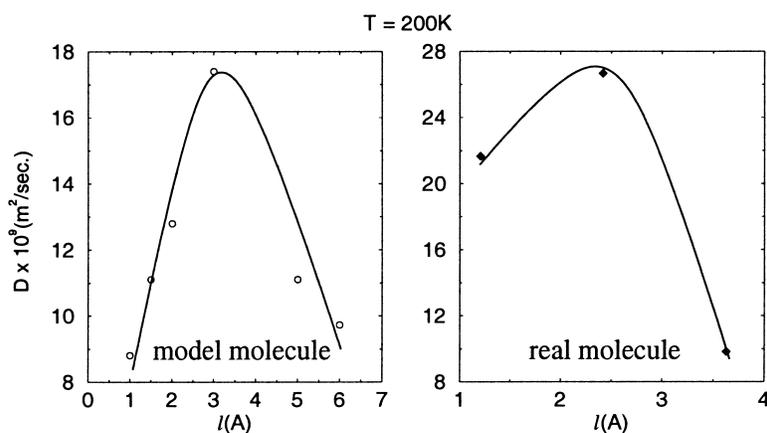


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Diffusion Anomaly as a Function of Molecular Length of Linear Molecules: Levitation Effect

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Abstract: Previous work on monatomic spherical sorbates has shown the existence of an anomalous peak in self-diffusivity (D) when plotted as a function of size of the diffusant. Molecular dynamics studies on linear molecules of different lengths l in zeolite NaY at 140 and 200 K are reported. It is seen that there is a peak in D as a function of l , suggesting that the levitation effect exists for linear molecules, the simplest member of polyatomics. This is confirmed by the lowering of the activation energy for the molecule whose length l exhibits highest D . Related quantities of interest such as the guest–host interaction energy and preexponential factor are discussed.

1. Introduction

Spherical monatomic guest species confined within porous solids have shown a surprising dependence of the self-diffusivity D on σ_{gg} , the Lennard-Jones parameter for guest–guest interaction. Two distinct regimes have been observed: (i) the linear regime, here D is linearly proportional to $1/\sigma_{\text{gg}}^2$ when σ_{gg} is small, and (ii) an anomalous peak in D for large σ_{gg} .^{1,2} While the linear regime is expected on the basis of kinetic theory, the anomalous or levitating regime is counterintuitive. The latter anomalous dependence of D on σ_{gg} (where σ_{gg} can be interpreted as the size of the diffusing guest species) arises from the fact that the sum of the forces on the guest due to the host is a minimum for the σ_{gg} corresponding to the maximum in D .³ The lowering of the net force leads to a weakly bound guest, which in effect increases D . For this reason the term levitation effect (LE) has been used previously since the guest molecules are not bound to any part of the inner wall of the host and therefore freely diffuse within the voids.

As can be discerned, existence of this behavior among polyatomic species is important not only to understand the underlying factors controlling diffusion but also for possible technological applications.^{4,5} There have been reports of unexpected maxima in diffusivity as a function of chain length among linear alkanes confined to zeolites. These are discussed below. However, n -alkanes are not *geometrically* linear in shape. There are many instances in chemistry involving linear molecules in porous solids such as N_2 , O_2 , CO , CO_2 , etc. Some of the hydrocarbon molecules such as ethane, ethylene, and but-

1,3-diene may also be considered effectively as linear. Molecular sieving is one of the important properties of zeolites and depends on the self-diffusivities of the guest species. Separation of mixtures of molecules can be possibly improved significantly by a careful study of factors influencing self-diffusivity.^{6–8} There are many instances where separation of mixtures of linear molecules are necessary: ethyne from ethylene or environmentally important separation of NO and CO from N_2 or O_2 involves essentially linear molecules.⁹ Recently, simulations of water and other molecular mixtures within zeolites have been reported.^{10–14} Further, there may be biologically important molecules that can be considered essentially as linear in geometry, and many of these exist as confined fluids. As a result, the existence or otherwise of LE will be important in these circumstances. It will also have relevance to lubrication that routinely involves fluids confined between moving walls.

Several decades ago, Goring¹⁵ reported that self-diffusivities, D , of n -alkanes (C_2 – C_{14}) in zeolite T exhibit a maximum in D at C_{12} and a minimum at C_8 . Cracking of long chain linear hydrocarbons in certain crystalline zeolites such as zeolite T revealed that the product distribution exhibits a maximum for C_{12} and a minimum for C_8 . Goring measured the diffusivities by gravimetric analysis of transient uptake of n -alkanes in zeolite T and found that the diffusivity of C_{12} is the highest and that of C_8 is lowest among alkanes with $n = 2, 3, \dots, 12$. Therefore the

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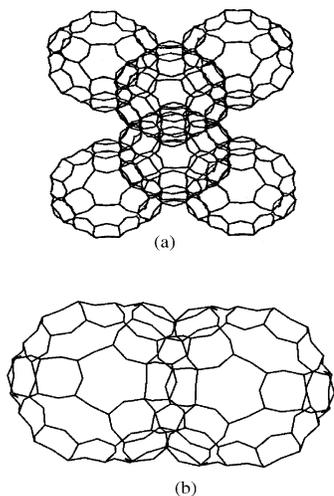


Figure 1. (a) One unit cell of zeolite NaY. There are eight α -cages, and each α -cage is connected tetrahedrally to four neighboring α -cages. (b) Two α -cages connected via 12-ring window is shown.

