

Levitation Effect and Its Dependence on Sorbate Concentration[†]

Chitra Rajappa[‡] and Subramanian Yashonath^{*,‡,§}

Solid State and Structural Chemistry Unit and Supercomputer Education and Research Centre,
Indian Institute of Science, Bangalore-560012, India

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Earlier work has reported the existence of a diffusion anomaly in porous solids at dilute sorbate concentrations. In this work we have carried out molecular dynamics simulations at higher sorbate concentrations. Results indicate the persistence of a diffusion anomaly even at significantly higher sorbate concentrations, which means that this anomaly can be used for separation of mixtures under conditions prevailing in industries.

Introduction

The subject of diffusion in porous solids is important in a number of areas.¹ In biology, there are several situations where diffusion of small and large species takes place in a porous environment. A typical example may be diffusion of ions across biomembranes.^{2,3} In chemistry, the subject attains importance among others in diffusion^{4–6} that takes place in, for example, zeolites, which provide molecular sized voids, cavities, and channels through which many organic molecules and inorganic cations diffuse. The subject is also important in understanding many of the processes that are of considerable interest in condensed matter physics. Recent work⁷ has shown that species diffusing in a porous media display—over a wide range of diameters of the diffusing species—a linear dependence of the diffusion coefficient on the reciprocal of the square of the diameter of the species. Further, there is a narrow range of diameters where this dependence breaks down. Instead, a peak is observed in the diffusion coefficient which is anomalous, and the effect is termed the levitation effect. It has been shown^{7–9} that this effect is universal; it persists in spite of differences in the topological and geometrical details of the void network, and consequently the effect is found to be quite general even in its manifestation and therefore is expected to be quite common and widely prevalent under diverse situations and in different processes.

All studies pertaining to this effect have so far been carried out at low sorbate concentrations close to the infinite dilution limit.^{7–10} At low sorbate concentrations, it is reasonable to expect the sorbate–zeolite interactions to play the predominant role in the diffusion of sorbate species. It has been demonstrated⁸ that the underlying cause for the observed levitation effect could be the decrease in the magnitude of the force on the diffusing species due to the porous host when the sorbate size corresponds to the levitation ratio, $\gamma \approx 1$. Here γ is defined as⁷

$$\gamma = 2.2^{1/6} \sigma_{sz} / \sigma_w \quad (1)$$

where σ_{sz} is the Lennard-Jones parameter for sorbate–zeolite interactions and σ_w is the window diameter.

Existence of this effect at high sorbate concentrations is of considerable importance fundamentally as well as for industrial

purposes. For purely scientific reasons it is of considerable relevance since many of the processes that occur in porous media do so at high sorbate concentrations,^{1,11} and therefore it would be of interest to learn whether the levitation effect still persists at high sorbate concentrations. Many of the industrial separation processes are carried out at high concentrations, and it would be useful to know whether the levitation effect has any relevance under these conditions.¹² Also, it would be of interest to know whether the effect can be used to separate mixtures at rather high concentrations.

In this study we report microcanonical ensemble molecular dynamics (MD) simulations at three different concentrations of the diffusing species at a series of different sorbate sizes. Simulations have been carried out at a temperature of 185 K, and diffusion coefficients have been obtained from the time evolution of the mean-square displacement and Einstein's relation

$$D = u^2(t)/2dt \quad (2)$$

where $u^2(t)$ is the mean-square displacement and d is the dimensionality. We have taken d equal to 3 throughout this study. Sufficiently long simulations have been carried out in view of a recent study,¹³ which suggests that rather long simulations are essential to obtain the value of D within reasonable accuracy.

Model and Method

The details of the zeolite NaY structure and intermolecular potentials are available from ref 7. In brief, the structure of zeolite NaY consists of eight cages, each of about 11.8 Å diameter interconnected via 12-membered rings of approximate diameter 8 Å. Calculations have been carried out at three different sorbate concentrations. Since sorbate species of differing sizes are being investigated, it is impossible to choose the same number of diffusing species, N , per α -cage for all sizes of the diffusing species. A better measure of the sorbate concentration is therefore the volume fraction, ρ , defined as

$$\rho = v_s / v_c \quad (3)$$

where v_s and v_c are the total volume of the sorbates and the total volume of the cage in which they reside. Simulations have been carried out at $\rho = 0.23, 0.3528$, and 0.46 . The sizes of the sorbates, σ_{ss} , and the corresponding number of sorbates, N , for these sizes are listed in Table 1. Sorbate–sorbate and sorbate–zeolite Lennard-Jones potential parameters are listed in Table 2. Interactions are restricted to sorbate–sorbate (ss),

* To whom correspondence should be addressed.

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[‡] Solid State and Structural Chemistry Unit.

[§] Supercomputer Education and Research Centre.

