

Molecular motion in restricted geometries

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Abstract. Molecular dynamics in restricted geometries is known to exhibit anomalous behaviour. Diffusion, translational or rotational, of molecules is altered significantly on confinement in restricted geometries. Quasielastic neutron scattering (QENS) offers a unique possibility of studying molecular motion in such systems. Both time scales involved in the motion and the geometry of motion can be studied using QENS. Molecular dynamics (MD) simulation not only provides insight into the details of the different types of motion possible but also does not suffer limitations of the experimental set-up. Here we report the effect of confinement on molecular dynamics in various restricted geometries as studied by QENS and MD simulations. An example where the QENS technique provided direct evidence of phase transition associated with change in the dynamical behaviour of the molecules is also discussed.

Keywords. Neutron quasielastic scattering; molecular dynamics simulation; confined geometry.

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1. Introduction

The problem of molecular motion in restricted geometries is encountered in a variety of systems in nature. Common examples are water in rock or sandstones and water in biological membranes. Other examples include polymer gels, clays, micelles, vesicles and microemulsions. Zeolites also are porous crystalline materials that absorb a number of molecules. Because of their properties of high void volume, regular pore distribution and shape selectivity, they are used extensively in industry as molecular sieves and catalysts. Both the catalytic as well as the sieving applications of the zeolites depend upon the diffusivities of the adsorbed molecules. In particular the cracking of large hydrocarbons inside zeolitic pores is known to be determined by the ease with which the reactants and the products can diffuse in the pores. Hence it becomes imperative to study the dynamics of hydrocarbons adsorbed within these pores. The diffusion of hydrocarbons in zeolite is determined by a variety of factors including the temperature, the shape and size of the pores and of adsorbed hydrocarbons, the concentration of guest molecules etc. 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 an understanding of the behaviour of guest molecules

in confined geometries. In general, 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 fluids under confinement: (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.

Neutron scattering is a powerful experimental tool for studying the structure and dynamics of atoms and molecules in condensed matter [1,2]. This is possible as neutron has a wavelength matching with the interatomic spacing 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, $\sigma_{\text{other element}} \sim 4\text{--}5$ barns). Thermally activated single particle motions can be studied using neutron scattering as they show up in Doppler-broadened elastic lines. This broadening of elastic lines due to stochastic motions is studied using a technique known as the quasielastic neutron scattering (QENS). The time-scale of the dynamical motion, its geometry as well as the nature of the hindering potential can all be obtained from the QENS experiments, which are carried out using either a triple axis or a time-of-flight spectrometer [1]. A few examples of molecular motion studies in various solids and liquids using QENS technique can be found in ref. [3]. Many a times there exists a variety of motions in a system and it is not easy to delineate the one corresponding to the experimental data. That way molecular dynamics (MD) simulation study [4,5] does not suffer limitations of the experimental set-up and provides insight into the details of the different types of motions present.

Here we report QENS and MD simulation studies investigating localization and dynamics of molecules in various confining environments and the role played by the symmetry and the structure of the guest molecule in addition to the physical characteristics of the sorbents. As examples, results of the investigation of water dynamics in porous media and modifications in the diffusivity of various hydrocarbon molecules in various zeolites are presented. QENS studies on the dynamics of alkyl chains in monolayer-protected metal clusters, which exhibit reverse confinement in the sense that the confining media is in motion in contrast to the confined clusters, are also discussed.

2. Theoretical details

In a neutron scattering experiment from a hydrogenous sample, the scattered intensity is proportional to the double differential cross-section which in turn is proportional to the incoherent scattering law $S_{\text{inc}}(Q, \omega)$. \mathbf{Q} is the wave-vector transfer and $\hbar\omega$ is the energy transfer. In general, the incoherent scattering law can be written as [1]

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

where the first term is the elastic part and second term is the quasielastic part. Contribution to the elastic part comes from the average position and fluctuation

from the average leads to quasielastic part. $L(\Gamma, \omega)$ is a Lorentzian and its half-width at half-maximum (HWHM) Γ is inversely related to the time constant of the motion. $A(Q)$, called the elastic incoherent structure factor (EISF), is the ratio of the elastic scattering to the total scattering and provides information about the geometry of the molecular motions. To analyse the QENS data, one in general, first separates elastic and quasielastic components by convoluting the model function (eq. (1)) with the instrumental resolution function, obtained by measuring the spectrum using vanadium sample, and least squares fit to the experimental data. The fitting parameters $A(Q)$ and Γ obtained in the fitting can then be studied as a function of Q to obtain information about the geometry of motion and time-scale of motion respectively.

