

Levitation Effect: Distinguishing Anomalous from Linear Regime of Guests Sorbed in Zeolites through the Decay of Intermediate Scattering Function and Wavevector Dependence of Self-Diffusivity

Pradip Kr. Ghorai[†] and S. Yashonath^{*,†,‡,§}

Solid State and Structural Chemistry Unit and Center for Condensed Matter Theory,
Indian Institute of Science, Bangalore-560012, India

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Previous work investigating the dependence of self-diffusivity, D , on the size of the guest diffusing within the porous solid such as zeolite has reported the existence of an anomalous maximum in the diffusion coefficient (*J. Phys. Chem.* **1994**, 98, 6368). Two distinct regimes of dependence of D on σ_{gg} , diameter of the guest were reported. $D \propto 1/\sigma_{gg}^2$, often referred to as linear regime (LR), is found when σ_{gg} is smaller than σ_v , the diameter of the void. A maximum in D has been observed when σ_{gg} is comparable to σ_v and this regime is referred to as anomalous regime (AR). Here we report the intermediate scattering function for a particle from LR and AR in zeolite faujasite. A particle from LR exhibits a biexponential decay while a particle from AR exhibits a single-exponential decay at small k . Variation with k of the full width at half-maximum of the self-part of the dynamic structure factor is nonmonotonic for a particle in the linear regime. In contrast, this variation is monotonic for a particle in the anomalous regime. These results can be understood in terms of the existence of energetic barrier at the bottleneck, the 12-ring window, in the path of diffusion. They provide additional signatures for the linear regime and anomalous regimes and therefore for levitation effect (LE).

1. Introduction

There have been many investigations on diffusion of guest molecules in zeolites.^{1–14} Many surprising observations have been made in the behavior of confining fluids such as single-file diffusion and superdiffusive motion of guests in carbon nanotubes.^{1,15,16} Another observation relating to confining fluid that is counterintuitive is the levitation effect. The levitation effect refers to the anomalous maximum in self-diffusivity, D , of the guest diffusing within the confines of the porous network of a zeolite or similar porous solids. For a guest diameter σ_{gg} diffusing within a void of diameter σ_v (provided by the zeolite or similar confining medium), two distinct regimes have been observed.¹ These regimes are not dependent on the size of the guest alone but instead depend on the ratio $\eta = \sigma_{gg}/\sigma_v$. When this ratio $\eta \ll 1$, the self-diffusion coefficient D of the guest is found to be inversely proportional to the reciprocal of the square of the guest diameter, that is, $D \propto 1/\sigma_{gg}^2$. This is often referred to as linear regime (LR) and this relation follows from kinetic theory. When $\eta \approx 1$, the self-diffusion coefficient D exhibits a maximum as a function of σ_{gg} . This regime is termed as the anomalous regime (AR). In the linear regime, the larger sized guest particles (larger σ_{gg}) has necessarily a D which is lower than D of a smaller sized guest particle (smaller σ_{gg}). This is however not always true for a particle in the anomalous regime.

Figure 1a shows the dependence of D on $1/\sigma_{gg}^2$ obtained from molecular dynamics simulations of spherical monatomic guest of varying sizes (σ_{gg}) confined to zeolite NaY reported by Yashonath and Santikary.¹ Interactions between the guest and

the O and Na of the zeolite in this study were modeled in terms of 6–12 Lennard-Jones potential. These calculations were carried out at 190 K. The potential energy of interaction between the guest and the host zeolite, U_{gh} was found to be different for a small sized guest in the linear regime and a large sized guest particle in the anomalous regime. Figure 1b shows that the interaction of the small sized guest from linear regime is not very favorable at the 12-ring window. This leads to a large barrier for a guest in the linear regime near the 12-ring window. The result is the curve shown in Figure 1c for LR where the variation of U_{gh} is shown against d . Here d is the distance of the particle from the plane of the 12-ring window. In contrast, for a particle in the anomalous regime, the interactions of the guest with the various atoms of the zeolite near the 12-ring window is favorable (see Figure 1b) leading to a lowering of U_{gh} . This leads to a lowering of the energetic barrier at the 12-ring window. The resulting energy profile for a particle from anomalous regime is shown in Figure 1c. Figure 1d shows eight α -cages of zeolite NaY while Figure 1e shows two α -cages along with the interconnecting 12-ring window.

