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MOLECULAR DYNAMICS IN LIQUID CYCLOPROPANE

I. — Self-diffusion Measurements by Quasielastic Neutron Scattering and N.M.R. Spin Echo

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Résumé. — Le coefficient de diffusion translationnelle du cyclopropane liquide a été mesuré dans une gamme de températures allant de 155 à 297 K par diffusion quasi élastique des neutrons (Q.N.S.) et par résonance magnétique nucléaire (N.M.R.) en utilisant la méthode des échos de spin. Les valeurs obtenues à l'aide de ces deux techniques sont en excellent accord.

Abstract. — The translational diffusion of liquid cyclopropane was studied by quasielastic neutron scattering (Q.N.S.) and by N.M.R. spin-echo in the temperature range 155-297 K. The values of the self-diffusion coefficient derived from the two techniques was the same within experimental accuracy (D = 0.78 x 10^{-5} cm^2 s^{-1} at 155 K, and D = 9.2 x 10^{-5} cm^2 s^{-1} at 297 K).

This shows that high-resolution Q.N.S. measurements at small momentum transfer give accurate information in the hydrodynamic region.

1. Introduction. — Neutron scattering is the only spectroscopic technique which realizes the appropriate energy and momentum transfer ranges to probe microscopic properties of condensed matter [1, 2]. Furthermore both individual and collective motions are reflected in the quasielastic and inelastic neutron scattering profiles.

It turns out, however, that it is always very difficult to extract selectively all this information and one is generally led to choose simple systems for which simplifying hypotheses are justified. Thus, for liquid cyclopropane for which the scattering is mainly incoherent, only the diffusive and vibrational motions of single molecules contribute to the scattering. In this case the relationship between the measured differential cross-section and the intermediate scattering law is:

\[
\frac{\delta^2 \sigma}{\delta \Omega \delta \omega} = Nb_{\text{inco}}^2 \frac{k}{k_0} \frac{1}{2 \pi} \int_{-\infty}^{+\infty} \times \left( e^{-iQ_0 \omega} \right) e^{iQ_0 \omega} e^{-i\omega t} dt , \tag{1}
\]

where \( N \) is the number of protons in the sample, \( b_{\text{inco}} \) their incoherent scattering length, and \( k_0 \) and \( k \), the incident and scattered neutron wavevectors which determine the momentum transfer \( Q \) according to...
The energy transfer $\hbar \omega$ is given by
\[
\frac{\hbar}{2m} (k^2 - k_0^2).
\]
The proton changes its position $r$ by translational, rotational and vibrational motions. As a working hypothesis it is usually assumed that there is no correlation between these different kinds of motions. Separation between vibrational and diffusive motions is certainly justified for cyclopropane, whose first vibrational level is at 92.5 meV [3].

As a consequence, the intermediate scattering law can be written as a product of the three contributions
\[
I(Q, t) = I_{\text{trans}}(Q, t) I_{\text{rot}}(Q, t) I_{\text{vib}}(Q, \infty) \tag{2}
\]
where $I_{\text{vib}}(Q, \infty)$ is related to the vibrational Debye-Waller factor, which is only a multiplicative factor of the quasielastic intensity (in our case, its value is close to unity). Hence, we are left with the problem of extracting the translational and rotational contributions from the quasielastic profile. The intermediate scattering law for the rotational process is given by the Sears’ expansion [4]
\[
I_{\text{rot}}(Q, t) = j_0^2(Qd) + \sum_{l=1}^{\infty} (2l + 1) j_l^2(Qd) F_l(t) \tag{3}
\]
where $j_l^2(Qd)$ are spherical Bessel functions of order $l$ and $d$ is the radius of gyration, i.e. the distance from the molecular center-of-mass to the scattering proton. $F_l(t)$ is some model-dependent function.

