

Diffusion Anomaly at Low Temperatures in Confined Systems from the Rare Events Method

Pradip Kr. Ghorai and Subramanian Yashonath*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India

Received: December 9, 2003; In Final Form: February 23, 2004

Size dependence of self-diffusivity of monatomic spherical sorbates within zeolite NaY has been investigated at low temperatures. Self-diffusivity, D , exhibits a pronounced maximum when the size of the diffuser is comparable to the void size. The value of D in the anomalous regime is 17 orders of magnitude higher as compared to the linear regime. The implication of these results on separation of mixtures is discussed. Frequency of the recrossing events across the barrier to diffusion and its dependence on the size as revealed by the transmission coefficient are discussed.

An understanding of the properties of fluids confined within another material such as porous solids is essential in developing better nanomaterials. Studies carried out in the past 10 years have shown that fluids confined within porous solids often exhibit properties that are remarkably different from those of the bulk. Examples of surprising properties of confined fluids are several in the literature: change in viscosity by a factor of 10 from one adsorbed layer to the next,¹ single file diffusion of molecules confined to one-dimensional channels,² and the maximum in self-diffusivity seen when the size of the diffuser is comparable to the void size, known as the levitation effect³ (LE).

Several attempts have been made to understand diffusion in bulk as well as in surfaces and even in confined systems such as zeolites particularly using the rare events method. For example, Chandler⁴ attempted to use the method of rare events to discuss the classical isomerization reactions of small nonrigid molecules in liquid solvents. Miller⁵ used a model that invokes the basic idea of the transition state to calculate the rate of chemical reaction. Chandler⁵ used the method of rare events to study the chair and boat isomerization dynamics of cyclohexane in liquid as a function of solvent pressure or viscosity. Voter and Doll⁶ mainly pioneered the application of the rare events method to surface adsorption. Auerbach and co-workers^{7,8} were the first to use the rare events method to study the motion within zeolites. He calculated the jump dynamics within zeolites.

The last of these, namely LE, refers to the maximum in self-diffusivity, D , seen in sorbates or guests confined within porous solids when the size of the sorbate is comparable to void size within which it is diffusing. This is referred to as the anomalous regime. For sorbate sizes significantly smaller than the void size, D is inversely proportional to the reciprocal of the square of the sorbate diameter. When the sorbate and the host are interacting via van der Waals interaction (typically modeled in terms of Lennard-Jones interactions), D varies as $1/\sigma_{g-g}^2$ where σ_{g-g} is the Lennard-Jones (LJ) parameter for guest–guest interaction. This is referred to as the linear regime. This behavior, however, is not restricted to guest–host systems with only van der Waals interactions but extends to ionic systems as well where long-range Coulomb interactions are predominant.⁹ Furthermore, this behavior is seen in all types of host structures, irrespective of the geometrical and topological details

of the pore network:⁹ it is seen in one-dimensional cylindrical channel systems as well as two-dimensional and three-dimensional pore networks.

Previously, temperature dependence of the peak height over the temperature range 150–300 K has been explored.¹⁰ It was found that the height of the maximum in the anomalous regime is generally 2–3 times that of the minimum. This minimum is seen at the transition between the linear and the anomalous regimes. Further, it was found that, at high temperatures, the height of the maximum decreases and eventually disappears.¹⁰

More recently, our work has shown that LE is also seen in real systems consisting of hydrocarbon molecules and zeolites. Molecular dynamics simulations of benzene, methane and ethane has shown that both rotational and translational mobility of these molecules in ALPO₄-5 and carbon nanotubes are altered by LE.¹¹ Padma Kumar and Yashonath⁹ have also demonstrated the existence of LE in solids leading to high ionic conductivity and to superionic conductors. We have also demonstrated that pentane isomers¹²—isopentane and *n*-pentane as well as geometrically linear molecules¹³—exhibit LE.

In this article, we attempt to investigate the nature of dependence of self-diffusivity on the size of the sorbate at rather low temperatures. In particular, we look at the LE. Since, at the temperatures we are interested in, the time scales associated with motion of the sorbate are larger than nanoseconds, we will resort to techniques such as the *rare events method* of Chandler,^{4–6} specially developed for such situations, instead of conventional MD.