observed product profile appears to be due to diffusion-limited reaction. While C_8 has a length that is equal to the distance between two windows, C_{12} has a length that is about $1\frac{1}{2}$ times that of this. The activation energy for C_{12} has been found to be the lowest. The window diameter in zeolite T is comparable to the size of the methyl (or methylene) group. This criteria seems crucial since in zeolites with larger-sized windows, no such maximum and minimum are seen. This effect has been termed the window effect or resonant diffusion for these reasons. Ruckenstein and Lee¹⁶ have studied a model of a one-dimensional rod moving through a one-dimensional periodic potential to understand the reasons behind these observations. By arguments based on symmetry considerations they show that for a rod extending over more than one cage as in C_{12} the potential barrier is lower. Subsequently, Derouane,¹⁷ Nitsche and Wei,¹⁸ and more recently Runnebaum and Maginn¹⁹ have investigated this effect. Clark et al. found no resonant diffusion in faujasite²⁰ since the window diameter is larger.

In this study, molecular dynamics simulations are reported on model linear molecules of different lengths l . Self-diffusivity D , the activation energy, E_a , and several other relevant properties are reported to verify the existence or otherwise of the levitation effect among model linear molecules. Simulations on real linear molecules have been carried out to provide data for experimental verification of these results. The molecules chosen are ethyne, prop-1,2-diene, and but-1,3-diyne. PFG-NMR or neutron scattering can be employed to measure self-diffusivities of these systems, which will provide a direct confirmation of the existence of LE. A comparison of these results is made with resonant diffusion in the Conclusions section.

2. Methods

2.1. Structure of Zeolite NaY. Synthesized zeolite NaY has the same framework structure as the natural mineral faujasite. Recently, its structure has been determined by neutron diffraction studies reported by Fitch et al.²¹ It crystallizes in the space

Table 1. Intermolecular Potential Parameters for Guest–Guest and Guest–Zeolite Interactions (model linear molecule)

atom	σ (Å)	ϵ (kJ/mol)
site–site	Guest–Guest	0.9977
	Guest–Zeolite	
site–O	2.55	1.1314
site–Na	2.96	0.1995

group $Fd\bar{3}m$, and the room-temperature phase has a unit cell dimension of 24.8536 Å. The framework consists of an array of sodalite units interconnected through six-membered oxygen bridges. Ten sodalite units are so arranged as to form a single large cage-like unit, known as the α -cage or supercage of diameter ~ 11.8 Å. Each supercage is connected to four neighboring cages through shared 12-membered oxygen rings of diameter ~ 7.5 Å (Figure 1b). Each crystallographic unit cell consists of eight α -cages, containing a total of 192 AlO_2 and SiO_2 tetrahedral units (Figure 1a). In the present study, for model linear molecules the zeolite framework has been assumed to have a Si/Al ratio of 3.0. Each unit cell contains 48 Na, 144 Si, 48 Al, and 384 oxygen atoms. The sodium atoms occupy all the SI and SII sites completely, and there is zero occupancy of all the other types of cation sites. For the three linear hydrocarbons, namely, ethyne, prop-1,2-diene, and but-1,3-diyne, the Si/Al ratio is ∞ . As a consequence, there are no extraframework cations in the zeolite structure.

2.2. Intermolecular Potentials. The interactions between the sorbate and sorbate as well as sorbate with the zeolite have been modeled by the (6–12) Lennard-Jones potential given by

$$\Phi(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

where ϵ_{ij} is the well depth, σ_{ij} is the diameter, and r_{ij} is the distance between the interacting atoms i and j . The parameters for the model linear molecule are listed in Table 1a. As the Si and Al atoms are surrounded by the bulkier oxygens, the close approach of guest to Si/Al atoms is not possible. For this reason, short-range interactions are included between the guest and the oxygens only.²² The Si/Al ratio is accounted through the presence of Na^+ ions which interact with sorbate species.

We have also simulated three real molecules (hydrocarbons), namely, ethyne ($CH\equiv CH$), prop-1,2-diene ($CH_2=C=CH_2$), and but-1,3-diyne ($CH\equiv C-C\equiv CH$), with a view to suggest possible systems on which laboratory measurements could be carried out. The CH and CH_2 groups are treated within the united atom model. The interaction parameters of the individual groups of the guests as well as between the groups of the guest and the zeolite are listed in Table 2.²³

The MD simulations have been carried out within zeolite NaY with a Si/Al ratio of 3.0 for model linear molecules and ∞ for real molecules. We have investigated the influence of the cations on self-diffusivity by carrying out simulations in faujasite with two different ratios: (1) Si/Al = 3.0 and (2) Si/Al = ∞ (that is, there are no extraframework cations). As we shall see, the

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Table 2. Intermolecular Potential Parameters for Molecule–Molecule and Molecule–Zeolite Interactions (hydrocarbons)

atom	σ (Å)	ϵ (kJ/mol)
Molecule–Molecule		
CH–CH	3.8000	0.11500
CH ₂ –CH ₂	3.8500	0.08000
C–C	3.7500	0.10500
Molecule–Zeolite		
CH–O	3.1728	0.38500
CH ₂ –O	3.1980	0.32110
C–O	3.1500	0.36790

presence of cations up to a Si/Al ratio of 3.0 leads to only a marginal change in self-diffusivity and no change in the dependence of D on molecular length, l .

We have chosen to neglect the polarization interaction between the guest molecules and the atoms of the zeolite. It is well known that the contribution from polarization interaction is typically only a few percent of the total interaction energy and may not alter the self-diffusivity significantly.