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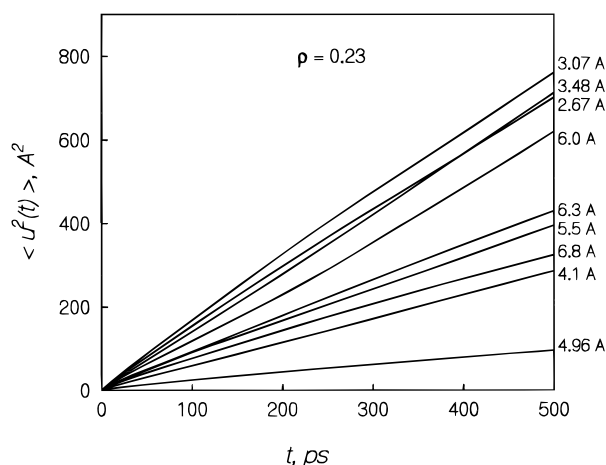
TABLE 1: Details of the Molecular Dynamics Runs Carried Out at $\rho = 0.23, 0.3528$, and 0.46

σ_{ss} (Å)	$\rho = 0.23$			$\rho = 0.3528$			$\rho = 0.46$		
	N	L (ps)	$\langle T \rangle$ (K)	N	L (ps)	$\langle T \rangle$ (K)	N	L (ps)	$\langle T \rangle$ (K)
6.8	8	6027	182	12	4958	178	16	4293	177
6.3	10	5430	178	15	4435	183	20	3839	183
6.0	12	4958	192	18	4047	190	23	3580	180
5.5	15	4435	179	23	3580	181	30	3135	182
4.96	21	3747	189	31	3084	185	41	2682	181
4.1	36	2862	187	55	2315	189	73	2009	189
3.48	60	2217	181	90	1810	180	119	1575	181
3.07	87	1841	190	130	1506	179	174	1301	182
2.67	132	1495	179	198	1220	191	264	1057	178

TABLE 2: Potential Parameters (in Å) for Sorbate–Sorbate and Sorbate–Zeolite Interactions^a

σ_{ss}	σ_{sO}	σ_{sNa}	σ_{ss}	σ_{sO}	σ_{sNa}
6.8	4.67	5.08	4.1	3.32	3.73
6.3	4.42	4.83	3.48	3.01	3.42
6.0	4.27	4.68	3.07	2.81	3.22
5.5	4.02	4.43	2.67	2.61	3.02
4.96	3.75	4.16			

^a ϵ_{ss} , ϵ_{sO} , and ϵ_{sNa} are 1.837 485, 1.539 079, and 0.268 502 kJ/mol, respectively.

**Figure 1.** Evolution of the mean-square displacement, $u^2(t)$, has been shown for various sorbate sizes at a volume fraction of 0.23. The sorbate sizes corresponding to each curve have also been indicated.

sorbate–oxygen (sO), and sorbate–sodium (sNa). The mass of the sorbate was that of xenon, viz., 131 amu. We employed the velocity Verlet scheme¹⁴ for integration of the equations of motion. Integration time step is 10 fs in all runs while the stored time step is 0.2 ps at the volume fraction of $\rho = 0.23$ and 0.1 ps at $\rho = 0.3528$ and 0.46. Duration of the run, L , for each of the sorbate sizes is different. As the number of sorbate atoms increase with decreasing sorbate size, the duration of the run is decreased (see Table 1). The runs reported here are much longer than those usually reported in the literature. The runs have been made sufficiently long to ensure that the error in the calculated diffusion coefficient is not large. Our recent study¹³ indicates that the error for the run lengths reported here vary between 15 and 25%. The cutoff radius was 12 Å for sorbate–sorbate and sorbate–zeolite interactions.

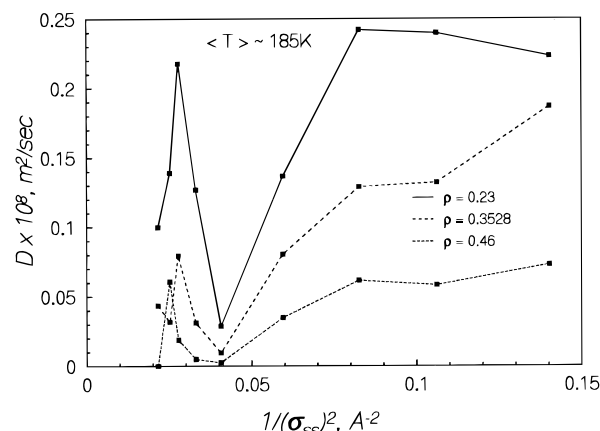
Results

Average temperatures of the trajectories obtained from the simulations are reported in Table 1. It is seen that the temperature of the runs lie between 178 and 192 K, the desired temperature being 185 K. Figure 1 displays the time evolution of the mean-square displacement for different sized sorbates at

TABLE 3: Diffusion Coefficients^a as a Function of Sorbate Size for the Volume Fractions $\rho = 0.23, 0.3528$, and 0.46

σ_{ss} (Å)	$D \times 10^8$ (m²/s)		
	$\rho = 0.23$	$\rho = 0.3528$	$\rho = 0.46$
6.8	0.099 703	0.043 387	0.000 003
6.3	0.138 974	0.031 643	0.060 730
6.0	0.217 735	0.079 279	0.018 839
5.5	0.126 778	0.031 109	0.004 961
4.96	0.028 972	0.009 515	0.002 561
4.1	0.136 718	0.080 436	0.034 852
3.48	0.242 016	0.128 875	0.061 573
3.07	0.239 648	0.131 976	0.058 228
2.67	0.223 186	0.186 782	0.072 946

^a D was calculated using the slope of the least-squares straight line fit to the range 200–500 ps of the msd curves.