The linear and anomalous regimes of the levitation effect have been observed to be associated with the following specific characteristics.

(i) A lower activation energy for diffusion for a particle from anomalous regime as compared to a particle from linear regime (obtained from the Arrhenius plot of $\ln D$ vs $1/T$).¹⁷

(ii) The velocity autocorrelation function of the guest from the linear regime shows a pronounced negative minimum while a guest from anomalous regime exhibits only a small foray into the negative regime, if at all.^{1,18}

(iii) The force exerted on the guest by the host (zeolite) is significantly lower for a particle in the anomalous regime as compared to a particle from the linear regime. The magnitude

* Corresponding author.

[†] Solid State and Structural Chemistry Unit, Indian Institute of Science

[‡] Center for Condensed Matter Theory, Indian Institute of Science.

[§] Also at the Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India.

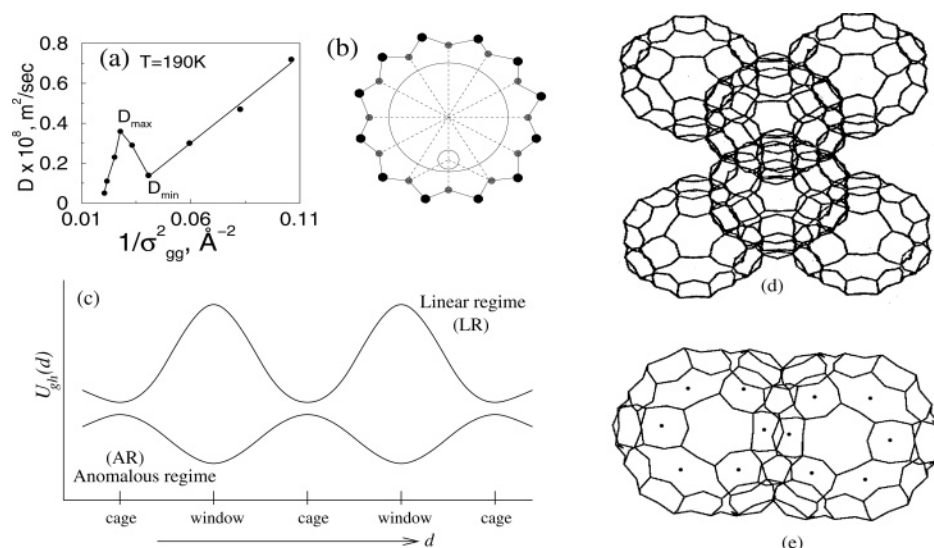


Figure 1. (a) Plot of self-diffusivity vs $1/\sigma_{gg}^2$ in NaY. (b) Bottleneck for diffusion. This is the 12-membered ring or window in zeolite NaY.¹ This is shown by the black and gray circles or dots. Si: larger filled circles. O: smaller filled circles. The line indicates the Si–O bond. The guest atoms are shown by unfilled circles. For the larger guest with diameter comparable to that of the 12-ring window, there is net cancellation of forces while this does not happen for the smaller guest. (c) Schematic illustration of variation of U_{gh} during diffusion. The potential energy landscape for linear and anomalous regimes is shown as a function of the distance the guest particle traverses. Note that at the window, the potential energy is a maximum for LR but minimum for AR. Further, potential energy landscape is less undulating for AR. (d) One unit cell of zeolite NaY. There are 8 α -cages and each α -cage is connected tetrahedrally to four neighboring α -cages. Only the α -cages are shown. (e) Two α -cages connected by 12-ring window. The positions of the six adsorption sites are shown within the α -cages by black dots.

of the force in the direction perpendicular to the plane of the window shows little or no dependence on σ_{gg} . However the magnitude of the force in the plane of the window is significantly reduced for a particle in the anomalous regime as compared to linear regime.¹

(iv) With the lowering of temperature the difference ($D_{\text{max}} - D_{\text{min}}$) (see Figure 1a) of the diffusion coefficients increases. The difference in the self-diffusivity between the LR and AR can be more than several orders of magnitude, as has been recently shown by us.¹⁹

