using only the two body dispersion and induction terms together with the repulsion term. It is clear that the overall 3-body contribution to the total potential can vary substantially when the polarizability of the adsorbate species is changed. In silicalite it turns out that this accounts for only 3% of the total potential energy for Ar, but is about 15% for Xe. This suggests

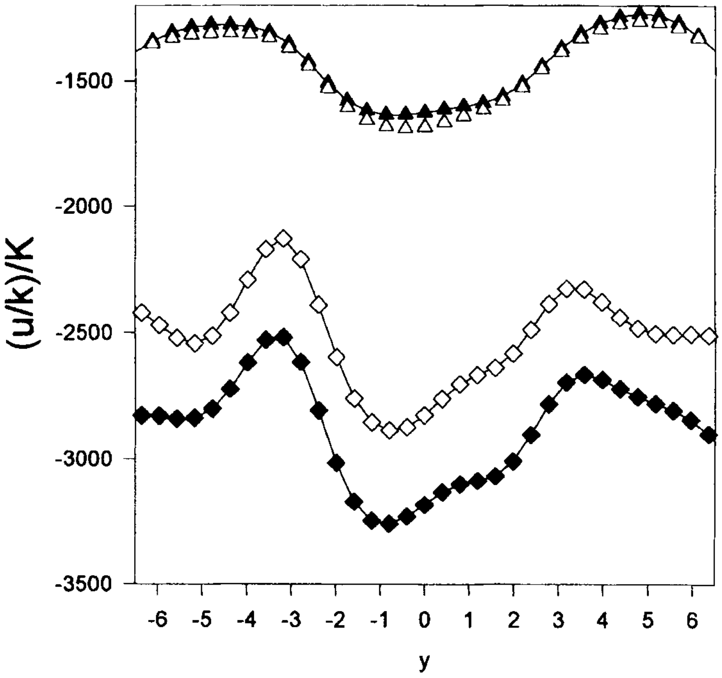

FIGURE 3 Potential energy along a line through the centre of the straight pore of silicalite ($x = 0, z = 0$) according to the PN potential. The triangles are for Ar and the diamonds for Xe. Filled points are the total potential function, open points are two body attractive terms only + repulsive terms.

that the good agreement with experimental heats at zero coverage, obtained for Ar in silicalite, using a potential function based on summation of two body interactions with oxygen only, may be fortuitous.

In order to explore further the contributions of the various terms in the PN type of potential functions, we now concentrate attention on the centre of the cross section through the straight channel (cf Fig. 1). Since there are only small quantitative differences between this position and other choices of pore cross section, it is possible to draw fairly general inferences about the nature of the potential energy from a consideration of this single position.

Figures 4 and 5 show the separate 2-body dispersion and repulsive components for adsorbate-O and adsorbate-Si interactions. As anticipated the O contribution is by far the most important part of the interaction ($\sim 80\%$), nevertheless the total interaction from the Si species is of the order of 12%. Perhaps of more interest is the significant contribution from the higher order (C_8 and C_{10}) terms. Since these also have a different distance dependence from

