

Molecular dynamics consideration of the mutual thermalization of guest molecules in zeolites

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Molecular dynamics (MD) is applied to simulate methane self-diffusion in a model zeolite ZK4. It is found that the mutual interaction of the adsorbed molecules is sufficient to guarantee their thermalization, so that in first-order considerations, the energy exchange with the zeolite framework may be neglected.

With the increasing possibilities of their technical application [1], in the last few years scientific interest has focused on the investigation of mass-transfer phenomena in zeolitic adsorbate-adsorbent systems [2]. In addition to the various experimental techniques involved, the advent of adequate computational facilities has initiated a series of attempts to simulate molecular transport by molecular dynamics (MD) calculations [3-8].

In general, the order-of-magnitude agreement of the thus calculated self-diffusion coefficients [5-8] with the results of the NMR pulsed field gradient measurements [9,10], has been considered as a reliable criterion for the feasibility of such calculations. A general shortcoming of these calculations consists in the fact that thermal equilibrium of the diffusants was either maintained artificially by a renormalization of the individual velocities after each iteration step [6] or has been completely left out of consideration. Such simplifications in the computational treatment are inevitable if one is considering

molecular dynamics under the influence of a rigid framework, i.e. in a fixed lattice without internal degrees of freedom and thus without the possibility of energy exchange between the zeolite framework and the diffusants. The steric effect of lattice vibrations on the diffusive motion of adsorbed particles can be approximately included by stochastic or harmonic oscillations of each individual lattice atom [8]. However, this simple model also gives no realistic description of the energy exchange between the zeolite framework (acting as a heat bath) and diffusants. But even with the fastest computers (e.g. CRAY versions) the examination of "long-range" diffusion phenomena would require unacceptably large computation times if lattice vibrations were included. It is the aim of the present communication to investigate up to which extent thermal equilibrium of the diffusants is already maintained by their mutual interaction. For this purpose as a model system we have considered methane in zeolite ZK4 with a silicon to aluminium ratio equal to infinity. The

geometry of this zeolite agrees with that of zeolite A except that it contains no cations, so that the windows between the individual supercages are unblocked [11]. The supercages may contain a maximum of about 10 methane molecules [12], the diameters of the windows (0.5 nm) slightly exceed those of the methane molecules.

In our paper, MD calculations have been carried out at a sorbate concentration of 1 to 6 molecules per supercage using the leapfrog algorithm [13]. The van der Waals radii, polarizabilities and diamagnetic susceptibilities used to calculate Lennard-Jones parameters as well as the corresponding procedure are the same as in ref. [14]. The diffusing methane molecules have been approximated by spherical particles. In comparison with the uncertainties in experimental examinations and with respect to the more general purpose of this paper, we think the accuracy of the model to be sufficient. We carried out runs of 100000 time steps per run. The size of the time step was 10^{-14} s. The MD box consisted of 8 large cavities (that means 576 lattice atoms) and periodic boundary conditions have been employed.

As a potential cutoff radius we have taken 2.5 times the Lennard-Jones parameter σ . Simulations with a potential cutoff radius [15] lead, of course, to somewhat too high values of the potential energy. This shift has been found to be of the order of about 1 kJ/mol for a single methane molecule being nearly uniform over the individual cavities. Thus it clearly contributes to the adsorption energy, but is of little influence on molecular dynamics since the attractive-force contributions arising from far lattice atoms in different directions nearly cancel each other. An additional (time-expensive) computational run without cutoff radius showed the same probability distribution and the same thermalisation effect as our other runs. Fig. 1 compares the density distribution following from our MD simulations with those of Monte Carlo (MC) calculations in a canonical (T, V, N) ensemble [15] since those correspond to an ideal thermalisation. $W(r)$ denotes the probability density to find an arbitrary particle at a distance r from the nearest cavity center. $W(r)$ is normalized by division by its mean value. In case a, the MD curve is the one with a small secondary maximum. In all other cases, MD and MC probabilities agree within the uncertainty of the results and, therefore, need