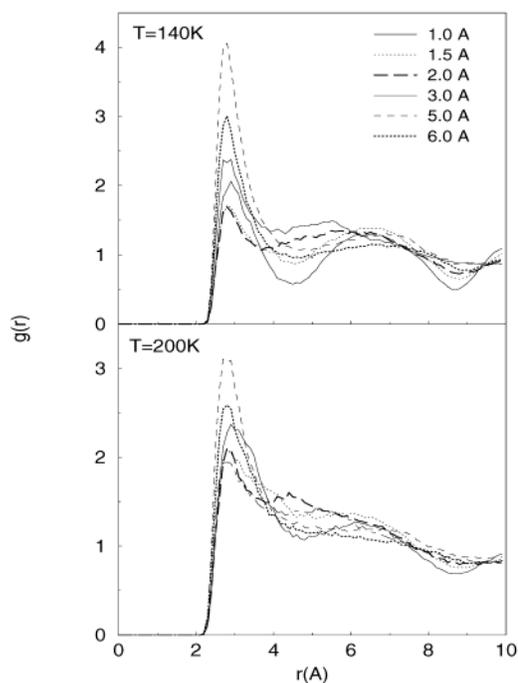
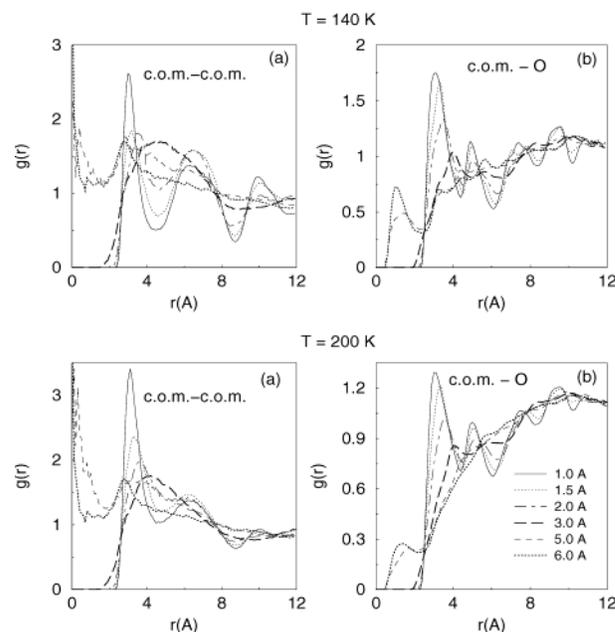
2.3. Computational Details. Unit cells ($2 \times 2 \times 2$) of NaY zeolite in a cubic simulation cell of length 49.70 Å have been employed in all simulations. Note that the Si/Al ratio is 3.0 for simulations on model guests and ∞ for real molecular systems. A concentration of 1 molecule/cage with a total of 64 model linear molecules has been simulated in the microcanonical ensemble at 140 and 200 K. The linear molecule consists of just two sites located at a distance l apart, which is its bond length. The mass of each site has been chosen to be 16 amu.

For model systems, typically, an equilibration for 140 ps was followed by runs of 1.26 ns, during which averages were computed. A time step of 7.0 fs has been used. Calculations have been carried out at $l = 1, 1.5, 2, 3, 5,$ and 6 Å all with a guest center of mass (com)–com and guest com–zeolite atoms cutoff of 13.0 Å. All simulations have been carried out using the constrained molecular dynamics algorithm.²⁴

Simulations of real molecules are reported at 100 and 200 K. Molecules are placed at the cage centers at the beginning. The molecular masses are the sum of the atomic masses. Unlike the model system where molecular masses not varied with l (32 amu), here molecular mass increases with molecular length l , defined as the distance between centers of two terminal carbons. The molecular lengths of the three molecules CH \equiv CH, CH₂=C=CH₂, and CH \equiv C–C \equiv CH are 1.21, 2.42, and 3.63 Å, and masses are 26, 40, and 50 amu, respectively. A time step of 1.0 fs was used for MD integration, which yielded good energy and momentum conservation (energy fluctuation less than 1 in 10^4). Equilibration was performed over a duration of 300 ps, during which velocities are scaled at every step to obtain the desired temperature. Properties are calculated from the configurations stored at intervals of 0.02 ps from a production run 1000 ps.

3. Results and Discussion

3.1. Model Linear Molecular System. Even though the present study focuses on the dynamical properties, in particular, the transport property, it is interesting to look at the equilibrium structure and energetics. These provide certain interesting trends as a function of l that are of considerable relevance.

**Figure 2.** Site–site radial distribution function (rdf) between the model linear guest molecules at 140 and 200 K.**Figure 3.** (a) Radial distribution functions (rdf's) between the center of mass (com)–com of the guests and (b) com of guest and O atoms of zeolite NaY at (a) 140 K and (b) 200 K at a loading of 1 molecule/ α -cage. Note that the rdf's are shown for the model linear molecule with six different molecular lengths: $l = 1, 1.5, 2, 3, 5,$ and 6 Å.

Structure. Figure 2 shows a plot of site–site radial distribution function (rdf) between the guest molecules. The site–site rdf exhibits a peak at around 3.0 Å corresponding to $2^{1/6}\sigma_{gg}$. There is no systematic change in the variation of intensities of the first peak with l . The $g(r)$ for $l \leq 3$ Å behave as expected. For $l > 5$ Å the com–com and com–O radial distribution functions shown in Figure 3a,b exhibit certain peculiarities: nonzero intensities below 1 Å are seen. For other values of l the $g(r)$ has nonzero intensity only beyond 2.0 Å, as one would

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expect. The reason for this unexpected behavior is the absence of an interaction site at the com; when the bond length l is significantly larger than $\sigma_{\text{site}}-\text{O}$ ($=2.55 \text{ \AA}$), it is possible for the com of one guest to be in close proximity of a neighboring guest molecule or the oxygen of the host.

