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Some unusual features in the behaviour of cyclohexane in confined geometry studied by neutron scattering

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1. Introduction

Cyclohexane, C_6H_{12} , is one of the simplest organic molecules due to its sixfold symmetry and weak van der Waals interaction. The dynamic characteristics have been extensively studied in the liquid and plastic crystal phases by spectroscopic means and have been analysed in terms of an unhindered rotator model. The transition from the liquid to the plastic crystal at $6.55^\circ C$ involves a low entropy change and leads to a fcc crystal with a large defect concentration. At lower temperatures, $-87^\circ C$, the rotational motion is frozen out to give a brittle crystal phase.

One of the more interesting aspects of cyclohexane is revealed when the material is confined in a meso-porous solid. Neutron and NMR studies of cyclohexane in a porous sol-gel silica [1] showed that the phase transition temperatures were substantially depressed. Further neutron diffraction studies [2] indicated that the plastic crystal phase exhibited structural changes over a wide temperature range and that there was a hysteresis effect in the temperature sequence. The large depression of the nucleation point was shown to be inversely proportional to pore size over most of the range and subsequently used for pore size characterisation by NMR cryoporometry [3]. Comparison with other organic liquids [4] has shown that cyclohexane exhibits one of the largest effects and this behaviour has led to a new interest in the properties.

Another unexpected phenomenon has been observed when cyclohexane liquid is added to the top of a granular powder of porous sol-gel silica in a sealed container. After a few minutes, an orange coloration develops in transmitted light (blue in reflected), which persists for up to a day. This behaviour indicates that there are spatial density variations on a scale comparable with that of light. Some test experiments using small-angle neutron scattering [5] showed that these features were changing on a time-scale of minutes; the effect could be observed in C_6D_{12} but not in C_6H_{12} , confirming that the effect was due to the liquid behaviour in the pores. As a consequence of these recent studies, it is now interesting to make a more detailed study of the phase behaviour of cyclohexane in confined geometry and the following sections outline some of the research which is currently in progress.

2. Theoretical background

a) Diffraction

Neutron diffraction formalism has been given elsewhere [6] and the following section is a brief overview to define the terms. The liquid structure factor, $S_M(Q)$ is composed of intra- and intermolecular terms by: -

$$S_M(Q) = f_1(Q) + D_M(Q)$$

Where $f_1(Q)$ is the form-factor and $D_M(Q)$ represents the liquid structure. The intermolecular spatial characteristics can be evaluated from the Fourier-Bessel transform relationship:-

$$d_L(r) = 4\pi r [g(r) - 1] = \frac{2}{\pi} \int_0^{\infty} Q D_M(Q) \sin QR \, dQ$$

In the case of C_6D_{12} , the relative contributions from the different partial pair correlation functions are:-

$$g(r) = 0.111 g_{CC}(r) + 0.444 g_{CD}(r) + 0.445 g_{DD}(r)$$

If temperature difference methods are used, many of the correction terms are eliminated and the change in the structure factor is given by

$$\Delta D_M(Q, \Delta T) = S_M(Q, T) - S_M(Q, T_0)$$

With a corresponding change in the spatial features given by

$$\Delta d_L(r) = \frac{2}{\pi} \int_0^{\infty} Q \Delta D_M(Q, \Delta T) \sin QR \, dQ$$

This formalism also applies to the plastic crystal phase although it has been more conventional to analyse the pattern in terms of elastic and diffuse scattering components, which separate out the ordered and disordered contributions.

b) Small angle neutron scattering

The SANS intensity profile, $I(Q)$ is representative of spatial variations in the mean coherent scattering length density $\rho(r)$. In the case of a two-phase porous solid, the $I(Q)$ function characterises the pore structure although approximate models are often needed to interpret the results [7]. In the case of pure liquids there is also an additional effect due to density fluctuations, which takes the form of a Lorentzian,

$$I(Q) = \frac{I(0)}{1 + Q^2 \xi^2}$$

arising from the Ornstein-Zernike relation, where ξ is a correlation length that varies with temperature.

The ρ -value for silica, corresponding to the mean coherent scattering length density, has a value of 0.60 relative to -0.05 for C_6H_{12} and 1.11 for C_6D_{12} . Density fluctuations in cyclohexane can therefore be more readily observed for C_6D_{12} than for C_6H_{12} . It is also possible to use a mixture of C_6H_{12} and C_6D_{12} to contrast match the silica for a direct check on the filling of the pores.