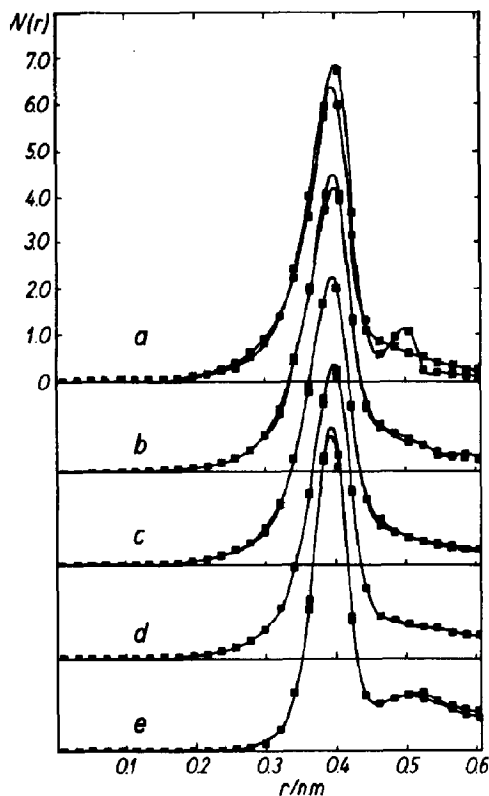


Fig. 1. The probability density $W(r)$ to find particles with a distance r from the nearest cavity center. $W(r)$ has been normalized to have a mean value of one. The labels a, b, c, ... are explained in table 1.

not be distinguished. Obviously, MD and MC lead to coinciding results. The labels a, b, c, ... together with the occupation numbers N_{oc} , the mean temperature of the corresponding run and the average potential energy per particle U are given in table 1. For U we find in all cases, even without interaction between diffusants, a good agreement between MD and MC values. Although it is well known that for macroscopic systems different ensembles lead to the same thermodynamic properties [16], in the present case, in view of the small number of molecules per cavity considered and the strong (local) variations of the potential energy within the zeolite, this result is not trivial. The narrow peak in the probability curves shows clearly that the particles in all cases considered moved during most of the time near the wall in the large cavity.

Fig. 2 shows the local temperatures of the methane

Table 1

List of the runs corresponding to the curves. The star in the first line means that the interaction between diffusants has been switched off in this run

N_{oc}	T (K)	U (kJ/mol)		Curve
		MD	MC	
3*	336.5	-11.6	-11.5	a
1	320.1	-11.9	-11.9	b
3	371.8	-12.2	-12.3	c
6	358.9	-13.2	-13.3	d
3	168.3	-13.9	-14.2	e
3	345.4	-12.3	-12.4	

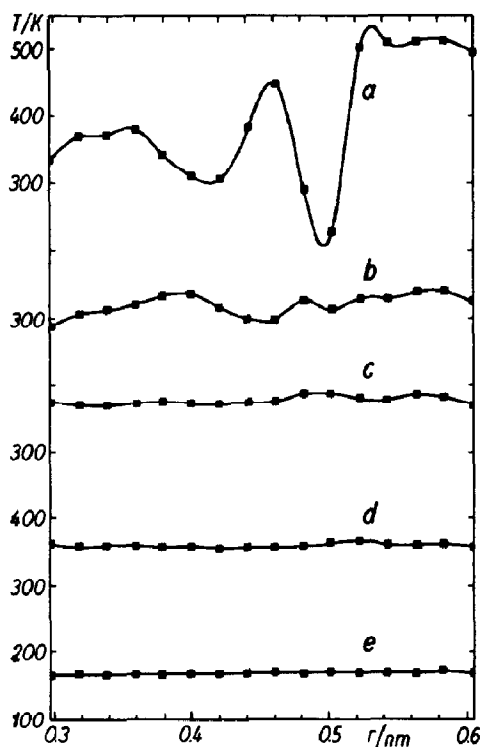


Fig. 2. The local temperature $T(r)$ at a distance r from the nearest cavity center.

molecules for different distances r from the cavity center. The temperature has been defined by

$$\langle E_{kin} \rangle = \frac{3}{2} k_B T. \quad (1)$$

Here $\langle \rangle$ means the (local) arithmetic average over many successive observations of single particles during a long MD calculation; E_{kin} is the one-particle