Another interesting observation is the presence of well-defined peaks in the com-com $g(r)$ for $l = 1.0 \text{ \AA}$, suggesting thereby that the guests are ordered and are more akin to a well-ordered solid phase. This receives further support from the guest-host (com-O) rdf. Guest-guest rdf for $l > 1.0 \text{ \AA}$ is similar to a fluid phase. As we shall see, the dynamical properties reported later are consistent with these structural properties.

Energetics. As the predominant interaction at low concentrations is the guest-host interaction, in Figure 4 we show a plot of the distribution of guest-host interaction energy of the i th molecule given by the equation

$$U_{\text{gh}}^i = \sum_{k=1}^{n_g} \sum_{j=1}^{n_h} \Phi(r_{(i,j)}^k) \quad (2)$$

Here n_h and n_g ($=2$, for the model molecular systems) are the number of zeolite and guest sites. The reported distribution has been averaged over all N guest molecules at all MD steps after equilibration. For $l = 3.0 \text{ \AA}$ the shift to the right is maximum. Such a shift is associated with an increased mobility, as we shall see. Further increase in the bond length beyond $l = 3.0 \text{ \AA}$ shows a shift to the left or increased binding to the host.

We have computed the site-zeolite interaction energy for the two sites $k = 1, 2$ of the i th linear molecule separately:

$$U_{\text{gh},k}^i = \sum_{j=1}^{n_h} \Phi(r_{(i,k,j)}) \quad (3)$$

Table 3 lists the variation of energy for different values of molecular length l . The lowest value of the two site-zeolite interaction energies is taken to be the second site. As can be seen, there is little change in site 2-zeolite interaction energy. In contrast, site 1-zeolite interaction energy shows a pronounced decrease in magnitude with increase in molecular length up to $l = 3.0 \text{ \AA}$. A small increase in magnitude is seen beyond $l = 3.0 \text{ \AA}$. The site 2-zeolite interaction energy remains largely unchanged, while the site 1-zeolite interaction energy shows changes similar to that of a total U_{gh} . Among monatomic sorbates, it is seen that the guest-host interaction energy increases monotonically with the diameter σ_{gg} .³ The linear molecule exhibits a decrease in U_{gh} (or an increase in magnitude) initially and an increase subsequently. The site 2-zeolite interaction energy remains largely unchanged, while the site 1-zeolite interaction energy shows changes similar to that of total U_{gh} .

The reason for the observed changes in these values is due to the spatial distribution of the physisorption sites within the supercage and the molecular geometry, which in the present case is specified by the molecular length l of the guest. Previous studies have shown the existence of physisorption sites, six in all, within each supercage. The energy within a region of about 1.0 \AA radius of the physisorption site is generally quite favorable.²⁵ Both guest interaction sites prefer the region in the

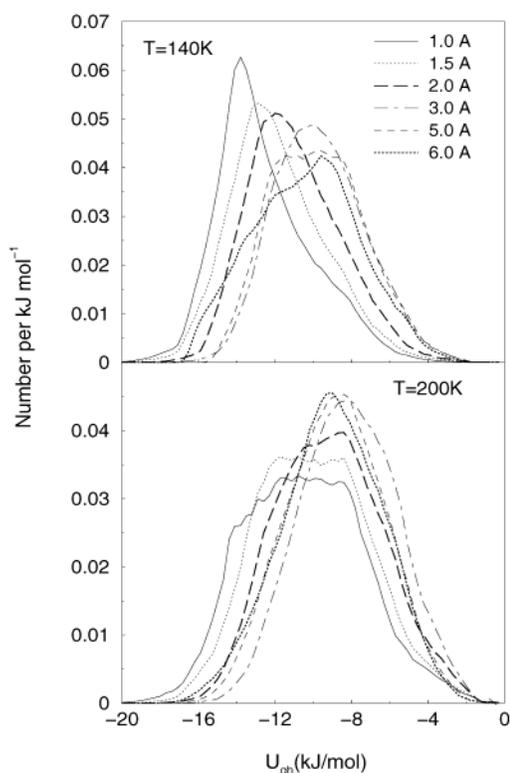


Figure 4. Distribution of guest-host interaction energy at 140 and 200 K for the model linear molecule with molecular lengths $l = 1, 1.5, 2, 3, 5,$ and 6 \AA .

vicinity of a physisorption site. When l is small (about 1 \AA), then it is possible to optimize the interaction of these sites with the zeolite. Both sites have a rather favorable interaction energy of -8.55 and -8.20 kJ/mol in this case. As l increases beyond 1.0 \AA , it becomes increasingly difficult to optimize the interaction energy of both guest sites. This leads to an increase in the energy to -6.10 kJ/mol of one of the sites, while the other site, at the physisorption site, still possesses rather favorable guest-zeolite interaction energy. Beyond $l = 3.0 \text{ \AA}$ it is possible to partially optimize both guest sites since now one of the sites can be in the vicinity of one physisorption site while the other site is close to a neighboring physisorption site.

