Molecular diffusion and confinement effect: Neutron scattering study

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Confined fluids generally have properties different from those of adsorbed layer or bulk phases. Diffusion, translational or rotational, is altered significantly on confinement. The molecular dynamics and its effect due to confinement in various environments as studied by Quasi-elastic Neutron Scattering (QENS) technique have been reported. QENS offers a unique possibility of analyzing spatial dimensions of atomic or molecular processes in their development over time. It is found that dynamics of a fluid confined in porous medium depending on the nature of the medium and interaction, can have a variety of modifications. The diffusivity of guest molecules embedded in zeolite or molecular sieves depends very much on the combination of the guest and host structures, shape and specific interactions.

Keywords: Molecular diffusion, Neutron scattering, Zeolites, Quasi-elastic neutron scattering

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1 Introduction

Neutron scattering is a powerful experimental tool for studying the structure and dynamics of atoms and molecules in condensed matter\(^1\). This is possible as neutron has a wavelength matching with the interatomic spacings in solids and also its energy is close to the excitations in the solid. It is particularly suited for studying the dynamics of protons because of the latter’s large scattering cross-section compared to that of other elements (\(\sigma_{\text{H}}\sim 81\) barns, \(\sigma_{\text{other element}}\sim 4-5\) barns). The inelastic neutron scattering experiments are used either for studying the periodic motions like vibrations or for studying the thermally activated single particle motions which show up in Doppler-broadened elastic lines. The latter are studied by using a technique known as the Quasi Elastic Neutron Scattering (QENS). It offers a unique possibility of analyzing spatial dimensions of atomic or molecular processes in their development over time. The time-scale of the dynamical motion, its geometry as well as the nature of the hindering potential can all be obtained from the neutron scattering experiments, which are carried out using either a triple axis or a time-of-flight spectrometer\(^3\). A few examples of molecular motion studies in various solids and liquids using QENS technique can be found in Ref. 3.

The problem of diffusion of molecules in restricted geometries (confinement) can be found in a large variety of physical situations. Common examples are water in rock or sand stones and water in biological membranes. Other examples of structures that impose spatial restriction include polymer gels, clays, micells, vesicles and micro-emulsions. Zeolites are also porous crystalline materials that absorb a number of molecules in relatively large quantities. This makes them useful in a number of industrial processes, mostly in petroleum and petrochemical industries, as catalysts and molecular sieves. An understanding of the role of various factors in the characteristics of molecular sieves could lead to tailor-made, highly efficient molecular sieves. This is largely determined by the diffusivity of the guest molecules within the cavities of molecular sieves. The sorption, binding and the transport characteristics of various adsorbents in zeolitic pore systems have been investigated extensively, both experimentally and theoretically, with an objective to achieve the fundamental understanding of the behaviour of guest molecules in confined geometries. It is also widely reported that the thermodynamic and transport properties of fluids are considerably altered on their physical confinement in well-defined channel and cavity system of porous materials. Two competing effects seem to be the main contributors to the modification of the dynamics of the confined fluid with respect to the bulk phase: (i) the geometric confinement and (ii) the interaction with the host cage. In other words, the problem can be addressed by asking how the properties of the porous medium, such as size, surface area or the chemical nature of the interface can modify the dynamical behaviour.
The QENS studies investigating localization and dynamics of molecules and the role played by the symmetry and the structure of the guest molecule in addition to the physical characteristics of the sorbents have been reported. The results of the investigation of water dynamics in porous media (alumina gel and hydrotalcite) and modifications in the diffusivity of various hydrocarbon molecules (benzene, cyclohexane, methanol etc.) in various zeolites (HZSM-5 and Na-Y) and a molecular sieve (MCM-41) are discussed.

