A Molecular Dynamics Simulation of the Temperature Dependence of the Diffusion of Methane in Silicalite

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Molecular dynamics (MD) methods can accurately predict the diffusion coefficients of hydrocarbons in zeolites; these techniques are used to construct an Arrhenius plot for the diffusion of methane in silicalite and the results agree accurately with experimental data. The success of the work confirms that simulation methods are predictive tools in modelling diffusion in molecular sieves.

The MD technique consists of an explicit dynamical simulation of the system modelled which is represented by an ensemble of particles (to which periodic boundary conditions are normally applied) and for which the equations of motion are integrated numerically using a specified time step (typically 10^{-4}–10^{-15} s), with the forces acting on each particle being calculated using specified interatomic potentials. A good account of the theory and practice of the technique, which has now been very widely applied is given in ref. 1.

The viability of MD simulations of molecular transport in zeolites has been shown by previous studies of Xe[2,3] methane and other hydrocarbons[4-7] in both silicalite and zeolite Y. The majority of these studies have used the rigid-framework approximation. Framework mobility was included using harmonic potentials in the work of Demontis et al.[5] on CH_4 in silicalite, while our own earlier study of CH_4 and C_2H_4 in this zeolite[6] included a full explicit treatment of framework dynamics employing Born model potentials which have been successfully used in modelling the structures and properties of other zeolite and silicate systems.[8,9]

In the present study we used the FUNGUS code to undertake simulations of CH_4 in the purely siliceous zeolite, silicalite, which we modelled using the potentials reported in refs. 6 and 8, with a simulation box comprising 576 framework atoms (i.e. three unit cells) (to which periodic boundary conditions were applied); 8 molecules were introduced into the simulation box. After equilibration, the simulations were run for 100 ps. Diffusion coefficients were calculated from the slope of the mean square displacement (MSD) of the carbon atoms with time; with a typical MSD plot being shown in Fig. 1. The simulations were run for a range of temperatures between 150 and 750 K. It would, of course, be desirable to run the simulations for longer periods. Indeed such work which is highly computationally demanding is currently in progress. However, the accurately linear nature of our MSD
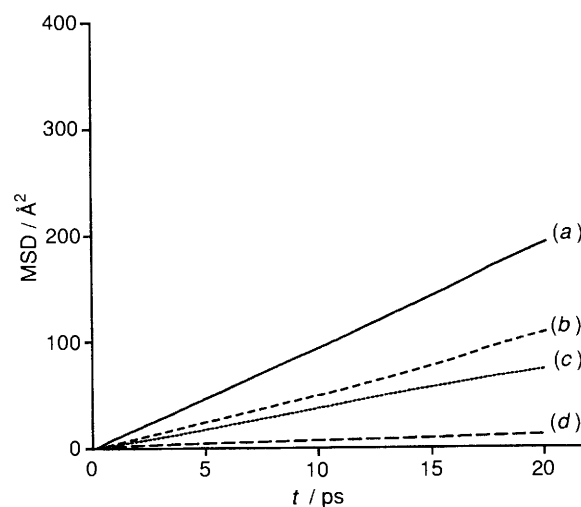

Fig. 1 Calculated mean square displacements (MSDs) for carbon in simulation at 300 K; (a) total MSD, (b) MSD of x direction, (c) MSD of y direction and (d) MSD of Z direction

Table 1 Calculated diffusion coefficients obtained from MSD plots

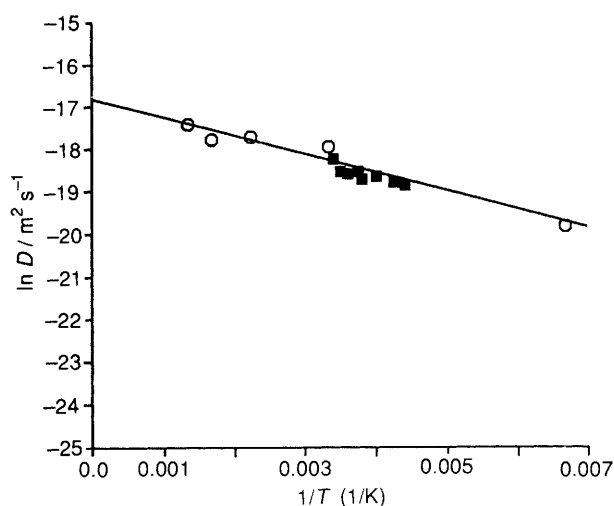| T/K	D $\times 10^{-9}/m^2 s^{-1}$
150	2.5
300	16.1
450	20.4
600	19.0
750	27.3

Fig. 2 Arrhenius plot for diffusion of CH_4 in silicalite using calculated diffusion coefficients; O = calculation, ■ = experiment.[10] Activation energy = 3.58 J.

plot suggests that for the purpose of calculating diffusion coefficients, the present simulations are satisfactory. The calculated diffusion coefficients are given in Table 1 and presented in the form of an Arrhenius plot in Fig. 2, on which we also indicate experimentally determined values. From the slope of the calculated Arrhenius plot we obtain an activation energy of 3.58 kJ mol^{-1} for methane diffusion.

The good measure of agreement between the simulated and experimental diffusion coefficients (D) and activation ener-

gies is most encouraging. In this context we should note that the inclusion of framework flexibility has an appreciable effect on the diffusion of even small molecules such as methane; imposition of a rigid framework can increase D by 70%. The calculations reported here show, however, that framework flexibility can be included straightforwardly in MD simulations of zeolites to yield results for molecular diffusion coefficients that are in good agreement with experiment.

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