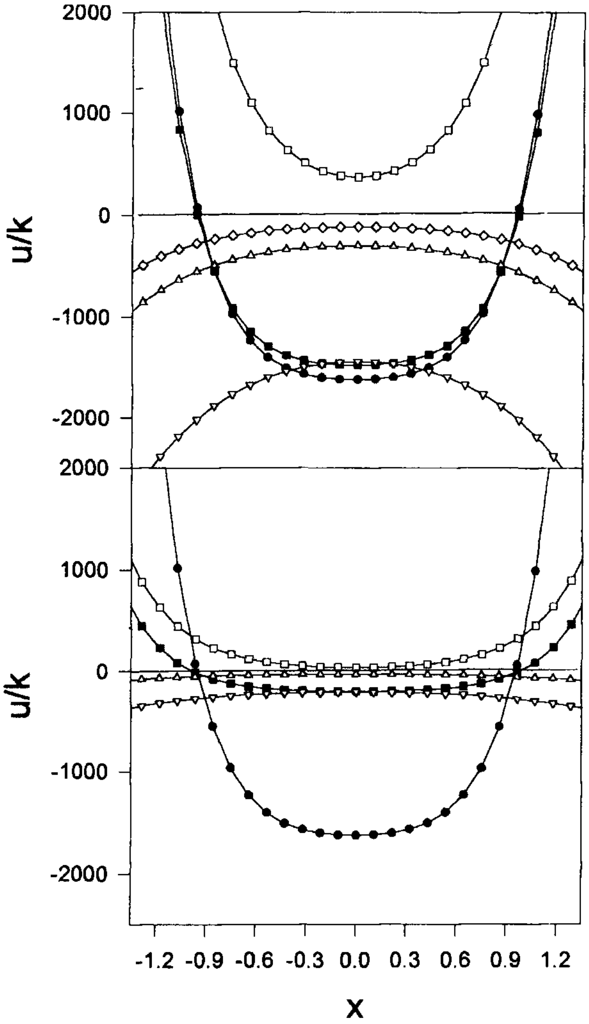

FIGURE 4 Two body contributions to the total PN potential for argon in the central section of the straight pore of silicalite. Top panel: Ar-O, bottom panel: Ar-Si. The total PN potential energy (also shown in Fig. 1) is shown as filled circles; the other symbols denote: (□) repulsive term, (▽) C_6 term, (△) C_8 term, (◇) C_{10} term, (■) total two body attractive term.

the dominant C_6 term, they play an important part also in determining the shape of the potential well. It is interesting to note that the relative contribution of these terms is not the same for the Xe probe as it is for the Ar probe.

The induced interaction is extremely small in these systems, being less than 0.3% of the total potential energy at the bottom of the well, even for

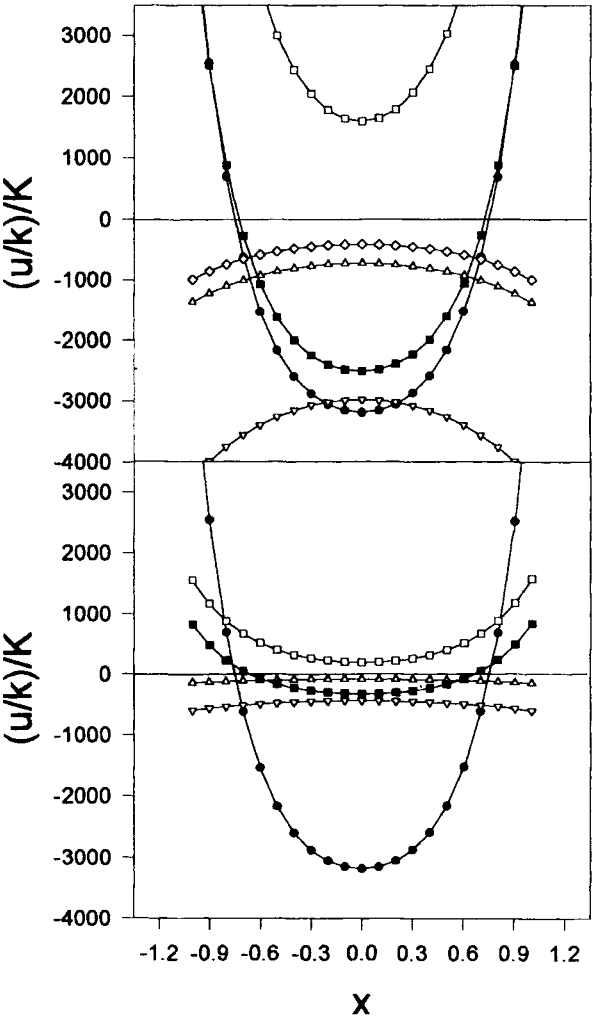

FIGURE 5 Two body contributions to the total PN potential for xenon in the central section of the straight pore of silicalite. Top panel: Ar-O, bottom panel: Ar-Si. The total PN potential energy (also shown in Fig. 1) is shown as filled circles: the other symbols denote: (□) repulsive term, (▽) C_6 term, (△) C_8 term, (◇) C_{10} term, (■) total two body attractive term.

the highly polarizable xenon. This is because the O^- and Si^{2+} contributions, which are individually quite large, tend to cancel out. When the probe is close to the surface, the absolute value of the induced potential is much larger (~10 K) but because the total potential is very steep in this region, the effect on the overall shape and on the effective pore width is negligible.