2 Theoretical Details

In a neutron scattering experiment the scattered intensity is analysed as a function of both energy and momentum transfer. The quantity measured is the double differential scattering cross-section representing the probability that a neutron is scattered with energy change $dE$ into the solid angle $d\Omega$:

$$\frac{d^2\sigma}{d\omega d\Omega} \propto \frac{k}{k_0} \left[ \sigma_{coh} S_{coh}(Q, \omega) + \sigma_{inc} S_{inc}(Q, \omega) \right] \quad \ldots (1)$$

$S(Q,\omega)$ is known as the scattering law and the subscripts $coh$ and $inc$ denote the coherent and incoherent components. $k$ and $k_0$ are the final and initial wavevectors. $Q = k - k_0$ is the wavevector transfer [$Q= 4\pi \sin\theta / \lambda$, where 20 is the scattering angle] and $\hbar \omega = E - E_0$ is the energy transfer. Incoherent scattering involves the same nucleus at two successive times, so there are no interference effects between the amplitudes scattered by different nuclei. Whereas in coherent scattering, the total intensity observed results from the sum of the different intensities scattered from the individual nuclei. In hydrogenous systems, such as benzene, cyclohexane and methanol, total scattering is dominated by the incoherent scattering of protons as $\sigma_{coh}$ (any element) $<< \sigma_{inc}$ (proton). So in the case of hydrogenous systems,

$$\frac{d^2\sigma}{d\omega d\Omega} \propto \frac{k}{k_0} \sigma_{inc} S_{inc}(Q, \omega) \quad \ldots (2)$$

In general, the incoherent scattering law can be written as:

$$S_{inc}(Q, \omega) \propto A(Q)\delta(\omega) + \left[1 - A(Q)\right]L(\Gamma, \omega) \quad \ldots (3)$$

where the first term is the elastic part and second term is the quasi elastic part. The contribution to the elastic part comes from the average position and fluctuation from the average leads to quasi-elastic part. $L(\Gamma, \omega)$ is a Lorentzian and $\Gamma$ is the half-width at half-maximum (HWHM) of the Lorentzian function inversely related to the time constant of the motion. It is convenient to analyse the data in terms of elastic incoherent structure factor (EISF), which provides the information about the geometry of the molecular motions. If $I_{el}(Q)$ and $I_{qe}(Q)$ are the elastic and quasi-elastic intensities respectively, the EISF is defined as:

$$EISF = \frac{I_{el}(Q)}{I_{el}(Q) + I_{qe}(Q)} \quad \ldots (4)$$

Therefore, $A(Q)$ in Eq. (3) is nothing but the EISF.

3 Results

Water in porous materials such as vycor glass, silica gel, nafion, lignite coal etc. has been actively under investigation because of its relevance in catalytic and separation processes. Alumina exemplifies the physio-chemical properties of this class of porous materials in that firstly, it has high surface area and in aqueous suspensions variable pH values and secondly, that it undergoes reversible chemical changes when exposed to water. These properties make alumina very useful in adsorptive and separation processes.

Hydrotalcite (HT), or the magnesium aluminium hydroxycarbonate, Mg$_6$Al$_2$(OH)$_{16}$(CO$_3$)$_4$H$_2$O, one of the representative materials belonging to the family of layered double hydroxides (LDH), has attracted much attention in recent times due to their practical applications as catalysts, catalyst supports, ion exchangers and composite materials. Since these materials provide three-dimensional structures characterized by superior porosity and ion exchange properties, these materials found some industrial applications. LDHs containing carbonate anions have been used as antacids. Those containing chloride anions are used as adsorbents of the phosphate ions contained in the human intestine.

The results found from the studies on water confined on alumina gel and in hydrotalcite material have been described.

Alumina gel is a porous material with average pore size of 50 Å dia. QENS experiments were performed on alumina gel heat treated at 700 °C with hydration level of 30 wt% using the high resolution LAM-80ET spectrometer (resolution 17 and 6.5 μeV) at KENS, KEK, Japan and the low resolution QENS
The data from the QENS spectrometer at Dhruva have a contribution from both the translational and rotational motions of the water molecules. A scattering law comprising the translational and rotational motions was used to analyse the data from the low-resolution spectrometer. For the rotational part of the scattering law, isotropic rotational diffusion as derived by Sears was assumed. The parameters corresponding to translational motion of water as obtained from high-resolution experiment are used as known parameters. Rotational diffusion constant obtained as 0.1 meV at room temperature. This is very similar to the bulk water diffusion constant at room temperature. So in the pores of the alumina gel, water exists in two dynamically different states, one attached to the surface and undergoes localized motion, other in the remaining volume undergoes hindered dynamics which approach the bulk like at low temperatures.