3. Experimental studies

a) Sol-gel silica:diffraction

The neutron diffraction measurements were made on the hot-source diffractometer, D4, at the Institut Laue Langevin, using a wavelength of 0.7 \AA . The samples consisted of cyclohexane C_6D_{12} , in several porous silicas. The samples were mounted in a cryostat and the diffraction pattern was measured by the usual method for several temperatures on a cooling and heating cycle. Details of the experimental procedure and analysis have been given in earlier papers [8] and a sample of the results is shown in Fig 1.

Figure 1: The diffraction pattern for C_6D_{12} in sol-gel silica showing the $D_M(Q)$ function

b) Sol-gel silica: SANS

The SANS measurements were made on the D22 instrument at the ILL. In this case, the dry silica samples were held in a 1mm thick Hellma cell which was mounted on a vertical translation table. The area detector was mounted in a fixed position and the incident beam was collimated to give a slit height of 0.38mm. A small quantity of liquid cyclohexane, C_6D_{12} , was introduced onto the top level of the dry silica powder as shown in Fig 2. At this time, the run was started by making a sequence of measurements of the SANS intensity profile as a function of time and position: the angular scattering intensity $I(\theta)$ was recorded for successive horizontal slices of the material, and the sample translated vertically in the beam by 0.5 mm between each measurement. Each measurement profile $I(\theta, z)$ was measured in less than 30 minutes. Several complete scans were made along the sample to provide a spatial and temporal record of the SANS signal $I(\theta, z, t)$.

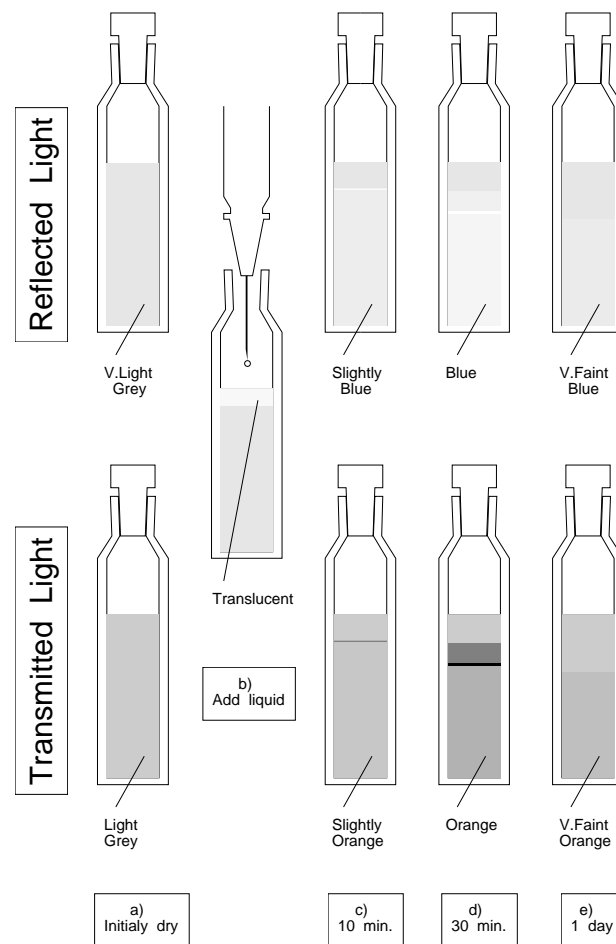
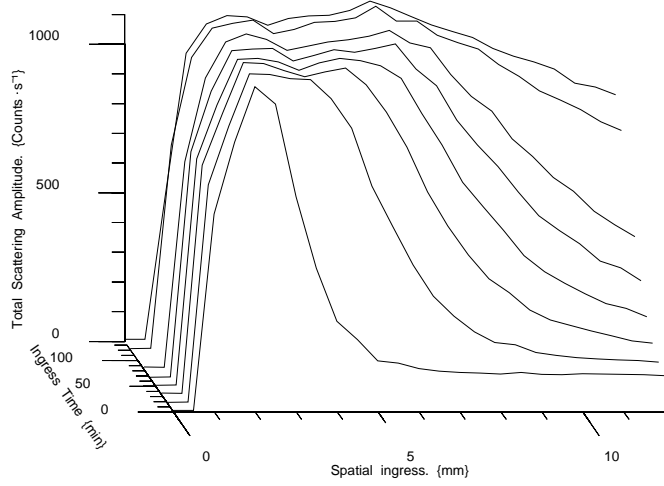
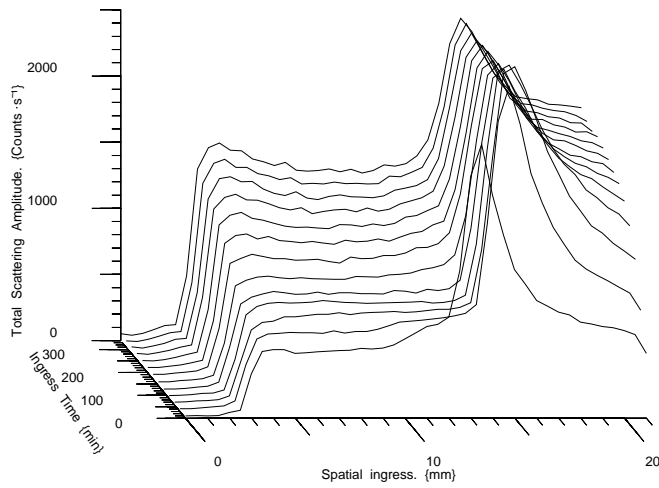