Figures 6 and 7 illustrate the way in which the various 3-body terms included in these calculations contribute to the interaction. Only those terms involving one or two oxygen lattice species have been considered, since the three body terms including two Si atoms are of negligible importance. It is striking that the total 3-body contribution is repulsive for Ar as would be intuitively expected, but attractive for Xe. It is also noticeable that the highly heterogeneous interactions involving probe + O + Si are quite different from those involving two oxygens. The latter tend to show the cancellation between terms involving quadrupoles (shown as squares in the figures) and fourth order triple dipole terms (shown as triangles), that is well known from studies of uniform homogeneous systems. The resultant from summing these two contributions (shown as heavy lines in the figures) is spatially non uniform for Ar, though not for Xe. There is a significant

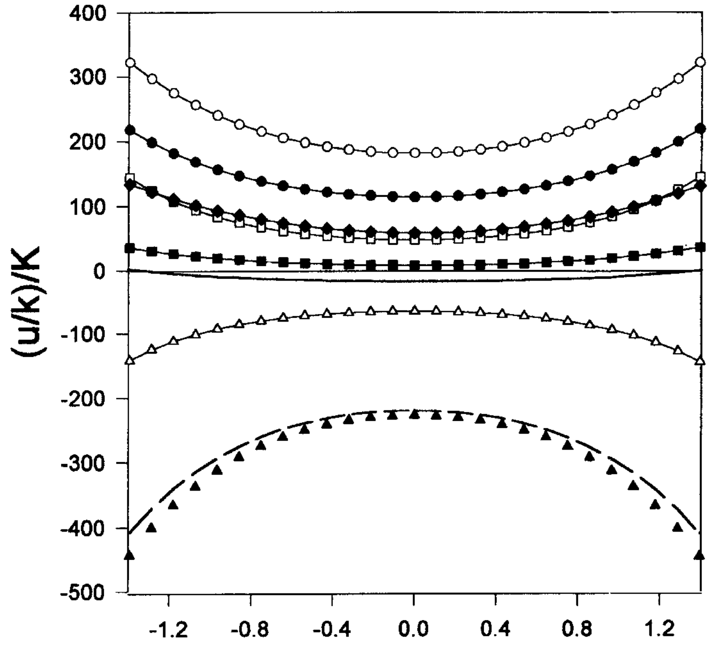

FIGURE 6 Three body dispersion contributions to the total PN potential for argon in the central section of the straight pore of silicalite. The total three body term is shown as filled diamonds. The remaining filled symbols are the Ar-O-Si terms, the open symbols the Ar-O-O terms. Circles denote the third order triple dipole (ATM) contribution, squares the sum of the contributions involving quadrupoles (DDQ, DQD, QDD, QQD, QDQ, DQQ and QQQ). The fourth order triple dipole terms are shown as triangles. The total contribution from the sum of fourth order + quadrupole terms is shown as a heavy full line for the Ar-O-O terms and as a heavy broken line for the Ar-O-Si terms.