Hydrotalcite with no excess water (Mg₆Al₂(OH)₁₆CO₃·4H₂O) did not show any quasi-elastic broadening over the instrumental resolution (ΔE=200 μeV). However, quasi-elastic broadening was seen in 9, 21, 30 and 50% excess water sample. The translational motion of water molecules can be described by a Lorentzian function. Since, rotational motion of a small water molecule (size ~ 2 Å) is not expected to get affected due to confinement between two layers with separation of about 8 Å, the rotational diffusion constant is assumed to be the same as that of bulk water. The QENS spectra of excess water sample are then fitted with a scattering function which consisted of both rotational and translation motions of water molecules. Only parameter to be found is the HWHM of the translational component at each Q value. QENS spectra can be fitted very well with this assumption at all the Q values. Fig. 2 shows the typical fitted QENS spectra with elastic (dotted) and quasi-elastic (dashed) components separated. With many other models for translational motion, obtained Γ(Q) is found to follow the random translational jump diffusion model which can be described by:

\[ \Gamma(Q) = \frac{D T Q^2}{1 + D T Q^2 \tau} \]  

where \( D_T \) and \( \tau \) are the translational diffusion constant and residence time in between jumps. Variation of \( \Gamma(Q) \) with \( Q^2 \) is shown in Fig. 3. Solid lines are the fit with Eq. (5). Translational diffusion constants and
residence time obtained for 9, 21, 30 and 50% excess water are given in Table 2. While the mean jump lengths have not changed much with different water content, residence time showed an increase when the water content is less. This essentially indicates that with the increase in water content, water molecules move faster. These values can also be compared with corresponding values obtained for bulk water. Mean jump length and residence time obtained for bulk water at 20°C were found to be 1.29 Å and 1.25 ps, respectively15.

Hence, even in 50% water content sample, though diffusion constant of excess water molecules is having a similar value as that of bulk water, residence time is still larger than that of bulk water. It is also found that the translational diffusivity decreases with the decrease of the amount of excess water. This is mainly due to the fact that when the amount of excess water is small they are mostly bound to the host layer. With increase amount of the excess water more and more of the water molecules are available away from the layer surface and are relatively free.1H T1 relaxation measurements by NMR have also clearly indicated that the hydration water at lower percentages (up to ~30%) shows that this water appears to be in a more bound state.
The role played by the pore geometry and by the framework acid sites of zeolites in the catalytic activity and selectivity of various hydrocarbons has been under extensive investigation. Dynamics of the guest molecule depends on the shape and size of the host zeolitic system. To understand the dynamics and binding states of various hydrocarbon molecules adsorbed in different size of pores in different zeolites, we have studied benzene, cyclohexane and methanol in HZSM-5 zeolites and in MCM-41 molecular sieve under ambient conditions\textsuperscript{18-20} and propane molecules in Na-Y zeolite at different temperatures\textsuperscript{21}.

First, we discuss the situation where the guest molecule is of similar size to the pores (HZSM-5 zeolite) and then when pore size is larger (MCM-41 molecular sieve) than the molecular size. In ZSM-5 zeolites, there are two types of channels consisting of 10 membered oxygen rings. The straight elliptical channels (5.7-5.2 Å) are interconnected by near-circular channels (5.4 Å) in a zig-zag fashion and there are four channel intersections per unit cell. In the experiment the guest molecules were loaded to the saturation. The MCM-41 sample (Si/Al ratio ~30) used in this study was synthesized by a conventional hydrothermal route; fumed silica and Al-isopropoxide being the source of Si and Al, respectively. The N\textsubscript{2} adsorption surface area, pore size and pore volume of a calcined sample were evaluated to be around 720 m\textsuperscript{2}g\textsuperscript{-1}, 34 Å and 0.68 cm\textsuperscript{3} g\textsuperscript{-1}, respectively.