Figure 2: Visually observed changes in silica with cyclohexane [see text for details]

SANS: Cyclohexane ingress into 40Å Silica.



SANS: Cyclohexane ingress into 200Å Silica.



SANS: Cyclohexane ingress into 500Å Silica.

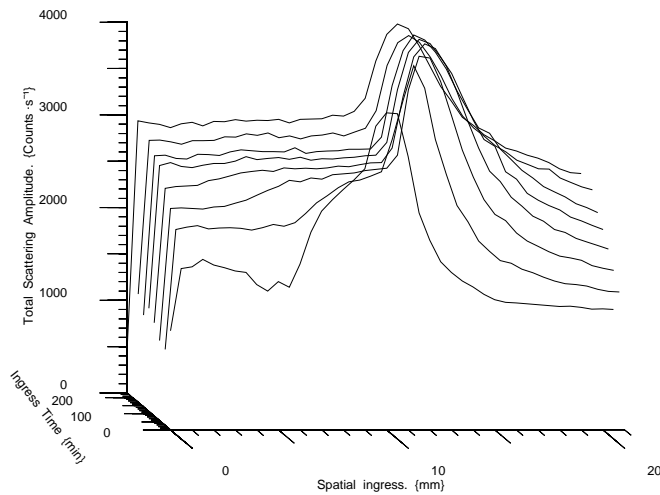


Figure 3: Time evolution of the SANS intensity through the sample volume; a) 40Å b) 200Å c) 500Å pore diameter.

The total recorded counts in the area detector for three different samples of sol-gel silica with pore sizes of 40 Å , 200 Å and 500 Å are shown in Fig 3. The changing profile represents the advancing liquid and vapour front through the granular silica powder. The data are discussed in the following section.

c) MCM silica: diffraction

Some preliminary diffraction measurements have been made on cyclohexane, C_6D_{12} , in two samples of MCM silica, characterised as MCM41 [hexagonal] and MCM48 [cubic]. The low-Q part of the diffraction pattern corresponding to the main diffraction peak has been investigated over a wide temperature range in a cooling cycle. The results are similar for the two samples and the datasets for MCM48 are shown in Fig 4.

Figure 4: The peak profile for C_6D_{12} in MCM48 as a function of temperature.

4. Results

a) Diffraction

The diffraction results for the sol-gel silica show the complex changes that occur with temperature variation throughout the plastic crystal phase. The use of the temperature difference function gives information on the changes and an example is shown in Fig 5 for the $\Delta D_M(Q)$ function for temperatures of 265 and 243K. The corresponding spatial correlation function, $\Delta d(r)$, is given in Fig 6 and has an oscillatory structure which indicates that the mean separation of molecular centres is decreasing as the temperature is reduced and effectively mimics the displacement of the main diffraction peak for the 002 reflection. A detailed analysis of the available diffraction data confirms that there are

orientational correlations between adjacent molecules in both the bulk and the confined state so the molecules do not undergo free rotation. It therefore seems that there is a complex interplay between the rotational motion and translation movement of the molecular centres as the temperature is changed. Another indication is provided by the finite value of $\Delta D_M(Q)$ at low Q-values which indicates a change in the isothermal compressibility with temperature. A more detailed analysis is in progress.

Figure 5: The temperature difference function for 265 and 243K

Figure 6: The change in spatial correlations corresponding to Fig. 5.

Clearly the plastic crystal phase of cyclohexane is not as simple as might have been supposed and it is this coupling at a molecular level that contributes to the large depression in the transition temperature for the confined state. As a result, cyclohexane makes an excellent material for use in NMR cryporometry, particularly for porous solids with pores sizes in the 200Å – 2000Å range where the depression for other liquids is relatively small. These studies use a melting cycle with increasing temperature to avoid the problems arising from possible super-cooling and hysteresis effects. A recent DSC measurement [8] using an oscillatory temperature control has been made to isolate the reversible and irreversible parts of the specific heat change arising from the formation of a metastable glassy state but it was found, somewhat surprisingly that there was no time evolution of the heat transport. This observation means that the measured changes are primarily linked to a variable pore size and the behaviour is thermodynamically reversible with a well-defined equilibrium state at any one temperature. However, time evolution was observed in a test measurement on a quenched sample [8] and this phenomenon will be further investigated.