We have carried out calculations on spherical monatomic van der Waals sorbates confined to zeolite NaY. Structure of zeolite NaY consists of three-dimensional network of large α -cages of 11.4 Å diameter connected tetrahedrally to four other similar cages through narrower 12-membered rings of diameter ~ 7.4 Å. Previous work has shown that the potential energy (PE) landscape within zeolites is a function of the size of the sorbate. For smaller sizes of sorbate, the PE surface consists of six energetic minima within each α -cage (the physisorption or the adsorption sites) and potential energy maxima at the windows. For larger sorbates, the latter change from maxima to minima.¹⁴ The exact location of the minima is a function of the sorbate size. Diffusion of sorbates consists of hops between two physisorption sites within the same cage (intracage hops) and

hops between sites located in different cages (intercage hops). The minimum energy pathway (MEP) between intracage as well as intercage hops reported recently⁶ suggests that the rate-determining step is the slower intracage rather than the intercage hop. Here, we compute the rate of intracage hops for spherical monatomic sorbates within zeolite NaY. We employ a modification of the method of rare events of Chandler⁴ for estimating rates of slow processes. He demonstrated that the interconversion between the chair and the boat forms of cyclohexane⁵ can be estimated from this method. Briefly^{5,6} the method consists of obtaining the transition state theory (TST) rate, k_{TST} , from the free energy profile along the reaction coordinate (here the diffusion coordinate, DC):

$$k_{\text{TST}} = \Lambda / L k_B T e^{-\Delta A / k_B T} \quad (1)$$

where $\Lambda = h / \sqrt{2\pi m k_B T}$ is the de Broglie wavelength associated with the sorbate, h is Planck's constant, L is the effective distance between the two adsorption sites, and ΔA is the free energy barrier between two adsorption sites. In a recent report, the way this can be obtained by a direct calculation of the canonical partition function has been discussed.¹⁵ We employ this method to obtain the free energy ΔA and calculate k_{TST} from eq 1. We then estimate κ as originally suggested in refs 4 and 5.

k_{TST} is generally higher than the actual rate indicated by k since TST does not take into account the possibility of returning to the initial state after traversing beyond the saddle point along the diffusion coordinate. In other words, TST does not account for the recrossing across the barrier after it has already crossed over the barrier. The corrected rate is given by

$$k = k_{\text{TST}} \times \kappa \quad (2)$$

where κ is the transmission coefficient estimated from: $\kappa = \lim_{t \rightarrow \infty} f_{ij}(t)$. $f_{ij}(t)$ is the dynamic correction factor (DCF) given by

$$f_{ij}(t) = \frac{\langle v_z(0) \delta[z(0) - z_w] \theta[z(t) - z_w] \rangle}{\langle v_z(0) \delta[z(0) - z_w] \theta[v_z(0)] \rangle} \quad (3)$$

where $v_z(0)$ is the z component of the velocity of the sorbate when it is on the dividing surface at $z = z_w$ at $t = 0$, and θ is the Heaviside function. $f_{ij}(t)$ is equal to 1 at short times and drops to a plateau at large t .

Structure of zeolite NaY (space group $Fd\bar{3}m$ with composition $\text{Na}_{48}\text{Si}_{144}\text{Al}_{48}\text{O}_{384}$ (Si/Al = 3.0) with $a = 24.8536$ Å) reported by Fitch et al.¹⁶ is used by us. The sodium atoms occupy all the SI and SII sites completely. The interaction between the sorbate and the zeolite is modeled in terms of the (6–12) LJ potential $\varphi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ where ϵ and σ are the LJ interaction parameters for the sorbate–sorbate and between the sorbate and the atoms of the zeolite (O and Na). The cross-interaction parameters were calculated using Lorentz–Berthelot combination rules.¹⁷ The short-range LJ interactions of the sorbate with the Si and Al atoms of the framework are negligible since the sorbates do not come in close proximity to Si or Al, being surrounded by the bulkier oxygens. ϵ_{g-g} , ϵ_{g-O} , and ϵ_{g-Na} (subscript g indicates sorbate) are 1.837485, 1.539079, and 0.268502 kJ/mol, respectively.