3. Hydrocarbons adsorbed in zeolites

As stated earlier, zeolites offer an example of restricted geometries in which several molecules can be confined. 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. To understand the dynamics and binding states of various hydrocarbon molecules adsorbed in different sizes of pores in different zeolites, we have studied benzene, cyclohexane, methanol, propylene etc. in ZSM-5 zeolites [6–8] and propane, acetylene, 1,3-butadiene, and propylene molecules in Na-Y zeolite [9–13]. Various combinations of guest and host systems were considered. Like, 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. Na-Y zeolite structure is made up of a network of tetrahedrally connected pores (α -cages) of diameter ~ 11.8 Å. The pores are interconnected through windows of diameter ~ 8 Å. Guest molecules are of the order of 4–6 Å. In the experiments the guest molecules were loaded to the saturation.

QENS data showed that rotational motion of benzene is best described by a six-fold jump rotation within the channels of ZSM-5, whereas cyclohexane adsorbed in ZSM-5 follows the three-fold jump rotation. We may also point out that the isolated benzene molecule has six-fold symmetry. The lowest energy conformation for isolated cyclohexane is the chair conformation of D_{3d} symmetry [14]. The three-fold jump rotation observed in the 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 obtained values of the residence times ($\text{HWHM} = \hbar/\tau$) for the benzene and cyclohexane molecules are found to correspond to that of bulk solid of the corresponding molecule indicating the effect of confinement. Methanol adsorbed in ZSM-5 zeolite did not show any quasielastic broadening indicating the absence of dynamical motion in the time-scale of 10^{-10} – 10^{-12} ps, which was attributed to the strong polar nature of the molecule as shown in IR studies.

As mentioned above, Na-Y has larger pores compared to the size of the adsorbed molecules considered here. We have studied the diffusion of several hydrocarbons

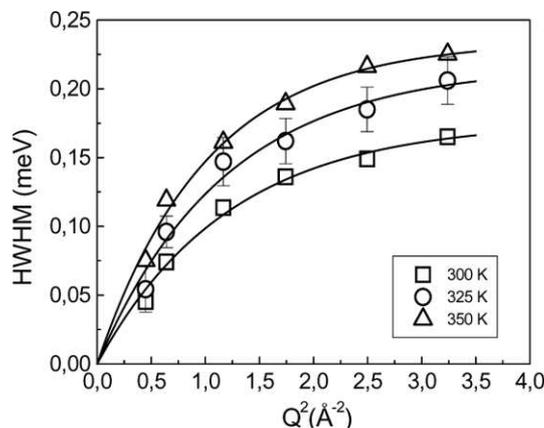


Figure 1. Variation of HWHM of the quasielastic component with Q for acetylene in Na-Y zeolite. Solid lines are the fit to the data assuming Hall and Ross model.