Dynamics. Figure 5 shows a plot of the evolution of the mean square displacement (msd) for different values of l and temperature. These msd curves during the first 200 ps may be approximated by a straight line, suggesting the behavior is diffusive. The self-diffusivity obtained using the Einstein relation²⁶

$$D = \frac{\langle u^2 \rangle}{2d_t} \quad (4)$$

where d_i is the dimensionality of the system, taken as 3 in the present case, is plotted in Figure 6 as a function of the molecular length, l . Table 4 lists the values of self-diffusivity (D) at both 140 and 200 K. D increases from $l = 1.0 \text{ \AA}$ to $l = 3.0 \text{ \AA}$. Beyond $l = 3.0 \text{ \AA}$ D decreases at both 140 and 200 K. This surprising behavior suggests that $l = 3.0 \text{ \AA}$ is the optimum molecular dimension for self-diffusion.

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Table 3. Molecule–Zeolite, Site 1–Zeolite, and Site 2–Zeolite Interaction Energies Obtained from the Minimization of the Molecule–Zeolite Interaction Energy for Linear Molecules with Different Molecular Lengths, l

molecular length (l) (Å)	U_{gh}^l (molecule–zeolite) (kJ mol ⁻¹)	$U_{\text{gh},1}^l$ (site 1–zeolite) (kJ mol ⁻¹)	$U_{\text{gh},2}^l$ (site 2–zeolite) (kJ mol ⁻¹)
1.0	-16.75	-8.20	-8.55
1.5	-15.87	-7.71	-8.16
2.0	-15.67	-7.37	-8.30
3.0	-14.13	-6.10	-8.03
5.0	-14.83	-6.21	-8.52
6.0	-15.27	-6.68	-8.59

Table 4. Self-Diffusivity Values Obtained from the Plot of Mean Squared Displacement for Linear Molecules with Molecular Lengths, $l = 1, 1.5, 2, 3, 5,$ and 6 Å at 140 and 200 K and a Loading of 1 Molecule/ α -Cage

l (Å)	$T = 140$ K		$T = 200$ K	
	$\langle T \rangle$ (K)	$D, 10^{-9}$ (m ² s ⁻¹)	$\langle T \rangle$ (K)	$D, 10^{-9}$ (m ² s ⁻¹)
1.0	138.18	2.32	204.73	8.82
1.5	134.56	3.13	194.82	11.10
2.0	135.87	4.31	204.24	12.80
3.0	138.43	7.53	204.85	17.41
5.0	136.82	4.56	199.80	11.16
6.0	139.88	3.90	210.34	9.75

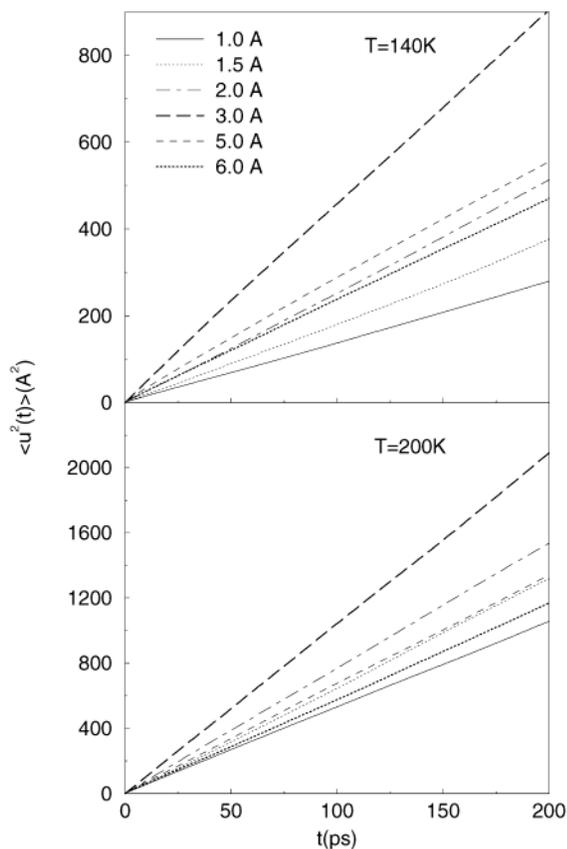


Figure 5. Mean squared displacement over the first 200 ps for the different molecular lengths of the model linear molecule at 140 and 200 K at a loading of 1 molecule/ α -cage.

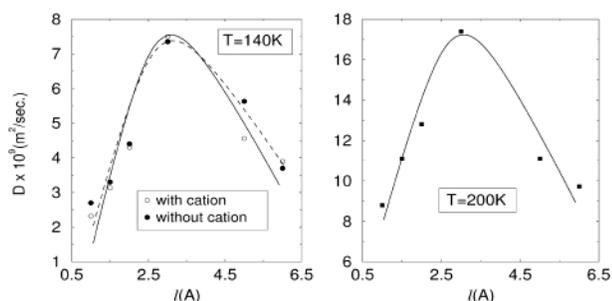


Figure 6. Self-diffusivity (D) of the model linear molecules at 140 and 200 K as a function of molecular lengths l . At 140 K, results with (for Si/Al ratio of 3.0) and without cations (Si/Al of ∞) are shown. Note that there is little difference in the dependence of D on l . This justifies our use of an extraframework cation free zeolite for real molecules.

As already stated, previous work on spherical monatomic sorbate has shown the existence of a peak in D as a function of σ .¹ Two distinct regimes were found: (i) a linear regime in

which $D \propto 1/\sigma^2$ and (ii) an anomalous or levitating regime where D exhibits a peak. Further, it was found that the frictional force on the guest due to the host does not change significantly in the linear regime.² In contrast, the frictional force exhibits a minimum for the value of σ corresponding to the maximum in D .