Further, it has been shown that the potential energy landscape associated with anomalous regime is relatively flatter.¹ In general, for a guest confined to a porous crystalline solid like zeolite, such undulations in potential energy landscape are correlated strongly with the structure of the porous host. For example, in zeolite Y and A the structure of the zeolite consists of large cages interconnected through narrow windows. The potential energy minima are located deep within the cages. The potential energy maxima are located in the proximity of the narrow window. This is the case for a particle in the linear regime. In contrast to this, for particle in the anomalous regime the potential energy maxima are located well within the cages and the minima at the window. The potential energy landscape for anomalous and the linear regime are thus quite different (see Figure 1c). The wavelength of the undulations in the potential energy landscape are the same for both the linear and anomalous regimes. However, the *height of the undulations* are *much larger* for a particle in the linear regime.

We emphasize that the levitation effect has been found in a variety of porous solids such as zeolite NaCaA,¹ NaY,^{1,20} VPI-5,²¹ silicalite,²¹ nasicon,²² and other porous solids. These results suggest that levitation effect exist in all type of porous solids irrespective of the geometrical and topological details of the pore network or chemical nature of the confining solid.²¹ In most of the above studies the guest was a spherical monatomic sorbate either charged (in the case of nasicon) or uncharged (in the case of zeolites and aluminophosphates). However, recent

simulations have shown that even in nonspherical polyatomic guest such as linear molecules²⁰ or nonlinear polyatomic molecules²³ exhibit levitation effect. For example prop-1,2-diene shows a higher diffusivity as compared to acetylene and but-1,3-diyne.⁸ Isopentane has higher diffusivity in AlPO₄-5 than *n*-pentane for similar reasons.²³ This demonstrates that levitation effect is not irrelevant to hydrocarbon diffusion in zeolites.

In view of the generic nature of levitation effect, it is necessary to understand levitation effect in all its aspects so as to obtain a more complete understanding of this interesting behavior. In fact, recently, there is evidence to show that the existence of diffusion maximum is *not restricted* to porous solids as presumed so far. In view of the universality of this, it is important to understand this behavior in greater depth.

The intermediate scattering function $F_s(\mathbf{k}, t)$, where \mathbf{k} and t are the wavevector and time, is a function that is accessible both experimentally and through simulation. In isotropic system the wavevector \mathbf{k} reduces to a scalar wavenumber k . Incoherent neutron scattering measurements give the dynamic structure factor, $S_s(k, \omega)$, where ω is the angular frequency. Its Fourier transformation gives the intermediate scattering function, $F_s(k, t)$. We look at the behavior of $F_s(k, t)$ for particles from the linear and the anomalous regime. We also look at the dependence on k of full width at half-maximum (fwhm) $\Delta\omega(k)$ of $S_s(k, \omega)$. In the limit of k approaching zero, the hydrodynamic limit, $\Delta\omega(k \rightarrow 0) \rightarrow 2Dk^2$.

2. Theory

2.1. Intermediate Scattering Function. In a typical neutron scattering experiment, the amount of sample required is rather large. As a result, only powder samples are used.²⁴ In contrast, simulations are carried out on very small sample size and are usually single-crystal samples. To facilitate comparison with experiment we compute from molecular dynamics the powder

average of the intermediate scattering function²⁴

$$F_s(k, t) = \sum_{i=1}^N \left| \frac{\sin(k|\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0)|)}{k|\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0)|} \right| \quad (1)$$

which may then be compared with experiment. The incoherent dynamic structure factor ($S_{inc}(k, \omega)$) is obtained from the Fourier transform of the intermediate scattering function ($F_s(k, t)$).