QENS data from dehydrated HZSM-5 zeolite showed presence of small amount of hydrogen but no quasi-elastic broadening was observed indicating that they are not mobile at least in the time window of the spectrometer. However, quasi-elastic broadening was observed for samples loaded with benzene as well as cyclohexane indicating the presence of dynamical motions associated with the guest molecules. Here saturation loading was used for both the cases. Experimental $S(Q,\omega)$ and the separated elastic and quasi-elastic components at typical $Q$-values are

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**Table 3**—Comparison of the dynamical parameters for rotational motion of various molecules adsorbed in HZSM-5

<table>
<thead>
<tr>
<th>Adsorbed species</th>
<th>Model</th>
<th>Residence time (ps)</th>
<th>Residence time for bulk solid (ps)</th>
<th>Residence time for bulk liquid at RT (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>No broadening observed</td>
<td>---</td>
<td>---</td>
<td>10.2</td>
</tr>
<tr>
<td>Benzene</td>
<td>6-fold Jump rotation</td>
<td>16.5</td>
<td>19.2 at 277 K</td>
<td>2.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>3-fold Jump rotation</td>
<td>8.2</td>
<td>6.0 at 180 K</td>
<td>1.7</td>
</tr>
</tbody>
</table>
shown in Fig. 4. The QENS spectrum of the dehydrated zeolite was subtracted from the spectrum of the corresponding hydrocarbon loaded samples. The presence of elastic line in the spectra of Fig. 4 reveals the presence of the rotational motion of the molecules occluded in HZSM-5. The values of the extracted EISF (using Eq. 3) are depicted in Fig. 5. On comparing these EISF values with different theoretical models, it is possible to delineate the nature of the rotational motion of the guest molecules inside the cages of HZSM-5 zeolite. Different models that may account for the rotational motion of guest molecules, benzene and cyclohexane in the present study, inside the cages of HZSM-5 zeolite are as follows: (1) In the isotropic rotational diffusion model, the molecules undergo small angle random rotations. Then, on an average, no most probable orientation exists. The incoherent scattering law for a scattering particle undergoing isotropic rotational diffusion on the surface of a sphere of radius $a$ with rotational diffusion constant $D_r$ is reported in the literature\textsuperscript{1, 2}. In jump diffusion model among $N$ equivalent sites on a circle, it is assumed that the motion is specified by jumps of certain angle with a characteristic time $\tau$ called the residence time. Barnes\textsuperscript{22} has worked out a scattering law for such a model. The theoretical EISF for isotropic rotational diffusion (curve d) and for a jump among $N$ equivalent sites on a circle (curve a: 2-fold, b: 3-fold and c: 6-fold rotation), are shown in Figure 6.

The experimental EISF values for benzene adsorbed in HZSM-5 closely follow the curve (c), it is apparent that the benzene molecules most likely perform a 6-fold jump rotation within the channels of HZSM-5 (Fig. 4).

However, experimental EISF for cyclohexane adsorbed in HZSM-5 follow the curve (b) indicating the 3-fold jump for cyclohexane adsorbed in HZSM-5 zeolite. We may also point out that the isolated benzene molecule has 6-fold symmetry. The lowest energy conformation for isolated cyclohexane is the chair conformation of $D_{3d}$ symmetry\textsuperscript{23}. The 3-fold jump rotation observed in case of cyclohexane is thus in accordance with the chair conformation of cyclohexane molecule. So, the molecular symmetry seems to play a major role in deciding the geometry of rotation. The value of the residence times (HWHM=$h/R$) for the benzene and cyclohexane molecules in the channel of HZSM-5 are given in Table 3. Residence times obtained for corresponding bulk solid or liquid are also given in Table 3. It can be seen that residence times obtained for benzene and cyclohexane adsorbed in HZSM-5 zeolite resemble that of bulk solid of the corresponding molecule.

However, no quasi-elastic broadening was observed for methanol adsorbed in HZSM-5 zeolite indicating absence of motion in the time scale of $10^{-10}$-$10^{-12}$ ps.