For this reason, this effect has been termed the levitation effect (LE). To verify whether the observed maxima in D versus l plot shown in Figure 6 has the same origin as the monatomic system, we computed the magnitude of the force on the guest due to the host, $\vec{F}_{\text{gh}} \cdot \vec{F}_{\text{gh}}$. This dot product exhibits a minimum corresponding to the position of the maximum in D (see Figure 7). This unambiguously demonstrates that the reason for the observed maximum in the self-diffusivity has the same origin as the levitation effect observed so far among monatomic species only.

The Arrhenius relationship

$$D = D_0 e^{-E_a/kT} \quad (5)$$

has two independent factors, namely, the preexponential factor D_0 and activation energy E_a , which determine D . An increase in molecular length l is expected to increase the collision cross section, leading to more frequent collisions. Consequently D_0 is expected to decrease with increasing l . The other factor determining diffusion rate is the activation energy. The values of E_a for different l are listed Table 5. E_a is smallest for $l = 3.0$ Å. Previous studies have also shown that E_a is lowest corresponding to the value of l for which D is maximum.

Velocity autocorrelation functions (vacf's) are shown in Figure 8 for $T = 140$ and 200 K. The curves exhibit significant negative correlations for all values of l except 3.0 Å at both temperatures. This suggests that the potential energy (PE) landscape is rather flat for $l = 3.0$ Å. Previous studies on monatomic sorbates have shown that for particles in the anomalous regime the PE surface is relatively flat in comparison to those in the linear regime.²⁵ The vacf's obtained here confirm that the PE surface is flat for the levitating regime even among the linear molecules.

3.2. Real Linear Molecular Systems. Even though the model systems we have employed are not far removed from real molecular systems, for purposes of experimental verification of the LE among linear molecules, it is necessary to choose real molecules. It will also show the relevance of the present study to practical problems faced in the laboratory and industry. Separation of O₂ from N₂, NO from N₂, and CO from CO₂ are important environmental problems. An understanding of their diffusion properties and their dependence on various factors is a prerequisite before an efficient solution can be designed for

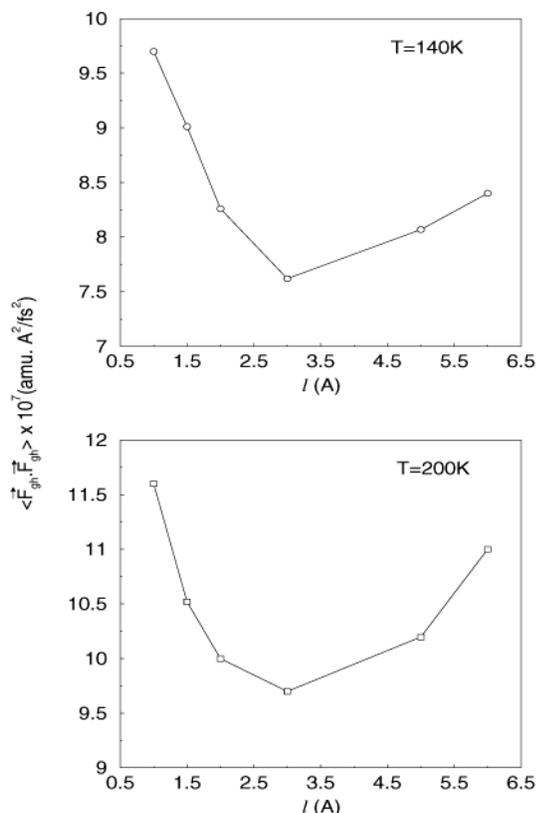


Figure 7. Average force on the guest molecule due to the host zeolite at 140 and 200 K for the model linear molecule with molecular lengths $l = 1, 1.5, 2, 3, 5, \text{ and } 6 \text{ \AA}$.

Table 5. Activation Energies (E_a) for Different Molecular Lengths, l

molecular length, l (Å)	E_a (kJ/mol)	molecular length, l (Å)	E_a (kJ/mol)
1.0	4.875	3.0	2.738
1.5	4.572	5.0	3.281
2.0	3.854	6.0	3.420

Table 6. Self-Diffusivity Values Obtained from the Plot of Mean Squared Displacement for Acetylene, Prop-1,2-diene, and But-1,3-diyne Hydrocarbons as a Function of Their Molecular Lengths, l

l (Å)	$T = 100 \text{ K}$		$T = 200 \text{ K}$	
	$\langle T \rangle$ (K)	$D, 10^{-9} (\text{m}^2 \text{ s}^{-1})$	$\langle T \rangle$ (K)	$D, 10^{-9} (\text{m}^2 \text{ s}^{-1})$
1.21	100.7	8.34	206.42	21.66
2.42	98.24	12.06	203.30	26.67
3.63	99.35	3.96	204.24	9.833

their separation. Apart from the above diatomic or triatomic molecule there are a number of hydrocarbon molecules whose separation from the mixture is essential, particularly in petrochemical industry.

We have chosen three hydrocarbon species, namely, ethyne ($\text{CH}\equiv\text{CH}$), prop-1,2-diene ($\text{CH}_2=\text{C}=\text{CH}_2$), and but-1,3-diyne ($\text{CH}\equiv\text{C}-\text{C}\equiv\text{CH}$). We have employed a united atom model for interaction between the various groups (C, CH, CH_2) and oxygen and the sodium of the zeolite.