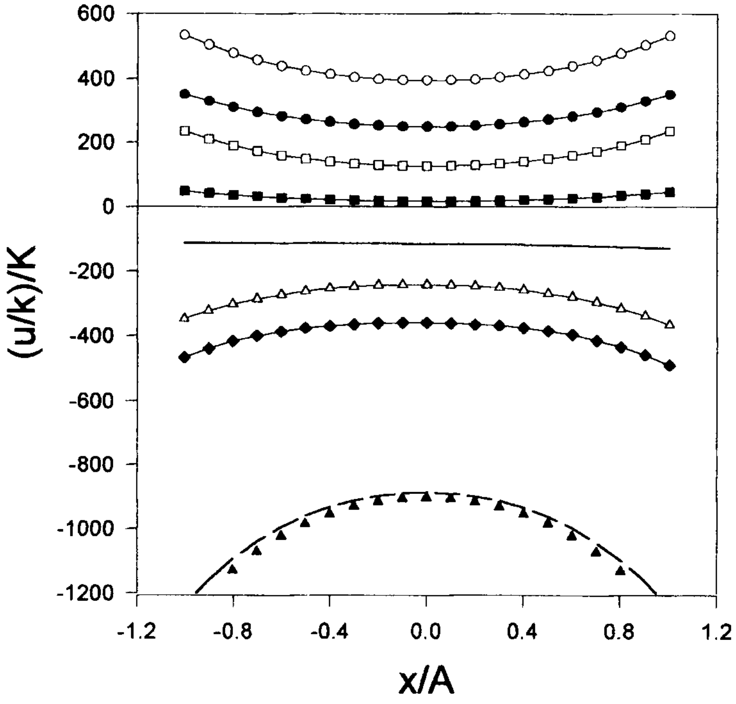

FIGURE 7 Three body dispersion contributions to the total PN potential for xenen in the central section of the straight pore of silicalite. The total three body term is shown as filled diamonds. The remaining filled symbols are the Xe-O-Si terms, the open symbols the Xe-O-O terms. Circles denote the third order triple dipole (ATM) contribution, squares the sum of the contributions involving quadrupoles (DDQ, DQD, QDD, QQD, QDQ, DQQ and QQQ). The fourth order triple dipole terms are shown as triangles. The total contribution from the sum of fourth order + quadrupole terms is shown as a heavy full line for the Xe-O-O terms and as a heavy broken line for the Xe-O-Si terms.

attractive contribution from these terms for Xe. This contrast with uniform homogeneous systems occurs because the sum of all the quadrupole terms is close to zero, but there is a rather large attractive contribution from the fourth order term, amounting to some 35% of the total potential energy. This observation underlines the sensitivity to spatial arrangement which can occur when some of the interacting species are fixed at lattice sites. In addition, the differences between Ar and Xe highlights the way in which the heterogeneity of the system - which is reflected in the different polarizabilities that are placed at different sites - can emphasise the contribution of a particular component in the overall interaction. In the case of the Ar probe, the total 3-body part of the potential energy, which is repulsive, almost exactly cancels the attractive contributions from Si 2-body interactions, as implied in models such as the Kiselev potential, where an effective 2-body potential is constructed using only the oxygen-probe interactions. It is clear that this does not occur when the probe is the more highly polarizable Xe.

We discuss below some of the defects of the PN potential in the light of the analysis given here. Despite these defects, comparisons with several experimental results have shown that it can be regarded as a very good approximation. However the establishment of a potential of this kind, in a form suitable for use in a simulation, involves a fairly substantial amount of labour and computing time in order to calculate enough points to set up an accurate interpolation grid for use in simulation. It is therefore of interest to ask whether an effective potential can be used as replacement. In order to examine this question, we have used the PN1 potential as a standard. We define a 12-6 fitting equation by the coefficients C and B, as

$$u=-\sum_{\mathrm{O,Si}}\frac{1}{r^6}+B\sum_{\mathrm{O,Si}}\frac{1}{r^{12}} \tag{28}$$

The coefficients B and C have been fitted to the attractive and repulsive parts of the potential energy curve through the centre of a cross section. It should be noted that this fitting procedure is not unambiguous, since the values of the coefficients can vary according to the range over which the fit is made. The coefficients can be related to effective Lennard-Jones parameters (ε,σ) by writing:

$$C=4\varepsilon\sigma^6; \quad B=4\varepsilon\sigma^{12} \tag{29}$$

An example for argon in silicalite is shown in Figure 8. The broken lines have been fitted, as described above, using the sums of the reciprocal 6th and 12th power terms over all species in the lattice for the range $-1.3<x<1.3$A. The dotted line in Figure 8, shows the total potential obtained in the same way but using sums over the oxygen atoms only. The values of the fitting parameters are shown in Table II together with the corresponding Lennard-Jones parameters. The effective σ for the oxygen in the silicalite lattice, calculated from the oxygen parameters, is 3.8Å (using σ for Ar = 3.405Å), this may be compared with the accepted value of 2.71Å, calculated on the basis of a van der Waals radius of 1.52Å. The larger value of σ that corresponds to the PN potential reflects the fact that this potential is more repulsive than one calculated on the basis of an oxygen van der