including acetylene (smallest unsaturated hydrocarbon), propane (saturated hydrocarbon with 3 carbon atoms), 1,3-butadiene (unsaturated hydrocarbon with four carbon atoms) and propylene (three carbon atoms and a double bond). The QENS spectra indicate that there is no elastic component and the quasielastic broadening corresponds to the translational motion alone. The rotational motion should be fast enough not to contribute to the present data, as it is very broad to go along the background. A detailed analysis of the QENS data shows that the translational motion of the guest molecules inside the cages of Na-Y zeolite is best described by a model where the molecules undergo jump diffusion with a Gaussian distribution of jump lengths (figure 1). Diffusion constants for the guest molecules have also been calculated. As stated above, we have also performed molecular dynamic simulation for all the systems discussed above. In our MD simulation studies, the adsorbed molecules were considered to be rigid and the positions of zeolitic atoms were held fixed. The interaction between the guest-guest as well as the guest-zeolite molecules was modelled by the (6-12) Lennard-Jones potential. Equations of motion were solved using a leapfrog form of the Verlet algorithm in microcanonical ensemble [4]. Intermediate scattering function corresponding to the centre of mass of the adsorbed acetylene molecule was found to consist of three functions – one Gaussian and two exponentials. The Gaussian function represents the noninteracting free particles at very short time intervals. Na-Y zeolite consists of pore topology of supercages and windows and this contributes to two distinct exponential functions corresponding to the motion of guest molecule within the supercages and window regions. The widths corresponding to the three different functions are given in figure 2. As shown in the figure the width as obtained from QENS data corresponds to the lowest value. MD simulation also showed that the rotational motion for propane in Na-Y zeolite is much faster compared to the translation and not expected to be observed in the experiment on MARX spectrometer [10]. In order to verify the MD prediction, further experiments have been carried out using triple axis spectrometer (TAS) having a much wider energy window ($\Delta E \sim 3$ meV)

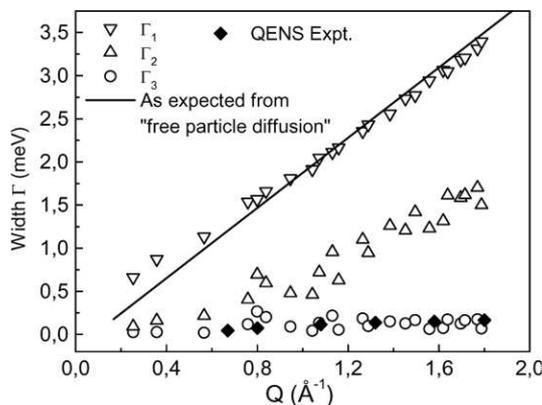


Figure 2. The behaviour of the widths corresponding to the three components of the intermediate scattering function with Q for acetylene in Na-Y zeolite. Filled diamond symbols correspond to the width as obtained from QENS experiment.

compared to 0.2 meV of the MARX spectrometer. The experimentally obtained $S(Q, \omega)$ was very well described by isotropic rotational diffusion model and was used to determine the rotational diffusion constant D_R . Radius of gyration equal to 1.89 Å, which is also the average distance of the hydrogen atoms from the centre of mass of the propane molecule and rotational diffusion constant $D_R = 1.05 (\pm 0.09) \times 10^{12}/\text{s}$ were obtained. These were in very good agreement with those obtained from MD simulation [10].

4. Dynamics of confined water

Water plays an important role in all biological processes. Most of the times it is found to be restricted within biological membranes. However, it is very difficult to study water confined in biological molecules because of the complexities of the structure of the confining part. Therefore, water confined in model systems with better-defined restrictive geometries is studied to mimic the biological systems. Besides, these model systems may exhibit their own applicative interests. For example, water in porous materials such as vycor glass, silica gel, Nafion, lignite coal etc. [15] has been under investigation because of their relevance in catalytic and separation processes. Alumina exemplifies the physiochemical 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. QENS data analysis revealed clear evidence of two types of water molecules in the pores of alumina gel. The water molecules attached to the surface of alumina perform very local motion, restricted within a localization radius of 5 Å as reflected in the low Q behaviour of the QENS data. On the other hand, the large Q region shows water molecules that are diffusing in

the available space within the pores. The diffusion constant (D_t) and the residence time (τ_0) of this motion are calculated from large Q region. D_t is found to be less than that of bulk water particularly in the high temperature range. Residence time τ_0 larger than that of bulk water implies a slower motion, due to confinement effect. Rotational dynamics of water molecules within the pores was found to be unchanged in comparison to bulk water at room temperature.