Figure 9 shows the time evolution of msd of these three real molecules over the first 50 ps. Table 6 lists the values of self-diffusivity along with molecular length l . The values of D are in the range 10^{-9} or 10^{-8} . In the literature, few groups have reported diffusivity of unsaturated hydrocarbons in zeolites. In

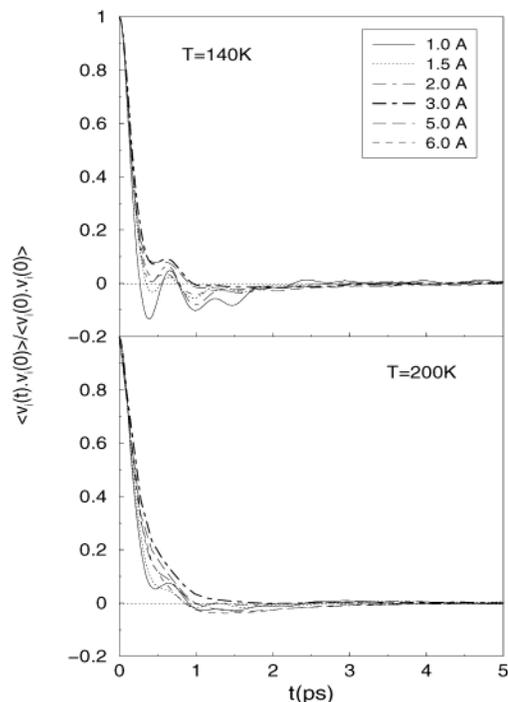


Figure 8. Velocity autocorrelation function (vacf) at 140 and 200 K as a function of time for different molecular lengths l .

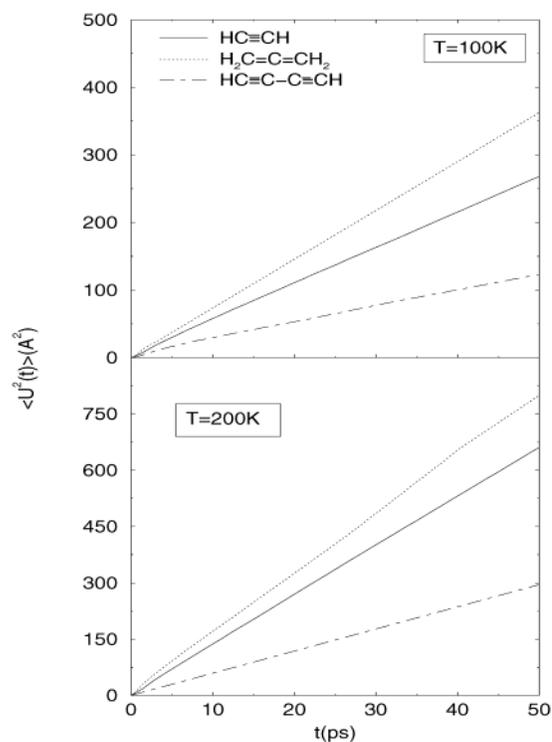


Figure 9. Mean squared displacement over the first 50 ps for the three different hydrocarbons, namely, $\text{CH}\equiv\text{CH}$, $\text{CH}_2=\text{C}=\text{CH}_2$, and $\text{CH}\equiv\text{C}-\text{C}\equiv\text{CH}$ at 100 and 200 K at a loading of 1 molecule/ α -cage.

comparison there are many authors reporting diffusivities of alkanes in zeolites. Germanus, Kärger, and Pfeifer²⁷ have reported the PFG-NMR diffusivities of ethene and but-1-ene in NaX zeolite. They are 1×10^{-9} and $3 \times 10^{-10} \text{ m}^2/\text{s}$, respectively, at 293 K. These may be compared with the values

(27) Kärger, J.; Pfeifer, H. *Zeolites* **1998**, *7*, 90.

Table 7. Self-Diffusivity as a Function of γ for Model and Real Linear Molecules (Hydrocarbons) at Different Temperatures

model linear molecules				real linear molecules				
$l(\text{\AA})$	γ	$D, 10^{-9} (\text{m}^2 \text{s}^{-1})$		hydrocarbons	$l(\text{\AA})$	γ	$D, 10^{-9} (\text{m}^2 \text{s}^{-1})$	
		$T = 140 \text{ K}$	$T = 200 \text{ K}$				$T = 100 \text{ K}$	$T = 200 \text{ K}$
1.0	0.665	2.32	8.82	CH \equiv CH	1.21	0.82	8.84	21.66
1.5	0.715	3.13	11.10	CH $_2$ =C=CH $_2$	2.42	0.95	12.06	26.67
2.0	0.764	4.31	12.80	CH \equiv C-C \equiv CH	3.63	1.07	3.96	9.833
3.0	0.863	7.53	17.41					
5.0	1.061	4.56	11.16					
6.0	1.160	3.90	9.75					

listed in Table 6, which are in the range $(9-26) \times 10^{-9} \text{ m}^2/\text{s}$ at 200 K. By fitting an Arrhenius expression to the 100 and 200 K calculated data we find that the diffusivities at 293 K are 2.98×10^{-8} , 3.56×10^{-8} , and 1.40×10^{-8} for the three molecules ethyne, prop-1,2-diene, and but-1,3-diyne, respectively. The MD calculations have been carried out in NaY zeolite with a Si/Al ratio of ∞ without any extraframework cations. This may be compared to a Si/Al ratio of 1.2 for the NaX zeolite sample employed by Germanus.²⁸ Since the Si/Al ratio is large in the calculation as compared to the experiment, it is not surprising that the D values we obtain are somewhat higher. The values we have obtained seem reasonable in view of this and the observation of Germanus et al. that the presence of even small amounts of water alters the D values significantly. It is possible that the self-diffusivity values in the presence of cations may change noticeably, but the trends are likely to be similar, as the results on model linear molecules demonstrate (see Figure 6).