MCM-41 is a relatively large pore (~34 Å dia) system. QENS spectra from the dehydrated MCM-41 did not show any quasi-elastic broadening. However, significant broadening was observed from the sample loaded with benzene, cyclohexane and methanol. In order to understand the contribution of occluded molecule, the QENS spectrum of dehydrated MCM-41 was subtracted from the spectrum of the loaded sample. The model scattering law given in Eq. (3) was convoluted with the instrumental resolution and the parameters ($A(Q)$ and $\Gamma$) were determined by least squares fit to the data. It was found that the elastic component ($A(Q)$) is almost zero at all the $Q$-values suggesting that the observed dynamics does not involve any elastic part and one Lorentzian function explains the data quite well. The HWHM values of the Lorentzian functions as obtained from the fit are given in Fig. 6. To arrive at an understanding of the dynamics of adsorbed molecules in the pores of MCM-41 different models for the translational motion of the guest molecules can be envisaged. The most simple motion that can be thought of is the Brownian motion where it is assumed that the particles move under the influence of the forces arising from the

![Fig. 6—Variation of HWHM with $Q^2$ for various molecules adsorbed in MCM-41. Lines are the fit with Chudley-Elliott model](image-url)
collisions between them. In this case, the scattering law shows a Lorentzian shape whose HWHM increases with the momentum transfer according to a \(DQ^2\) law and provides a direct method of determining the diffusion constant. However, Half Width at Half Maxima (HWHM) of the quasi-elastic component deviates from the linear behaviour at high \(Q\) values which suggests that simple Fick’s law is not adequate in describing the experimental data (Fig. 6). The other model formulated by Chudley and Elliott\textsuperscript{24} assumes that for a time interval \(\tau\), the particle remains at a given site, vibrating about equilibrium position, building-up a thermal cloud and then jumps to another site in a negligible time. The jump length \(l\) is assumed to be the same for all such jumps under consideration.

This model is also called a fixed jump model. The powder averaged scattering law in this case can be written as a Lorentzian with HWHM,\[\Gamma = \frac{1}{\tau} \left[1 - \exp\left(-\frac{Q^2 l^2}{6\tau}\right)\right].\] ... (6)

One can also find out the diffusion constant, \(D\) from Einstein’s relation \[D = \frac{l^2}{6\tau}\] ... (7)

In Fig. 6, the fit of the HWHM values of the Lorentzians as per the Chudley-Elliott model is also shown. As seen in Fig. 6, the experimental values fit quite well with this model. The values of residence time \((\tau)\), jump length \((<l>)\) and the diffusion constant \((D)\) as obtained from the fitting are indicated in Table 4 for various adsorbed molecules. On comparing this \(D\) value with the value reported for the diffusion constant of liquid methanol at 298 K \((D = 2.4 \times 10^{-5} \text{ cm}^2/\text{sec} \text{ (Ref. 25)}\) or \(2.6 \times 10^{-5} \text{ cm}^2/\text{sec} \text{ (Ref.26)}\), we may conclude that the translational diffusion constant of methanol in MCM-41 is much less than that of bulk liquid methanol. However, the diffusion constants obtained for benzene and cyclohexane adsorbed in MCM-41 did not show any change compared to the diffusion constant obtained from its bulk liquid value\textsuperscript{27,28}. This as well as absence of rotational dynamics of methanol in HZSM-5 may be attributed to the fact that methanol is a polar molecule (dipole moment 1.7 D) whereas benzene and cyclohexane are non-polar. Polar molecule while passing through the cavities experiences forces from different framework or extra-framework sites and in the process diffusivity of the polar molecule reduces. However, for non-polar molecules such as benzene and cyclohexane, molecular symmetry plays an important role in deciding their diffusion parameters such as jump lengths, residence time as indicated in Table 4.

The dynamics of hydrocarbon molecule when the size of the molecule is smaller than the pore size has been investigated. Na-Y zeolite structure is made up of a network of tetrahedrally connected pores (\(\alpha\)-cages) of diameter \(\sim11.8 \text{ Å}\). The pores are interconnected through windows of diameter \(\sim8 \text{ Å}\). Propane (‘size’ \(\sim6 \text{ Å}\) coverage of 4.5 molecules per zeolitic supercage was used for the experiment. Translational motion of propane in Na-Y zeolite was studied using QENS spectrometer (\(\Delta E=200 \mu\text{eV}\)) at Dhruva. The data were interpreted in terms of the translational motion of the propane molecule inside the supercage of Na-Y. The analysis of the experimental data was done using several available models of the dynamics. But, the model of Hall and Ross\textsuperscript{29} was found adequate and consistent with our experimental data. In this model unlike Chudley and Elliott model, the jump lengths \(s\) are not fixed but Gaussian distributed Scattering law in this case is a Lorentzian with HWHM,\[\Gamma(Q) = \frac{1}{\tau} \left[1 - \exp\left(-\frac{Q^2 \langle l^2 \rangle}{6}\right)\right].\] ... (8)

here, \(\tau\) is the residence time and \(<l^2>^{0.5}\) is the root mean square jump length. Diffusion constant, \(D\) can be calculated from Einstein’s relation as defined in