The preliminary measurements made with the MCM silica represent an extreme situation with a small pore size in two of the three dimensions. The 002 diffraction peak is much broader than that for the sol-gel silica, primarily due to diffraction broadening effects, but the displacement of the peak shows a similar general behaviour with temperature. There is no evidence of a phase transition in these measurements but the low-Q behaviour indicates a continuous reduction in the compressibility. It therefore seems that there is a gradual change from the liquid to a disordered solid state without any clear phase transition. This behaviour appears similar to that created by super-cooling a bulk organic liquid through the glass transition to give a metastable state. Such systems are of much topical interest in the investigation of the relaxation modes in glassy systems [9]. The present findings suggest that the phenomena seen for molecular systems, such as cyanoadamantane and TPP, may be repeated for many other molecules in the confined state.

b) Small Angle Neutron Scattering

Small angle neutron scattering arises from spatial variation of the component ρ -values through the sample volume irradiated by the incident beam. Thus there will be no signal from either the bulk liquid or the normal vapour phases as they will be homogeneous and of relatively large volume. The sol-gel silica is meso-porous and the dry sample gives a scattering intensity that depends on the pore characteristics. As the cyclohexane vapour condenses in the pores the contrast distribution, $\Delta\rho(\mathbf{r})$, is subject to change and gives an increased intensity distribution that has a much sharper profile due to longer range effects. The enhanced scattering intensity at low Q-values is presumably related to the amount of material in the pores and the resulting density variations arising either from a distributed volume of liquid or alternatively from density fluctuations within the fluid itself. The time sequence shown in Fig 3 therefore displays the variation in the condensation through the sample as a function of time. The diffusion of individual cyclohexane molecules around the silica granules leads to an advancing vapour front that becomes depleted through capillary condensation, leading to a non-equilibrium system involving the two competing processes.

The SANS intensity appears to saturate in the region close to the liquid layer but then extends throughout the sample as a function of time. The behaviour in the 40Å pore indicates a continuing process of filling the pores and the advancing front seems to become wider as the process continues. The total intensity distributions for the 200Å and the 500Å pores have a different shape with a well-defined maximum in the pattern which changes position initially and then becomes stationary. This feature is correlated with the position of the ‘white/dark line’ revealed in the optical characteristics shown in Fig 2. There is an intense scattering of both light and neutrons for this region indicating large local variations in $\Delta\rho(\mathbf{r})$ over a wide length-scale. This phenomenon is not fully understood but must be related to and dependent on the spatial characteristics of the fluid phase of the cyclohexane. However, it is reasonable to expect that the initial condensation phase will involve the filling of the small pores in preference to the larger ones, as confirmed by NMR measurements [10] in the same sol-gel silicas. The subsequent time evolution of the SANS intensity may therefore represent either the spatial distribution of the condensation sites or the density fluctuations within the distributed fluid phase. The current results are based on the total SANS intensity in the detector and further analysis will be made to see if there are any changes to the individual profiles which can be correlated with the time and spatial variables.

5. Discussion and Future Studies

The present results have shown that there are some interesting and unexpected characteristics concerning the behaviour of cyclohexane in mesoporous solids. It is not known whether other liquids exhibit similar effects. The diffraction data emphasise that the orientational correlations between the molecules are affected by the confined geometry and it seems likely that this phenomenon contributes directly to the large depression in the phase transition temperatures. Further studies of the dynamics by NMR are in progress to try to understand the reason for this behaviour. Other measurements [11] have indicated that the rotational behaviour is quite complicated even in the bulk phase with significant variation in the shape of the NMR signal as a function of temperature. The study of cyclohexane in MCM silicas is at a very early stage but current indications suggest that the system enters a ‘frustrated nucleation’ phase as the temperature is reduced. Further structural and dynamic measurements with spatial and temporal variation will be needed to determine the full characteristics of this system.

The SANS data probably represent the first direct measurement of a spatially-resolved, time-resolved SAS intensity profile for vapour diffusion in a granular porous matrix. Further work is needed to extract additional information about the density fluctuations and to provide a theoretical basis for a quantitative interpretation of the results. The technique developed in these measurements is expected to have applications to other diffusion problems and it may be useful to extend the range of the measurements to smaller Q-values using USAXS to define the profile more accurately. Corresponding proton NMR imaging techniques [12] have also been used to observe the developing vapour front and it seems likely that the complementarity of these two methods will

provide a firm basis for an extended investigation of the phenomenon. A more detailed treatment of the data will be presented in a later publication [13].

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