3. Methodology

3.1. Structure of Hosts. Laboratory synthesized Zeolite NaY has the same structure as the natural mineral faujasite, as shown by neutron diffraction studies reported by Fitch et al.²⁵ NaY belongs to the space group $Fd\bar{3}m$ and room-temperature phase has a cubic unit cell with $a = 24.8536$ Å. The framework consists of a tetrahedral array of sodalite units interconnected through six membered oxygen bridges (Figure 1d)). Ten sodalite units form a single large cage-like unit, known as α -cage or supercage of diameter ~ 11.8 Å. Each supercage is connected to four neighboring cages through 12-membered oxygen rings of diameter ~ 7.5 Å. Two α -cages interconnected through 12-ring windows is shown in Figure 1e. The crystallographic unit cell consists of eight α -cages, containing a total 192 AlO_2 and SiO_2 tetrahedral units and extraframework cations.

In the present study, faujasite with a Si/Al ratio of 3.0 has been chosen. Unit cell composition is $\text{Na}_{48}\text{Si}_{144}\text{Al}_{48}\text{O}_{384}$ and the sodium atoms occupy all the SI and SII sites completely.

3.2. Computational Details. Molecular dynamics calculations have been carried out in the microcanonical ensemble (fixed N , V , and E). The zeolite framework is assumed to be rigid and only the coordinates of the sorbate atoms are included in the MD integration. MD integration was carried out by using the velocity Verlet scheme.²⁶ $3 \times 3 \times 3$ unit cells of zeolite NaY have been used in the simulations. Cubic periodic boundary conditions have been employed. Two different sizes of the guest have been considered; one from the linear regime ($\sigma_{gg} = 4.96$ Å) and another from the anomalous regime ($\sigma_{gg} = 6.0$ Å).¹ An example of a guest species of close to 6.0 Å size is neopentane or CCl_4 or SF_6 . The sorbate mass is taken to be 131 amu and a time step of 40 fs is used. A cutoff radius of 12 Å has been employed for sorbate–sorbate and sorbate–zeolite interactions. All runs were equilibrated up to 600 ps. The production runs have been carried out for 7 ns with 216 sorbate atoms. All the calculations have been carried out at 190 K.

3.3. Intermolecular Potential. The intermolecular potential parameters between the monatomic sorbate and zeolite were taken from the literature.^{27,28} Lorentz–Berthelot rules were used to compute the cross interaction parameters. The potentials employed here are of the (6–12) Lennard-Jones form. The guest species are assumed to interact only with the oxygen and sodium atoms of the zeolite framework. The Si and Al atoms are largely shielded by the surrounding oxygens, thus making the short-range interaction of these with the guest species insignificant. Table 1 lists the potential parameters for the sorbate–sorbate and sorbate–zeolite interaction.^{1,27,28}

TABLE 1: Potential Parameters for Sorbate–Sorbate (gg) and Sorbate–Zeolite Y ($g\text{--O}$ and $g\text{--Na}$) Interaction, for a Particle in the Linear ($\sigma_{gg} = 4.96$ Å) and Anomalous ($\sigma_{gg} = 6.0$ Å) Regimes

σ_{gg} (Å)	$\sigma_{g\text{--O}}$ (Å)	$\sigma_{g\text{--Na}}$ (Å)	ϵ_{gg} (kJ/mol)	$\epsilon_{g\text{--O}}$ (kJ/mol)	$\epsilon_{g\text{--Na}}$ (kJ/mol)
4.96	3.75	4.16	1.837	1.539	0.2685
6.0	4.27	4.68	1.837	1.539	0.2685