One unit cell of zeolite NaY consisting of eight α -cages has been used to calculate the free energy profile for intracage migration at 40 K for different sorbate sizes (Figure 1). Simulations are carried out in the microcanonical ensemble with velocity Verlet algorithm at a loading of 1 sorbate/cage with

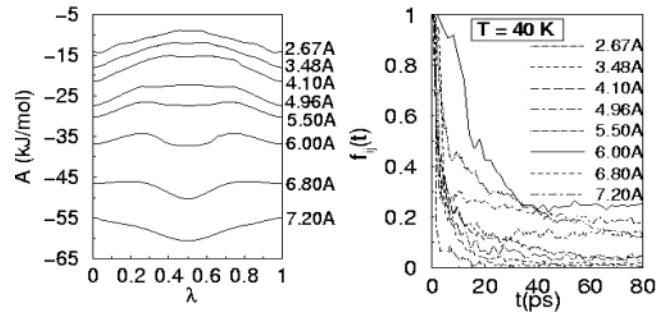


Figure 1. Free energy A and dynamical correction factor f_{ij} for different sorbate sizes in NaY zeolite for intracage hops.

TABLE 1: Values of k_{TST} and κ at 40 K

σ_{g-g} (Å)	k_{TST} (m^2/s)	κ
2.67	2.4×10^3	0.120
3.48	1.2×10^3	0.015
4.10	2.4×10^2	0.070
4.96	1.5×10^4	0.013
5.50	6.6×10^5	0.068
6.00	4.5×10^5	0.250
6.80	6.1×10^6	0.015
7.20	5.4×10^4	0.012

64 guests (with one fixed at the saddle point). For more details of the method see.¹⁵ The zeolite framework ions and cations are assumed to be rigid. The sorbate mass is 131 amu. Integration time step is 40 fs. Cutoff radius is 13.0 Å. Equilibration is over 800 ps and configurations are stored every 2 ps during a run of 400 ps. Of these, the first 100 stored configurations are later used to generate trajectories for the downhill motion of the sorbate placed at the top of the free energy surface. For each 100 configurations, 20 different velocities are chosen from the Maxwell–Boltzman distribution of the right temperature, giving the total of 2000 trajectories. Initially, the sorbate is placed at the saddle point.

Since the rate-determining step is the intracage hops, we have carried out free energy and MD calculations for the intracage site-to-site hop. Figure 1 shows the variation of the free energy along the DC and the decay of the DCF with time for different sorbate sizes for intracage at 40 K. The free energy profile along the MEP connecting the two minimum energy sites (the physisorption sites) for the intracage site-to-site hop shows undulations. The p.e. landscape for $\sigma_{g-g} = 6.0$ Å is rather flat. Other sizes show larger undulations suggesting that the barrier for intracage site–site migration is larger. The TST rate for intracage site-to-site hops, k_{TST} , is computed from eq 1.

The decay is slowest for $\sigma_{g-g} = 6.0$ Å suggesting that significant number of recrossing events occur even after 20 ps for this sorbate. Previous work³ has shown that the potential energy landscape for this particle is rather shallow. It is therefore not surprising that the dynamic correction factor $f_{ij}(t)$ does not attain a plateau even after 20 ps. Value of $f_{ij}(t)$, as $t \rightarrow \infty$ (i.e., κ) is also large. The 4.96 Å sized sorbate, shows significant recrossing at large times ($\kappa = 0.013$) while the 6.0 Å sorbate shows a relatively lower rate of recrossing ($\kappa = 0.250$). One would think that the magnitude of the transmission coefficient would be close to unity if the barrier height is large and close to zero if the barrier is shallow. This rather anomalous behavior suggests that there are other factors that may determine the recrossing. The values of κ are computed for all sorbate sizes. The rate k was then computed from eq 2.