In the limit of low $Q$, $I_{\text{rot}}(Q, t)$ tends to $j_0^2(Qd)$. It turns out (see point 1 of the discussion) that the total intermediate scattering law reduces to the translational contribution, which is given by
\[
I_{\text{trans}}(Q, t) = \exp(-DQ^2 | t |) \tag{4}
\]
$D$ is the self-diffusion coefficient. The resulting quasielastic profile $S(Q, \omega)$ is a simple Lorentzian
\[
S(Q, \omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2} \tag{5}
\]
with full width at half peak height (F.W.H.H.) of $\Delta E = 2 \hbar DQ^2$.

In order to check the validity of eq. (5), we propose to compare the value of $D$ obtained by Q.N.S. with its value measured by N.M.R. spin-echo [5].

In this technique, diffusion of the spin system is observed by the attenuation of the echo amplitude in an inhomogeneous magnetic field, according to the relation
\[
M_x(2 \tau) = M_0 \exp \left( -\frac{2 \tau}{T_2} \right) \exp \left( -\frac{2}{3} \gamma^2 G^2 D \tau^3 \right) \tag{6}
\]
where $M_x(2 \tau)$ is the transverse magnetization component at time $2 \tau$, $M_0$ is the initial magnetization, $T_2$ the transverse relaxation time, $\gamma$ the gyromagnetic ratio and $G$ the magnetic field gradient along the $Z$ axis.

2. Experimental part. — The neutron scattering experiments were performed at the Institute Laue-Langevin, Grenoble, with the multichopper time-of-flight machine IN5 [6] and the back-scattering spectrometer IN10 [7]. The experimental conditions are summarized in table I.

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th>time of flight IN5</th>
</tr>
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<tbody>
<tr>
<td>IN10</td>
<td>6.275</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Incident wavelength (Å)</th>
<th>9.061</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scattering angles (degrees)</td>
<td>10, 15, 23.5, 28, 33</td>
</tr>
<tr>
<td>Elastic momentum transfer (Å⁻¹)</td>
<td>0.12, 0.18, 0.28, 0.335, 0.39</td>
</tr>
<tr>
<td>Elastic resolution (µeV)</td>
<td>0.15, 0.31</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>36.7, 35.7, 36.6, 36.5, 37.5</td>
</tr>
<tr>
<td>Back-scattering</td>
<td>1.28, 1.26</td>
</tr>
<tr>
<td>IN10</td>
<td>155, 194, 251</td>
</tr>
<tr>
<td>156, 174, 195</td>
<td></td>
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</tbody>
</table>

In both experiments the cyclopropane sample was contained in an aluminium cell which contributed about 4 % to the scattering. The cyclopropane sample thickness was designed to give about 10 % scattering. In fact the measured percentage of scattering was of the order of 20 % because of a wall deformation. This high value implies a non negligible multiple scattering contribution that we shall discuss later.

The cyclopropane (Matheson, purity 99.5 %) was deaerated in a vacuum line by successive trappings at liquid nitrogen temperature and thereafter condensed in the sample cell. Its vapor pressure is 5 bars at room temperature, its melting point is at 145 K.

Reduction of the neutron data was performed in two steps. Standard correction procedures of empty container subtraction, detector efficiency, self-shielding and normalization to vanadium were applied first [8, 9].

Then, in order to determine the diffusion coefficient, the resolution function given by the vanadium experiment was folded by a Lorentzian, a flat background was added, and the final result fitted to the experimental profile.

The N.M.R. spin-echo measurements on the proton resonance line at 60 MHz were done using a spectrometer built by one of us (P.L.) [10].

The cyclopropane was deaerated as for the neutron experiments and sealed in a calibrated glass tube of 7 mm diameter.