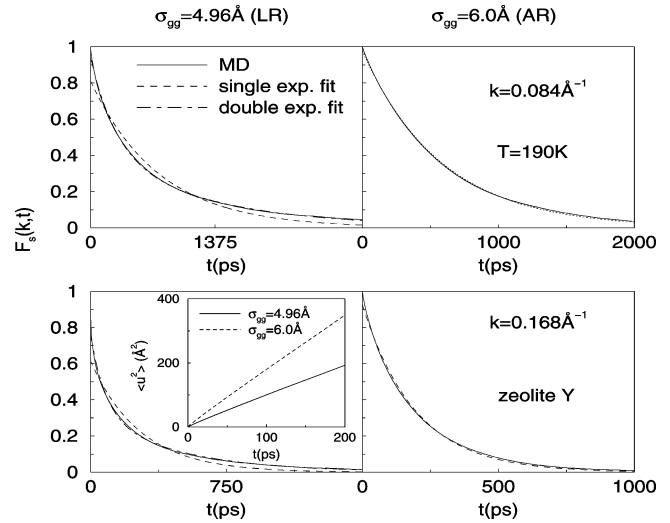


Figure 2. Intermediate scattering function, $[F_s(k, t)]$ for the particle in the linear ($\sigma_{gg} = 4.96$ Å) and anomalous ($\sigma_{gg} = 6.0$ Å) regimes in zeolite Y at 190 K for $k = 0.084$ Å⁻¹ and 0.168 Å⁻¹ along with single (e^{-t/τ_1}) and double exponential ($e^{-t/\tau_1} + e^{-t/\tau_2}$) fit. Inset shows the mean square displacement against time for the particle in the linear ($\sigma_{gg} = 4.96$ Å) and anomalous ($\sigma_{gg} = 6.0$ Å) regimes in zeolite Y at 190 K.

TABLE 2: Self-Diffusion Coefficients at 190 K for the Particle in the Linear ($\sigma_{gg} = 4.96$ Å) and Anomalous ($\sigma_{gg} = 6.0$ Å) Regimes in Zeolite Y Obtained from Einstein's Relation

σ_{gg} (Å)	$D \times 10^8$ (m ² /s)
4.96	0.14 ± 0.017
6.0	0.34 ± 0.021

4. Results and Discussion

The inset to Figure 2 shows the time evolution of mean square displacement, $\langle u^2(t) \rangle$, for the particle in the linear ($\sigma_{gg} = 4.96$ Å) and anomalous ($\sigma_{gg} = 6.0$ Å) regimes in zeolite Y at 190 K. The self-diffusion coefficient, D , is obtained from the long time slope of $\langle u^2(t) \rangle$ vs time curve from Einstein relation.²⁶ In Table 2, we list the D values for linear ($\sigma_{gg} = 4.96$ Å) and anomalous ($\sigma_{gg} = 6.0$ Å) regime particles.

We have calculated the intermediate scattering function, $F_s(k, t)$ for the particle in the linear ($\sigma_{gg} = 4.96$ Å) and anomalous ($\sigma_{gg} = 6.0$ Å) regime in zeolite Y at 190 K. The $F_s(k, t)$ is calculated for two different k values, $k = 0.084$ Å⁻¹ and $k = 0.168$ Å⁻¹, in multiples of 0.084 Å⁻¹. This (0.084 Å⁻¹) is the smallest value of k which can be accessed in the present molecular dynamics study, because of the requirement that each Cartesian component of k must be an integral multiple of $2\pi/l$, l being the length of the cubic simulation box. This requirement arises as a consequence of the periodic boundary conditions used in the simulation.²⁹

The decay of $F_s(k, t)$ for the particle in the linear ($\sigma_{gg} = 4.96$ Å) and anomalous ($\sigma_{gg} = 6.0$ Å) regimes are shown in Figure 2 at 190 K along with a fit to a single (e^{-t/τ_1}) and double exponential ($e^{-t/\tau_1} + e^{-t/\tau_2}$) decay for different k values. The decay of $F_s(k, t)$ of the guest are shown for small k . The value of l ($l = 2\pi/k$) corresponding to k is ≈ 50 Å. A guest would have traversed through several α -cages in covering a distance of 50 Å. It is seen that a single-exponential decay provides a good fit to $F_s(k, t)$ for the particle in the anomalous regime ($\sigma_{gg} = 6.0$ Å) but not for the particle in the linear regime ($\sigma_{gg} = 4.96$ Å).

In zeolite NaY, two α -cages are connected through 12-ring window. The window is the bottleneck for the cage-to-cage

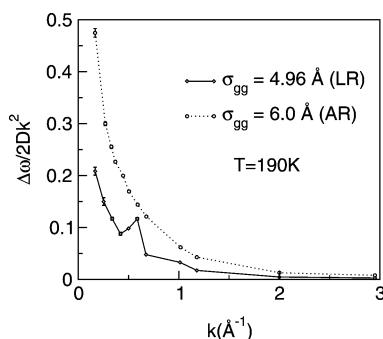


Figure 3. $\Delta\omega(k)/2Dk^2$ as a function of k for the particle in the linear ($\sigma_{gg} = 4.96$ Å) and anomalous regimes ($\sigma_{gg} = 6.0$ Å) in zeolite Y at 190 K. Error bars for $\Delta\omega(k)/2Dk^2$ are shown. For $k < 0.5$ Å⁻¹ the errors are somewhat larger than the size of the symbol used to indicate the value.