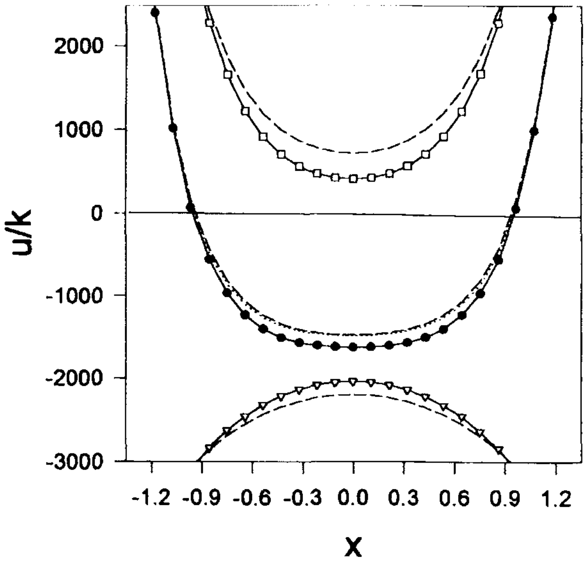

FIGURE 8 Summed 12-6 effective potential compared to the PN model for Ar in the central section of the straight pore in silicalite. Filled circles are the total PN potential. The total dispersion contribution to the PN potential is shown as triangles, the Born-Mayer repulsive contribution is shown as squares. The fits from the 12-6 potential summed over all the lattice atoms (Si and O) are shown as broken lines, those for summations over oxygen only as a dotted lines.

TABLE II Values of C, B, σ and ε from fitting attractive and repulsive parts of the potential energy to 12-6 functions

	Oxygen and silicon sums		*Oxygen sums only*	
	Ar	*Xe*	*Ar*	*Xe*
$(C/k)/\mathrm{K}$	3.80×10^5	8.24×10^5	5.2×10^5	1.14×10^6
$(B/k)/\mathrm{K}$	1.014×10^9	3.22×10^9	1.14×10^9	3.775×10^9
$\sigma/\mathrm{\AA}$	3.72	3.97	3.60	3.86
$(\varepsilon/k)/\mathrm{K}$	35.6	52.7	59.3	86.1

Waals radius (see Equation (29)). The effective ε/k for oxygen is 29.3 K, using the standard value of 120 K for argon. The heat of adsorption at zero coverage depends on the integral over the Boltzmann factor ($\exp(-u/kT)$) for the overall potential. Figure 8 shows that the overall potential energy from the effective 12-6 function is in close agreement with the PN1 function and therefore results in a similar adsorption heat.

A similar fitting procedure was applied to the Xe probe (Fig. 9) the resulting parameters are given in Table II. The effective values of σ and ε/k for oxygen are 3.87Å and 26.3 K, using 3.85Å for σ and 281K for ε/k for Xe. These values are quite close to those obtained from the argon results above. Nevertheless transferability for the simple effective potential cannot be claimed since the potential well for Xe turns out to be more than 20% more repulsive than that obtained from the PN1 potential. This large discrepancy can be attributed to the different weighting of the various contributions to the total potential discussed above, and explains the poor agreement between experiment and theory for q_{st} and k_H, when the 12-6 function is treated as a transferable potential [2].

From both examples it is clear that a single inverse 6th power term cannot adequately account for the more accurate attractive terms calculated here. As the foregoing demonstrates, much of this failure can be attributed to the large contribution from the C_8 term, although 3-body interactions