Note the D values are in the order ethyne < but-1,3-diyne < prop-1,2-diene at both 100 and 200 K. The length of these molecules is in the order $l(\text{ethyne}) < l(\text{prop-1,2-diene}) < l(\text{but-1,3-diyne})$. The molecule with highest D is that of intermediate length. This suggests that there is an optimum length of the molecule at which the self-diffusivity is highest.

Levitation Parameter for Linear Polyatomics. Previous studies on monatomic guest species have shown that the peak in D is found in different zeolites and other porous solids irrespective of the geometrical and topological details of the host pore network. The peak in D occurs at different values of the Lennard-Jones parameter σ_{gg} for different porous solids. The levitation parameter defined as

$$\gamma = \frac{2^{7/6} \sigma_{\text{gh}}}{\sigma_{\text{w}}} \quad (6)$$

provides a universal parameter. Here σ_{gh} is the guest–host Lennard-Jones interaction parameter and σ_{w} is the void dimension. According to eq 6, the peak in D is observed when γ approaches unity.¹ The present study suggests that such a peak may be seen in linear polyatomics as well. The definition of γ , however, needs to be modified for the linear guest species. We redefine the levitation parameter for linear polyatomics:

$$\gamma = \frac{l + 2^{7/6} \sigma_{\text{gh}}}{\sigma_{\text{w}}} \quad (7)$$

Here l is the end-to-end distance between the atomic centers of the guest. The above expression reduces to that of monatomic

systems when $l = 0$. Values of γ for model and real systems studied here are reported in Table 7. It is evident that the peak in both model and real systems occurs at a value of γ close to unity.

4. Conclusions

The present study demonstrates the existence of levitation effect for both the model and real linear molecular systems, similar to what has been observed in the case of monatomic systems. This study shows that the levitation effect is not confined to monatomic species, but it exists among linear polyatomic systems as well. It should be possible to verify these findings experimentally with ethyne, prop-1,2-diene, and but-1,3-diyne. Proton PFG-NMR could be one of the techniques that could provide direct evidence of this. It is important that these experiments be carried out in faujasite with high Si/Al ratio. Even though we have used a Si/Al ratio of 3.0, our studies essentially correspond to a high Si/Al ratio since we have included only the short-range interactions between the guest and zeolite. Further, when the Si/Al ratio is large, the presence of cations will not block the motion of these guest species near the bottlenecks (windows) and strong interactions between the extraframework cations and the π -electron clouds of the guest will be absent. Effort is under way to verify the above findings experimentally.

These findings are interesting because of a large number of situations in chemistry, physics, biology, and material science where diatomic or polyatomic linear species (guests that can be effectively considered as linear or linear molecules) diffusing through porous solids are encountered. The present study may be said to be a prelude to studies on diffusion of nonlinear polyatomics within confined regions. Molecules that are one-dimensional such as chains or short peptides and other species may also behave similarly. These can be of great significance in transport of biomolecules within the living cell.

However, the results reported here are different compared to resonant diffusion^{15–20,29} seen in n -alkanes confined to zeolites. As discussed in the Introduction, resonant diffusion or window effect refers to the maximum in diffusivity observed for n -alkanes in zeolite T (and a few other zeolites) whenever the length of the n -alkanes is a half-integral multiple of and greater than the distance between the two windows. This occurs for C₁₂. When the chain length of n -alkane is an integral multiple of the distance between the two windows, it is seen that the diffusivity is a minimum, as is seen for C₈. Such maxima and minima are seen only among zeolites that have a window (cross section) dimension comparable to the size of the methyl or methylene groups.

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(29) Talu, O.; Sun, M. S.; Shah, D. B. *AIChE J.* **1998**, *44*, 681.

The effects that is reported in the present study, viz., levitation effect and resonant diffusion, have certain similarities as well as certain differences at a fundamental level. Basically both arise from a decrease in the influence of the host on the diffusant, i.e., the guest molecule. However, in practice, the levitation effect and resonant diffusion manifest themselves in quite different ways. The levitation effect is an effect that is seen in *any* porous solid irrespective of the void structure and void topology^{30,31} and appears to be a universal behavior. In the resonant diffusion, the maximum and minimum are observed only for linear alkanes and only when the bottleneck void dimension is comparable to the size of the CH₃ or CH₂ group *and* the length of the alkane is a half-integral multiple of and greater than the distance between two windows. The last condition is not necessary for the levitation effect. As pointed out by Tsekov and Smirniotis,³² the window effect is seen only among crystalline zeolites with regular periodicity. In contrast, recent work from some of us suggests that the levitation effect can be seen even among disordered solids or even liquids.³³

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(32) Tsekov, R.; Smirniotis, P. G. *J. Phys. Chem. B* **1998**, *102*, 9385.

The present work suggests that the maximum in D is seen when the *length* of the linear molecule matches the *diameter* of the bottleneck (here 12-ring window) through which it is passing. This may be contrasted with the resonant diffusion or window effect of Goring,¹⁵ where the maximum in D occurs when the *length* of the linear *alkane* molecule is a half-integral multiple of the *distance between two windows*. In fact, in resonant diffusion, the molecule is not a linear molecule but a linear alkane. That is, it is not geometrically linear. A more thorough comparison needs to be made between the two effects. However, it is beyond the scope of the present work to go into a more detailed comparison of the two effects.

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