migration of the sorbate inside zeolite.¹ A particle in the linear regime ($\sigma_{gg} = 4.96$ Å), as we have already seen, encounters a positive energetic barrier at the 12-ring window. The motion within the cage (intracage) is relatively facile. In contrast, motion from one cage to another (intercage) is less facile. Therefore, for a particle in the linear regime there are two distinct types of motion; intracage and intercage motion. This leads to two well separated time scales for the decay of the density–density correlation function, $F_s(k, t)$. This separation is possible since the particle in the linear regime ($\sigma_{gg} = 4.96$ Å) encounters a significant barrier during its passage from one α -cage to the neighboring α -cage through the window. For the particle in the anomalous regime no energetic barrier is seen for intercage migration due to mutual cancellation of forces.¹ As a result, there is a single time scale associated with its motion. The particle in the anomalous regime ($\sigma_{gg} = 6.0$ Å) thus sees a homogeneous potential energy landscape and therefore the decay of the intermediate scattering function, $F_s(k, t)$ can be fitted to a single-exponential function. This is consistent with the rather flat potential energy landscape of the particle in the anomalous regime.

Figure 3 shows variation of $\Delta\omega(k)/2Dk^2$ with k for a particle in the linear and anomalous regimes. We have shown the error in $\Delta\omega(k)/2Dk^2$ for a given k . The errors are larger at small k . For $k < 0.5$ Å⁻¹, the error is larger than the size of the symbol. For $k > 0.5$ Å⁻¹, the errors are smaller than the size of the symbol used to indicate the points. In the hydrodynamic limit ($k \rightarrow 0$), the width of $S_s(k, \omega)$ approaches $2Dk^2$. As $k \rightarrow \infty$, the guest behaves like a free particle. However, in the intermediate k regime the behavior of $\Delta\omega(k)$ is strongly influenced by the nature of interactions between itself and other particles (guest as well as host). The particle from the linear regime ($\sigma_{gg} = 4.96$ Å) exhibits a minima and a maxima around $k = 0.5$ Å⁻¹. In contrast, the particle from anomalous regime ($\sigma_{gg} = 6.0$ Å) shows a smooth decrease of $\Delta\omega(k)/2Dk^2$ with k . This is

surprising. One expects the smaller particle to diffuse through the void space without difficulty, i.e., without reduction in the diffusion rate at intermediate k values. A larger particle, in fact, should encounter barrier at the window and consequently a minimum in the vicinity of the window. This also would be consistent with the nonmonotonic variation of $\Delta\omega(k)/2Dk^2$ observed by Nijboer and Rahman³⁰ for a pure fluid at high density and low temperature (see Figure 4a) and the observation that fluids at low density and high temperatures exhibit a simple monotonic decrease in $\Delta\omega(k)/2Dk^2$ with increase in k reported by Levesque and Verlet³¹ (see Figure 4b). Thus, what is found here is the exact opposite of what one expects. The results obtained by us here are therefore counterintuitive. The present calculation has been carried out for both the linear and anomalous regimes at a low concentration of 1 particle/ α -cage. This obviates any possibility of such behavior arising due to the presence of other guest atoms. Therefore, we conclude that the nonmonotonic variation in $\Delta\omega(k)/2Dk^2$ has its origin in the host or, more appropriately, in the guest–host interaction. As we already know, the guest particle from the linear regime encounter an energetic barrier at the window. The distance between two windows which is also the diameter of the α -cage is around 11.8 Å. The value at which the minimum in $\Delta\omega(k)/2Dk^2$ ($k = 0.5$ Å⁻¹) occurs is consistent with this distance. As a particle from the anomalous regime encounters no barrier at the window, a monotonic variation is observed. Thus, the present results suggest that a particle in the LR exhibits a minimum and a maximum in the rate of diffusion or wavevector dependent diffusion coefficient at intermediate k values, corresponding to the passage through the bottleneck, the 12-ring window. In contrast, a larger particle in the anomalous regime exhibits a smooth decrease in $\Delta\omega(k)/2Dk^2$ with k over all k .

