MOLECULAR DYNAMICS STUDIES OF SIMPLE SORBATES IN ZEOLITES

BY

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Certificate

This is to certify that the thesis titled **"Molecular Dynamics Studies of Simple Sorbates in Zeolites"** being submitted by Sudeshna Kar to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy, is a record of bona-fide research work carried out by her under my guidance and supervision. In my opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other university or institute for the award of any degree or diploma.

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To my mother

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Abstract

Zeolites are three-dimensional, microporous, inorganic crystalline polymers which can accomodate mobile cations and neutral molecules in the pore spaces. They form a very important category of industrial adsorbents and shape-selective molecular sieves. The physisorption properties of simple atomic and molecular sorbates in zeolites can be understood on the basis of just two parameters, their van der Waal radius and polarizability. In this thesis, microcanonical ensemble molecular dynamics simulation has been used to explore several aspects of sorption and diffusion of such simple Lennard-Jones sorbates in zeolites. The aim has been to show how computer simulations of such simple systems can provide considerable insight into unusual diffusional properties that emerge as a consequence of confinement of fluids in zeolites. In addition to adding to our understanding of diffusion phenomenon, such simulations illustrate methodological issues of relevance to simulations of fluids in porous media.

The first chapter contains an introduction to the field of zeolites. Structural features of zeolites from the perspective of their molecular sieve properties are reviewed. Some key conceptual aspects of sorption and diffusion of molecular sorbates in zeolites are discussed followed by a brief review of the recent developments in computer simulations of sorption and diffusion in zeolites. The final section of the chapter contains the scope and chapter plan of the thesis.

The primary input in any computer simulation is the potential energy surface (PES).

The parametrisation of potential energy surface for physisorbed molecules in zeolites is discussed in Chapter 2. The exact parametric form of the PES used for the simple sorbates studied in this work and its range of applicability is described in detail.

Chapter 3 discusses the computational techniques used in this work. The primary simulation technique, molecular dynamics (MD), is described with reference to the MD algorithm as implemented in my simulations. The calculation of the various quantities related to diffusional behaviour are discussed. A discussion of the estimation of chemical potential by the Widom particle insertion method is also given. Instantaneous normal mode analysis and its usefulness as an indicator of short-time dynamical information is reviewed.

Chapter 4 applies instantaneous normal mode analysis to understand the correlated changes in diffusivity and in the PES that occur as a result of variations in sorbate size. From simple geometrical considerations, it would appear that the self-diffusion coefficient, D, will be maximum for very small sorbates and will decrease with increasing sorbates size. However, under certain circumstances, a nonmonotonic increase in D with increasing sorbate size is observed for sizes close to the minimum channel width. This anomalous peak in transport properties is termed the levitation effect. In this chapter we perform instantaneous normal mode analysis, in conjunction with MD simulations, for Lennard-Jones sorbates of variable size and polarizability diffusing in NaY zeolite. The size-dependence of the diffusivity, including the anomalous levitation peak, is reflected in various properties of the instantaneous normal mode spectrum, such as the fraction of imaginary modes and the Einstein frequency. The existence of clear signatures of the levitation effect in the instantaneous normal mode properties indicates a close connection between the anomalous diffusivity peak and the curvature distribution of the potential energy surface. My work shows that an INM analysis provides a very simple simulation test for the levitation effect since the anomalous peak in the diffusivity is strongly correlated with the fraction of imaginary frequency modes and the mean curvature of the potential energy surface. This work on instantaneous normal mode analysis of the levitation effect leads one to expect that the INM spectra can be used provide important clues to qualitative changes in diffusional dynamics of sorbates in porous media, specially when the system dynamics is largely controlled by the topography of the potential energy surface.

Our results on estimation of Henry's constants and isosteric heats of sorption at infinite dilution for Lennard-Jones sorbates in zeolites are presented in Chapter 5. Henry's constants are obtained by an integration method which corresponds to the infinite dilution limit of the Widom particle insertion method for determining the chemical potential. Isosteric heats of sorption at infinite dilution are calculated using MD simulations as well as from the temperature dependence of the Henry's constant. The systems studied are: (i) CH_4 in silicalite (ii) Ar, Kr and Xe in Na-Y and (iii) variable size Lennard-Jones sorbates in Na-Y. The first two sets of sorbate-zeolite systems provide a way to test the accuracy of the potential energy surfaces used in this thesis in predicting sorption and related properties. The third set of simulations highlights an important difference between molecular dynamics simulations and insertion techniques when applied to adsorbates in porous media since the MD techniques sample the dynamically connected pore space whereas insertion techniques sample all available, low potential energy pore regions.

Diffusional anisotropy is a phenomenon which is characteristic of sorbates in porous crystaline solids because the structural properties of confining solids are direction-dependent. This is expected to result in inequality of the three principal components of the diffusion tensor. A more unusual effect is an interdependence of the components of the diffusion tensor due to geometrical correlations which arise as a result of special features of the channel network and have been studied in detail in ZSM-5. I have studied the diffusional anisotropy of several Lennard-Jones sorbates in all-silica compositional variants of three zeolites: ZSM-5, ZSM-11 and ferrierite. All of them are low porosity zeolites but only ZSM-5 and ZSM-11 can show diffusion along the z-direction due to correlated motions along the x- and y- directions. The most unexpected result that emerges from my study of diffusional anisotropy in ZSM-5 and ZSM-11 is the very slow crossover from ballistic to diffusional motion and the existence of a protracted period of subdiffusional motion along the correlated z-direction. The results also suggest that the extent of subdiffusional behaviour will be partly determined by the size and polarizability of the sorbate, with helium showing the least tendency to subdiffusional behaviour. An important methodological point which emerges from our study of diffusional anisotropy is the importance of checking the applicability of the Einstein relations and the possibility of deviations from Fickian behaviour when fluids are confined in nanoporous media.

Chapter 7 highlights the various results and conclusions arrived at in the chapters 4 to 6 and outlines the implications for future computational and experimantal work.

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