Layered double hydroxides with their lamellar structures offer another example of confined geometries in which water can be found. Hydrotalcite (HT) is one of the representative materials belonging to the family of layered double hydroxides (LDH). Hydrotalcites have attracted much attention in recent times [16] due to their practical applications as catalysts, catalyst supports, ion exchangers and composite materials [17]. Hydrotalcites, because of their relatively open hydroxide lattice, offer a unique advantage in terms of studying water dynamics in the interlayer region of the LDH frameworks [18–20]. The excess water, other than the water of crystallization, exhibits slightly reduced thermodynamic water activities, and, thereby reduced tendency for water loss from hydrated HT materials. This excess water seems to make the structure more stable; therefore it is important to study its behaviour. Varied content of excess water inside the hydrotalcite sample was used for a QENS study of water confined within hydrotalcite. Both translational and rotational motions were taken into account in analysing the data. It was seen that the translational motion for excess water can be best described by random translational jump diffusion model (figure 3). Rotational motion is described by isotropic diffusion model. Both translational and rotational diffusivities were found to increase with increasing amount of excess water suggesting that with increased amount of the excess water, more and more water molecules are available away from the layer surface and are relatively free to move. This is indicated by larger values of HWHM (Γ) of the translational Lorentzian obtained for higher water content samples as shown in figure 3. It is established that there is a clear difference in the magnitude of the translational and rotational motions between the layers that is attributable to the bonding interactions between water and the interlayer species.

5. Dynamics of alkyl chains in monolayer-protected metal clusters and their superlattices

In all the above systems discussed so far, dynamics of the molecules, which were confined, was studied. Contrary to this we shall here discuss a molecular system in which it is the confining media, which is dynamic. Monolayer-protected clusters (MPCs) are nanoparticles capped with monolayers, typically having a hydrocarbon chain [21]. These monolayers may form three-dimensional self-assembled monolayers (3D SAMs), or planar (2D SAMs) structures. Due to interactions of monolayers, the isolated clusters may crystallize to yield particle crystals, called superlattices as they possess double periodicity, one due to the metal core and the other due to the organized particle assembly. Orientational freedom of the alkyl chain assembly is one of the critical issues concerning the structure of the monolayers. Applications of monolayer systems in several areas, utilizing distance-specific organization of molecules, depend on the structural and conformational rigidity of the monolayer chain.

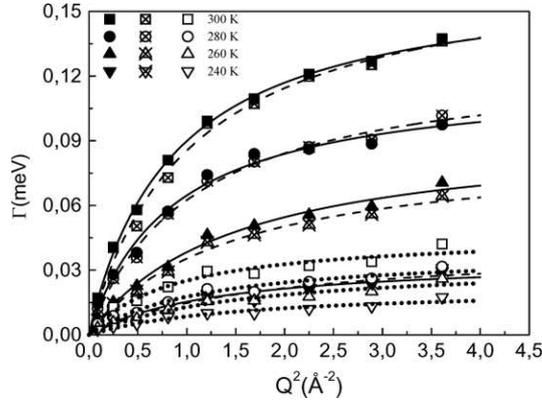


Figure 3. Variation of HWHM of the translational Lorentzian with Q^2 for water absorbed in hydrotalcite with a concentration of 40% (filled symbols), 30% (crossed symbols) and 10% (open symbols). Lines are the fits with random jump diffusion model.

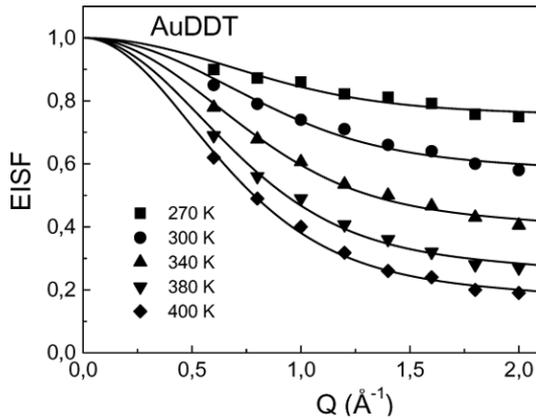


Figure 4. Experimental EISF, as obtained from QENS data for Au-DDT (isolated MPC) system, fitted with the model described in the text.