5. Conclusions

The results of Nijboer and Rahman³⁰ in a normal single component pure liquid (not confined within a zeolite) at high density, low temperature suggest that the behavior of $\Delta\omega(k)/2Dk^2$ with k shows a nonmonotonic variation. This is associated with the correlations in liquid structure of these dense liquids. These liquids at lower density, higher temperatures showed a monotonic variation.³¹ Our studies here are for particles in porous solid such as zeolite. The results obtained by us here suggest that a *smaller* diameter guest particle from the linear regime exhibits a behavior of $\Delta\omega(k)/2Dk^2$ with k akin to what Nijboer and Rahman found in high density, low-temperature pure liquids! Both $F_s(k, t)$ and $\Delta\omega(k)/2Dk^2$ show that a behavior within these zeolites are consistent with each other. Surprisingly, a *larger* diameter guest particle from anomalous regime exhibits a monotonic dependence of $\Delta\omega(k)/2Dk^2$ with k which is found only in low density, high-temperature normal pure liquids as seen by Levesque and Verlet.³¹ The single-exponential decay

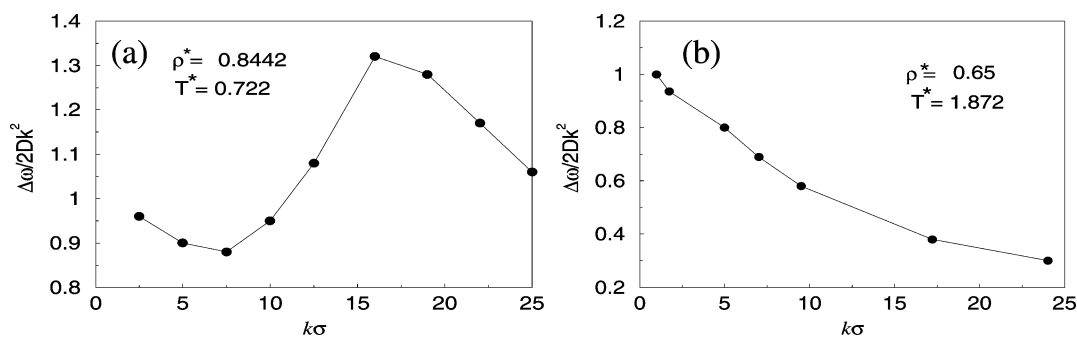


Figure 4. $\Delta\omega(k)/2Dk^2$ as a function of k for a Lennard-Jones liquid at (a) $T^* = 0.722$ and $\rho^* = 0.8442$ ³⁰ and (b) $T^* = 1.872$ and $\rho^* = 0.65$.³¹

of $F_s(k, t)$ is again consistent with the monotonic behavior of $\Delta\omega(k)/2Dk^2$.

These results provide additional evidence for relatively facile nature of diffusion of a particle in the anomalous regime relative to a particle in the linear regime. They also provide insight into the nature of motion at the intermediate k regime. The diffusion coefficient obtained from Einstein relation²⁶ provide only value of D in the long time limit. This however does not lead to any insight into the reasons behind the higher self-diffusivity of the particle in the anomalous regime. The decay of $F_s(k, t)$ and $\Delta\omega(k)/2Dk^2$ suggests that energetic barrier at the window does play an important role. Finally, the variation of $F_s(k, t)$ and $\Delta\omega(k)/2Dk^2$ are consistent with the four principle characteristics of linear and anomalous regime listed in introduction, namely lower activation energy and less undulating potential energy landscape associated with anomalous regime.

As incoherent neutron scattering experiments can provide the dynamic structure factor at various k values, the results of these experiments can provide validity or otherwise of the calculations. An appropriate choice of the systems, one for linear regime and another for anomalous regime need to be made. An accurate choice of intermolecular potential between the guest and host is essential if the results of calculations are to reproduce the experimental measurements.

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