Table 1 lists the values of the TST rate, k_{TST} , and κ , the transmission coefficient for all sizes at 40 K. Insights into the levitation effect can be gained from the trend shown by the

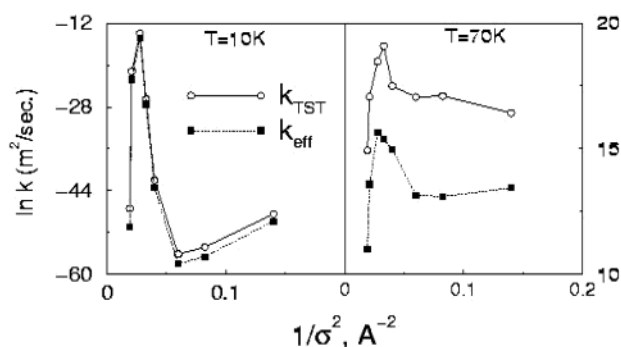


Figure 2. TST rate plotted at two temperatures without κ (k_{TST}) and with κ (k_{eff}) against $1/\sigma_g^2$.

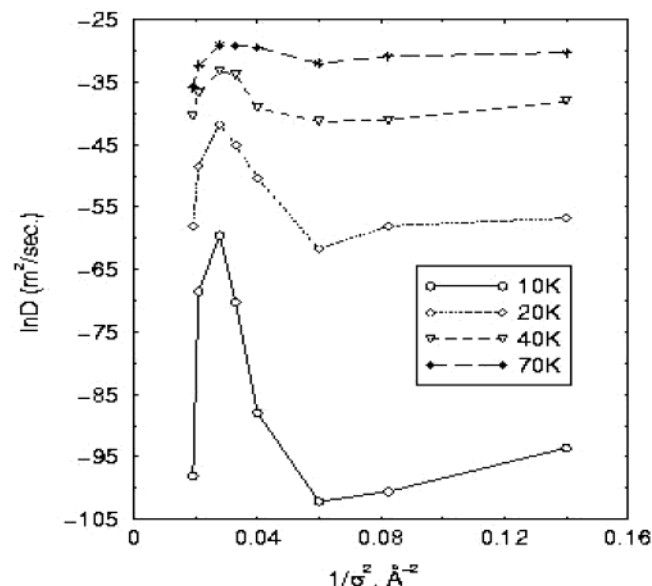


Figure 3. Logarithm of the self-diffusivity (D) plotted inversely as a function of the square of the sorbate sizes.

TST rate, k_{TST} , and that of the transmission coefficient, κ . κ exhibits a trend similar to that seen in D . Thus, the recrossing events for the guest with dimension close to the void dimension are minimum (κ maximum). As a comparison of the results at 10 K with those at 70 K suggest, at higher temperatures, recrossing events become increasingly important (κ small; see Figure 2).

The values of the rate of intracage site-to-site hops k and the distance, l , between two neighboring physisorption sites are functions of the size of the sorbate.^{14,9} We evaluated the self-diffusivities for various sizes of the sorbate from

$$D = \frac{l^2}{2k_c^{-1}} \quad (4)$$

As self-diffusivity varies over several orders of magnitude we have plotted the natural logarithm D against reciprocal of the square of the sorbate size in Figure 3 for several different temperatures. Note the pronounced maximum varying over at least 3 orders of magnitude. This may be compared with just a factor of 2 or 3 observed at around 150K in the same zeolite.³ Calculations at 10 K gave a value of D for the anomalous regime that was 17 orders of magnitude higher than D for the linear regime (see Figure 3). We note that Auerbach^{6,7} has applied the rare events method to study the jump dynamics of benzene in zeolite NaY at room temperature and discussed the various possibilities in that context.

Previous work¹⁸ suggests that superior separation is achieved when the LE is exploited as opposed to use of just the linear regime. In other words, separation is better when one of the components of the mixture lies in the anomalous regime while the others lie in the linear regime as opposed to when all components lie in the linear regime. The present study suggests that better separation can be achieved at lower temperatures and using the anomalous and linear regimes. As the difference in self-diffusivity is 3 orders of magnitude at 40 K (see Figure 3), the separation is expected to be superior.

The magnitude of self-diffusivity is significantly lower at low temperatures making the process of separation slower. However, through the use of the blow torch effect of Landauer,¹⁹ it has been shown by Bekele²⁰ et al. that, in a bistable potential, placing a hot spot between one of the p.e. minimum and maximum separating the two minima enhances the escape rate of the particle across the barrier asymmetrically. The latter enhances the self-diffusivity. This technique can be used to enhance D at low temperatures to obtain separation within a reasonable time.