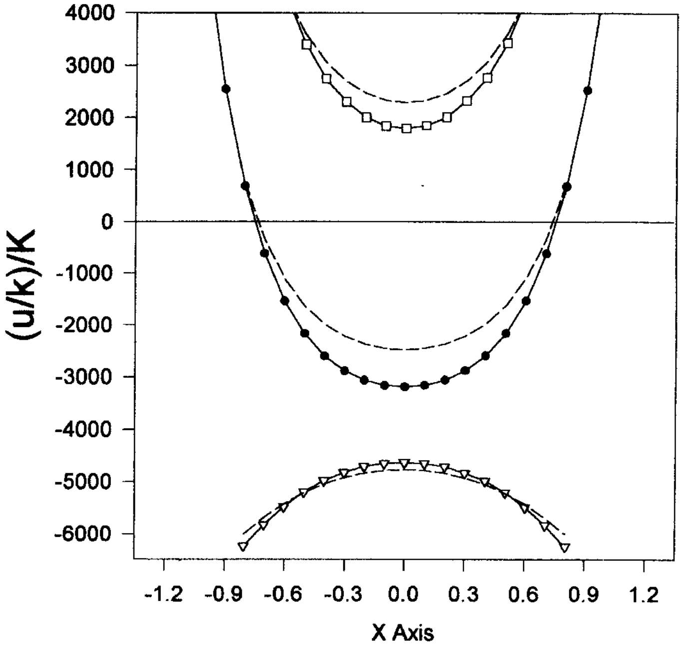

FIGURE 9 Summed 12-6 effective potential compared to the PN model for Xe in the central section of the straight pore in silicalite. Filled circles are the total PN potential. The total dispersion contribution to the PN potential is shown as triangles, the Born-Mayer repulsive contribution is shown as squares. The fits from the 12-6 potential, summed over all the lattice a atoms (Si and O), are shown as broken lines.

are also important. It is remarkable that the failure of the inverse 12th power repulsive term to match the more accurate Born-Mayer exponential function actually compensates for much of the inadequacy of the r^{-6} fit. It follows that a 6-exp (Buckingham) potential function would not be expected to be a better choice of effective potential than the 12-6 function, since in this case the repulsive term could be fitted exactly, leaving the r^{-6} function as a poor fit and thereby exposing the inadequacy of an inverse 6th power term to represent attractive interactions.

In constructing the PN potential several limitations were imposed. The present analysis demonstrates that this type of potential function is likely to be an improvement on simple 12-6 models. Nevertheless it raises the question of whether even higher order terms than those included in this work need to be considered. For example the contribution from the fourth order three body term is found to represent a very significant part of the total interaction when this is calculated for different lattice species and the cancellation with 3-body terms involving quadrupoles does not occur. The neglected terms beyond C_{10} in the two body interactions seem to be of less importance, except perhaps for highly polarizable adsorbates. Of course overall properties of the potential function are determined to a very large extent by the repulsive part of the interaction; since there is no way of accurately obtaining the repulsive term, many of the shortcomings of the present approach are hidden in the repulsive part of the interaction. The remarkable success of transferability for the PN potential is an encouragement to believe that the most important features are already present in a potential of the type described here.

CONCLUSIONS

The two and three body dispersion terms included in the PN potential, with the exception of the induced interactions and possibly the C_{10} terms, each make a significant contribution when compared with the total potential energy function. This creates distortions in the attractive part of the interactions by comparison with a simple inverse sixth power attraction. It seems fortuitous that there is a nearly perfect cancellation of the deviations from attractive and repulsive parts of the interaction for argon, and that furthermore the oxygen atoms alone account for very nearly all of the potential energy. When the polarizability of the adsorbate is altered, as for example for Xe as exemplified here, these compensations vanish. In a similar way the cancellation between three body quadrupole terms and fourth order triple dipole terms which occurs in uniform heterogeneous systems does not occur in these heterogeneous systems. Of course there are other 3-body terms, involving two adsorbate atoms or all three adsorbate atoms, which do not enter into the present considerations, but which can play a role in dense adsorbates [19]. It is disturbing to find that the fourth order triple dipole term can be a very large part of the total potential energy since this implies that even higher order terms may not be negligible. No method of handling damping in a simple and convincing way for these terms is presently available. A great deal depends on the shape of the repulsive interactions, and on the validity of the repulsive parameters. It would be an important advance to be able to calculate the repulsive terms in a reliable way using a quantum mechanical approach. Some progress has been made in this respect [20], but there is great scope for improvement. From the present study it would appear that carefully tuned 12-6 potentials can be used as input to adsorption simulations in the type of zeolites considered here, but it would appear to be advisable to include all atoms (rather than oxygens only) and not to place any reliance on transferability of the parameters obtained.

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