It is therefore of interest to study the dynamical behaviour of these chains. Here we report the dynamics of alkyl chains in both isolated and superlattice systems with varying chain lengths, using QENS [22–25]. Isolated MPCs investigated are 6, 12 and 18 carbon n-alkyl chain thiolate-protected 4 nm diameter gold clusters while the superlattices are their silver analogues. QENS data for both the systems were found to be consistent with a model where the chain undergoes uniaxial rotational diffusion with additional body axis fluctuation. The EISF for this model can be written as

$$\text{EISF} = [p_x A_0 + (1 - p_x)], \quad (2)$$

where A_0 is the model structure factor (rotation about chain axis and additional body axis fluctuation) and p_x is the fraction of alkyl chains that are mobile [24,25].

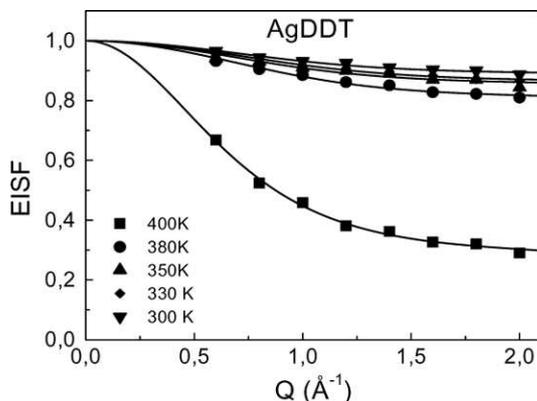


Figure 5. Experimental EISF, as obtained from QENS data for Ag-DDT (superlattice) system, fitted with the model described in the text.

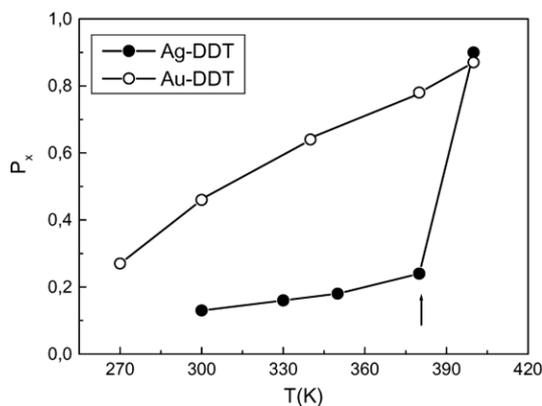


Figure 6. Fraction of alkyl chains which are mobile, p_x , as in eq. (2), vs. temperature. The point of abrupt change in the case of Ag-DDT system corresponds to the superlattice melting.

The experimental EISF and the calculated EISF have been compared for the two systems of monolayers protected with dodecanethiol (DDT) molecules in figures 4 and 5. The variation of p_x with temperature for the superlattice systems (figure 6) shows an abrupt change indicating that increasing proportion of the chains contribute to the dynamics whereas this variation was found to be continuous for the isolated MPC system. The dynamics in isolated MPCs of the monolayer was thus found to evolve continuously whereas in superlattice systems an abrupt change in the dynamics occurs at the superlattice melting temperature detected in calorimetry measurements. This is a clear demonstration of the QENS technique providing a direct evidence of the phase transition connected to the evolution of the dynamical motion. The chains are found to be held by strong interchain interactions below the superlattice melting. The data from the planar silver thiolate systems show similar behaviour like the superlattice systems, consistent with the calorimetric data.

6. Summary

Dynamical behaviour of molecules confined in various environments as studied by quasielastic neutron scattering (QENS) and molecular dynamics simulations are reported. It is shown that diffusion, translational and/or rotational, is altered significantly on confinement in a variety of systems, like water in porous media, hydrocarbon in zeolite or molecular sieves. It is found that diffusivity of guest molecules in zeolites depends very much on the combination of the guest and host structures, their shapes and mutual interactions. Symmetry of the adsorbed molecule is also found to affect the dynamical properties of the adsorbed molecules as observed for benzene and cyclohexane in ZSM-5. An example of dynamics of alkyl chains in monolayer-protected metal clusters and their superlattices, as also their dynamical evolution is discussed. It is shown for this system how QENS can provide direct evidence of phase transition in the system corresponding to the changes in the dynamical behaviour.

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