The self-diffusivity at 40 K for the anomalous and the linear regimes are respectively 10^{-15} and 10^{-18} m²/s. It is evident that D for a sorbate which lies in the anomalous regime is reasonably high even at low temperatures. One could utilize this fact in situations where high diffusivity is required at low temperatures. At these low temperatures, the quantum effects are likely to be important. However, for sorbates such as xenon or heavier guest atoms, the present classical results would not change significantly. For lighter hydrocarbons, one expects the quantum effects, which have been discussed by Miller,⁵ to be of importance. However, as is evident, even then one would expect more than a few orders of magnitude difference in the self-diffusivity and therefore the LE at low temperatures may still be exploited for any application especially in kinetic based separation methods.

Mechanical gating in biomembranes is one way of controlling the passage of ions. It is known that gating operates through controlled opening of the channel. The present results suggest that the principle of LE provides a natural method of gating if one ion or solute (whose passage across the biomembrane is required) lies in the anomalous regime and others lie in the linear regime. This obviates the need for large changes in the opening. The results of the present study suggests that a natural gating is most effective at low temperatures.

Acknowledgment. The authors thank the Department of Science and Technology, New Delhi, India, for support of this research.

References and Notes

- Israelachvili, J.; McGuigan, P. M.; Homola, A. M. *Science* **1988**, *240*, 189.
- Kärger, J. *Phys. Rev. E* **1993**, *47*, 1427.
- Yashonath, S.; Santikary, P. *J. Phys. Chem.* **1994**, *98*, 6368.
- Chandler, D. *J. Phys. Chem.* **1978**, *68*, 2959.
- Miller, W. H. *J. Chem. Phys.* **1974**, *61*, 1823. Kuharski, R. A.; Chandler, D.; Montgomery, J. A.; Rabii, F.; Singer, S. J. *J. Phys. Chem.* **1988**, *92*, 3261.
- Voter, A. F.; Doll, J. D. *J. Chem. Phys.* **1985**, *82*, 80.
- Auerbach, S. M.; Henson, N. J.; Cheetham, A. K.; Meitu, H. I. *J. Phys. Chem.* **1995**, *99*, 10600.
- Auerbach, S. M. *Intl. Rev. Phys. Chem.* **2000**, *19* (12), 155–198.
- Padmanabhan, P. K.; Yashonath, S. *J. Phys. Chem.* **2002**, *106*, 3443.
- Bandopadhyay, S.; Yashonath, S. *J. Phys. Chem.* **1994**, *99*, 4286.
- Anil Kumar, A. V.; Yashonath, S. *J. Chem. Phys.* **2000**, *112*, 965.
- Yashonath, S.; Rajappa, C. *Faraday Discuss.* **1997**, *106*, 105.
- Shreyas, Y. B.; Yashonath, S. *J. Chem. Phys.* **2002**, *116*, 2175; *J. Phys. Chem. A* **2002**, *106*, 7130–7137; *J. Phys. Chem. B* **2000**, *104*, 11977–11986.
- Shreyas, Y. B.; Yashonath, S. *J. Am. Chem. Soc.* **2003**, *125*, 7425.
- Ghorai, P. K.; Yashonath, S. *J. Am. Chem. Soc.* **2003**, *125*, 7116.

- (14) Rajappa, C.; Yashonath, S. *J. Chem. Phys.* **1999**, *110*, 1. Ghorai, P. K.; Yashonath, S. *Chem. Phys. Lett.* **2002**, *359*, 507.
- (15) Ghorai, P. K.; Yashonath, S.; Lynden-Bell, R. M. *Mol. Phys.* **2002**, *100*, 641.
- (16) Fitch, A. N.; Jobic, H.; Renouprez, A. *J. Phys. Chem.* **1986**, *90*, 1311.

- (17) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*, Clarendon Press: Oxford, England, 1987.
- (18) Rajappa, C.; Yashonath, S. *Mol. Phys.* **2000**, *98*, 657.
- (19) Landauer, R. *J. Stat. Phys.* **1988**, *53*, 233.
- (20) Bekele, M.; Rajesh, S.; Ananthakrishna, G.; Kumar, N. *Phys. Rev. A* **1999**, *59*, 143.