**Figure 2.** Diffusion coefficient, D , has been shown as a function of $(1/\sigma_{ss}^2)$, the reciprocal of the square of the sorbate diameter. The solid line, the dashed line, and the dotted line correspond to $\rho = 0.23, 0.3528$, and 0.46, respectively.

$\rho = 0.23$. The absence of deviation from a straight course of the mean-square displacement (msd) curves suggests that the long runs reported here do yield reliable diffusion coefficients. Diffusion coefficients were calculated from the msd curves using the slope of the least-squares-fit line to the points in the range 200–500 ps. The reasons for this choice of the range are discussed in ref 13. The diffusion coefficients for the various sorbate sizes obtained from Einstein's relation (eq 2) and the msd curves are listed in Table 3. Figure 2 gives a plot of the diffusion coefficient as a function of the reciprocal of the square of the sorbate diameter, σ_{ss} , for different values of ρ . It is evident that the diffusion coefficient decreases with increase in the sorbate diameter. The average temperatures of the runs for different sorbate sizes are different. They are usually within ± 10 K of the desired temperature (185 K). Recently,¹⁵ we have calculated the activation energies for sorbates of different sizes confined in zeolite NaY from long molecular dynamics simulations at different temperatures. The difference in the values of D arising from the difference in the average temperatures

attained (listed in Table 1) is insignificant as compared to the difference in the values of D shown in Figure 2.

Earlier studies⁷ reported a linear relationship

$$D = c/\sigma_{ss}^2 \quad (4)$$

between D and $1/\sigma_{ss}^2$ when the sorbate concentration was fixed at a specified value of sorbates per α -cage close to infinite dilution. Here c is the constant of proportionality. In the present study, this is not the case since we have fixed the volume fraction. Therefore, no such linear dependence is expected and also obtained. However, this region is characterized by a decrease in D with increase in σ_{ss} , which we shall refer to as the normal region. From Figure 2 it is clear that the anomalous behavior is found when $\rho = 0.23$. What is interesting, however, is that even at the higher values of ρ , viz., 0.3528 and 0.46, this anomaly persists. The diffusion coefficient is attenuated on increasing ρ to 0.3528 and subsequently to 0.46. However, this attenuation extends to the normal region as well. Thus, it appears that diffusion anomaly persists even at higher sorbate concentrations. This implies that the sorbate–zeolite interactions are still playing a predominant role at these high sorbate concentrations where one would normally expect the sorbate–sorbate interactions to predominate. This result is of considerable significance since many of the processes in chemistry and biology occur at high sorbate concentrations. The present result suggests that one should take into account the possibility of the levitation effect while trying to understand diffusion processes in these systems. Industrially, many catalytic reactions that involve the diffusion of products through the pores of zeolites and other porous solids as well as molecular sieve processes for separation of mixtures occur at high sorbate

concentrations. The present results indicate that the levitation effect can exist in these systems as well. Further, it should be possible to make use of the levitation effect for separation of mixtures. Studies on separation of mixtures are presently under way in this laboratory.

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References and Notes

- (1) Karger, J.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*; John Wiley and Sons: New York, 1992.
- (2) De Loof, H.; Nilsson, L.; Rigler, R. *J. Am. Chem. Soc.* **1992**, *114*, 4028.
- (3) Kovacs, H.; Mark, A. E.; Johansson, J.; van Gunsteren, W. F. *J. Mol. Biol.* **1995**, *247*, 808.
- (4) Complete issue of *J. Chem. Soc., Faraday Trans 2* **1991**, *13*.
- (5) Martens, J. A.; Perez-Pariente, J.; Sastre, E.; Corma, A.; Jacobs, P. A. *Appl. Catal.* **1988**, *45*, 85.
- (6) Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: New York, 1978.
- (7) Yashonath, S.; Santikary, P. *J. Phys. Chem.* **1994**, *98*, 6368.
- (8) Bandyopadhyay, S.; Yashonath, S. *J. Phys. Chem.* **1995**, *99*, 4286.
- (9) Yashonath, S.; Bandyopadhyay, S. *Chem. Phys. Lett.* **1994**, *228*, 284.
- (10) Santikary, P.; Yashonath, S. *J. Phys. Chem.* **1994**, *98*, 9252.
- (11) Cunningham, R. E.; Williams, R. J. J. *Diffusion in Gases and Porous Media*; Plenum Press: New York, 1980.
- (12) Ruthven, D. M.; Lee, L.-K. *AIChE. J.* **1981**, *27*, 654.
- (13) Chitra, R.; Yashonath, S. *J. Phys. Chem.*, in press.
- (14) Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids*; Clarendon Press: Oxford, 1987.
- (15) Chitra, R.; Subramanian, Y. *Faraday Discuss.*, in press.