<table>
<thead>
<tr>
<th>Adsorption in MCM-41</th>
<th>Jump length ((&lt;l&gt;)) (Å)</th>
<th>Residence time ((\tau)) (ps)</th>
<th>Diffusion constant ((&lt;l^2&gt;/6\tau)) ((\times10^{-5} \text{ cm}^2/\text{sec}))</th>
<th>Bulk liquid Diffusion constant ((\times10^{-5} \text{ cm}^2/\text{sec})) at RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2.3 ± 0.6</td>
<td>5.8 ± 0.5</td>
<td>1.5 ± 0.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Benzene</td>
<td>3.1 ± 0.3</td>
<td>7.5 ± 0.6</td>
<td>2.2 ± 0.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.4 ± 0.7</td>
<td>5.7 ± 0.7</td>
<td>1.7 ± 0.4</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Eq. (7). Fig. 7 shows the variation of HWHM of the quasi-elastic line with $Q^2$. Solid lines are the fit with Hall & Ross Model (Eq. 10). Residence time $\tau$, root mean square jump length, $<l^2>^{0.5}$ and diffusion constant, $D$, are obtained for each temperature $21$. The obtained diffusion constant, $D (=<l^2>/6\tau)$, is $2.3 \times 10^{-5}$ cm$^2$/s at 300 K and found to increase with increase in temperature. As molecular dynamics simulation studies carried out by us have showed that the propane molecules undergo very fast rotational motion (6-8 times faster than the translational motion in terms of the diffusion constant) and not expected to be observed in the experiment on MARX spectrometer$^{20}$. In order to verify the MD prediction, further experiments have been carried out using Triple Axis Spectrometer (TAS) having a much wider energy window ($\Delta E \approx$ 3.3 meV, at fixed final energy$^{30}$ of 20 meV). Data were recorded in the wavevector transfer ($Q$) range of 0.8 - 2.5 Å$^{-1}$. Dehydrated zeolite sample did not show any quasi-elastic (QE) broadening, whereas propane loaded sample did show significant QE broadening at room temperature indicating the presence of dynamical motion of propane molecules. To analyse the data, in the first instant the elastic and quasi-elastic components in the total spectrum were separated, which involves convolution of the model scattering function $S(Q,\omega)$ with the instrumental resolution function. Then, the model parameters were estimated by least squares fit with the experimental data. The fitting parameters were the EISF and the half width at half maxima (HWHM) of the Lorentzian function. The contribution from the bare zeolite, towards elastic scattering only, was subtracted from the data with the propane-loaded sample. The extracted EISF is as shown in Fig. 8. The theoretically calculated EISFs for isotropic rotational diffusion and uniaxial rotational diffusion$^1$ are shown by solid and dashed lines in Fig. 8. The isotropic rotational diffusion model describes the experimental EISF quite well. Thereafter, we have used the model $S(Q,\omega)$ for isotropic rotational diffusion to fit with the experimental QENS data and determine the rotational diffusion constant $D_R$. Very good fit was obtained at all the $Q$-values with radius of gyration equal to 1.89 Å, which is also the average distance of the hydrogen atoms from the center of mass of the propane molecule. $D_R=1.05 \pm 0.09 \times 10^{12}$/s, is the value obtained from QENS experiment, is found to be close to the value of $0.82 \times 10^{12}$/s obtained from MD simulation$^{31}$.

4 Conclusion
Molecular dynamics and its effect due to confinement in various environments as studied by Quasi-elastic neutron scattering (QENS) technique are reported. It is shown that diffusion, translational and/or rotational, is altered significantly on confinement in variety of system, like water in porous media, hydrocarbon in zeolite or molecular sieves. It is found that diffusivity of guest molecules depends very much on the combination of the guest and host
structures, their shape and mutual interactions. Gas behaves as liquid and liquid behaves as solid due to confinement effect.

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References