kinetic energy. In order to check whether the local distribution of successive observations of E_{kin} is in fact of the Boltzmann type, we have evaluated the second moments of the so-defined local temperature distributions at different places. Within an uncertainty of 10%, the values obtained for $\langle (T - \langle T \rangle)^2 \rangle / \langle T \rangle^2$ were (except in the case without interaction between diffusants) found to be everywhere in satisfactory agreement with the theoretical value of 2/3 which easily can be derived from the well-known variance of the kinetic energy of a particle in a canonical ensemble [16], i.e. the Boltzmann distribution. So we may assume that it is possible to define a local temperature corresponding to (1), irrespective of the fact that the local regions in our evaluation are partially so small that at most one particle can be found there. Note that (except case a) everywhere the local temperature is essentially the same, irrespective of the fact that the moving particles meet regions of considerably different potential energy. Corresponding to (1), a difference in the kinetic energy of 1 kJ/mol would correspond to a temperature difference of about 80 K. The particles in the window ($r=0.6$ nm) have average potential energies of about 2 kJ/mol less than those of all other particles. Only the mutual interaction between diffusants prevents these potential-energy differences from occurring with opposite sign also, as local differences of the kinetic energy (energy conservation). The resulting temperature difference in the absence of methane-methane interaction can be seen in curve a of fig. 2. Note that the considerable fluctuation near $r=0.5$ nm corresponds also to a fluctuation in $W(r)$ in the MD curve a of fig. 1. This fluctuation, which occurred at other places or was missing in additional runs with the same parameters but different initial positions and velocities, is clearly due to the strange behaviour of such an artificial ensemble without interaction of the diffusants in which the total energy of each individual particle is conserved even if it, for instance, were situated in a potential minimum with zero kinetic energy, i.e. at rest.

Imagine that polar coordinates have been introduced to describe the density distribution in an individual cavity, the origin being the centre of the cavity. Then fig. 1 corresponds to the density distribution with respect to the radius r , where an integration over all angles has been performed. Fig. 3

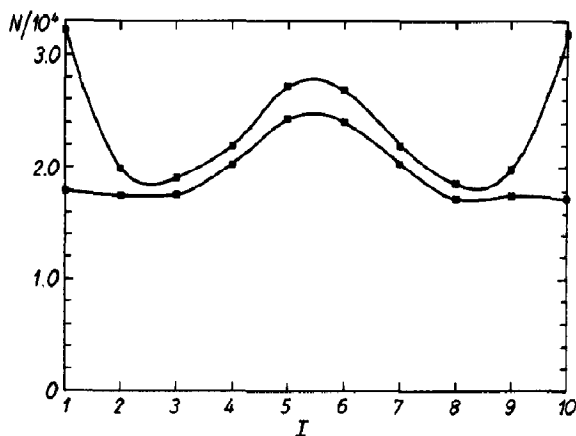


Fig. 3. The angular distribution of particles in the large cavity (see text).

shows the density distribution with respect to the angle in the xy plane if an integration over the other angular coordinate and up to certain values (see below) over r has been carried out. For ten intervals between zero and $\pi/2$, the number of particles found in the corresponding interval has been registered during the whole run; I is the number of the interval. The upper curve gives this distribution for all particles and the other one only for those within $r < 0.43$ nm, i.e. without particles that have been found in windows. Intervals 1 and 10 correspond to windows and the other maximum corresponds to a potential minimum at an additional window into the sodalite unit which is too small for methane to penetrate.

In fig. 4, the nature of the interaction of methane molecules located in the window with other methane molecules has been examined by registering all the distances to other particles whenever a methane has been found in a window. N means in this case the number of methane molecules found at given distances from that in the window. As can be seen, neighbours in the repulsive region < 0.4 nm appear relatively seldom. So the interaction must take place mainly by attractive forces and the strong thermalization found seems to us to be surprising. Figs. 3 and 4 have been taken from the last run in table 1.

From the calculations, we conclude that the mutual thermalization of the diffusants is very good even for small occupation numbers. One of the effects of lattice vibrations on diffusion consists in the thermalization of the kinetic energy of diffusing particles

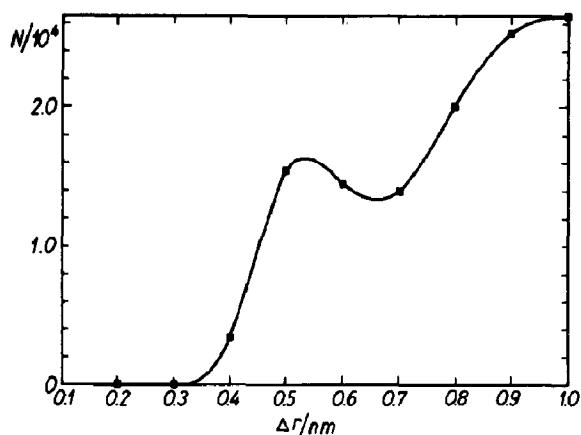


Fig. 4. The number of other diffusants at given distances around a methane molecule situated in a window. The registration has been performed whenever a methane molecule has been found in a window.

to a Boltzmann distribution at any place within the zeolite. But, as we could show in this paper, this is also performed by the diffusants themselves in the case of a rigid lattice.

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