To avoid the determination of $T_2$, we followed the method described by Hahn [11] which consists in
using two different field gradients $G_1$ and $G_2$. The ratio

$$Y_{(2)} = \log \frac{M_{xy}(2 \tau)}{M_{xy}(2 \tau)} = 2/3 \gamma^2 (G_2^2 - G_1^2) \Delta \tau^3$$

was plotted as a function of $\tau^3$ to obtain the slope $2/3 \gamma^2 (G_2^2 - G_1^2) D \Delta \tau^3$. The same procedure was applied to a reference compound of well known self-diffusion coefficient, $D_{ref}$. The ratio of the slopes gives $D/D_{ref}$, i.e. $D$. The liquid was investigated at three temperatures: 297 K with reference to water [12], and at 219 and 182 K with reference to pentane [13].

3. Results. — 3.1 Quasielastic Neutron Scattering. — Typical corrected data are represented in figure 1 on an energy transfer scale, together with the best fitted profiles.

These pictures illustrate clearly the advantage of using both spectrometers. The back scattering experiment at very high resolution but with a small energy transfer window ($\pm 7.8 \text{ $\mu$eV}$) is complemented by the time-of-flight experiment at lower resolution but with much larger energy transfer. As a result, we have been able to measure accurately a large continuous range of broadening, ranging from a few $\mu$eV to more than 100 $\mu$eV. This is shown in figure 2, where the F.W.H.H. of the Lorentzian is plotted versus $Q^2$ at 194 K and 155 K. All the experimental points lie on a straight line. The same is true for the other temperatures.

The self-diffusion coefficients were determined from the slope of the straight lines and their values are given in table II together with the activation energy.

It has to be pointed out that we have considered the momentum transfer $Q$ to be constant and equal to $Q_{elastic}$ in all the Q.N.S. measurements. This approximation which leads to a simplification in the calculations is justified in view of the very small energy transfers investigated.

3.2 N.M.R. Spin-Echo Measurements. — Figure 3 shows, as an example, the experiment results at 297 K using water as a reference. All our results are summarized in table II.

4. Discussion. — 4.1 Comparison between Q.N.S. and N.M.R. Results. — Figure 4 shows the experimental self-diffusion coefficient of liquid cyclopro-
Translational diffusion coefficients in units of $10^{-5}$ cm$^2$ s$^{-1}$ and energy of activation for liquid cyclopropane from quasielastic neutron scattering and N.M.R. spin-echo.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Q.N.S.</th>
<th>N.M.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>155</td>
<td>0.78 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>174</td>
<td>1.3 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>181.5</td>
<td>2.26 ± 0.10</td>
<td>1.68 ± 0.09</td>
</tr>
<tr>
<td>194</td>
<td>5.98 ± 0.24</td>
<td>3.55 ± 0.18</td>
</tr>
<tr>
<td>251</td>
<td>9.2 ± 0.5</td>
<td></td>
</tr>
</tbody>
</table>

Activation energy
Kcal/mole          1.60 ± 0.06

pane as a function of temperature. The agreement between the Q.N.S. and N.M.R. measurements is surprisingly good in view of the following experimental and theoretical limitations:

a) multiple scattering contamination in the Q.N.S. experiment,

b) mixing of the rotational and translational contributions in the quasielastic profile,

c) fundamental differences in the $(Q, \omega)$ region probed by the Q.N.S. and N.M.R. techniques.

FIG. 2. — F.W.H.H. of best fit Lorentzians versus $Q^2$ for liquid cyclopropane at 155 and 194 K in the back-scattering (•) and time-of-flight experiments (○).

FIG. 3. — N.M.R. spin echo measurements at 197 K for cyclopropane and water.

FIG. 4. — Q.N.S. and N.M.R. spin echo measurements of the self diffusion coefficient of liquid cyclopropane as a function of reciprocal temperature.
We shall successively discuss these different problems. As already pointed out, the cyclopropane sample scattered about 20\% of the incident neutrons. In order to estimate the amount of multiple scattering in the quasielastic region, we have used a computer program based on Monte-Carlo calculations [14] up to the third scattering order. Figure 5 shows that the F.W.H.M. of the profile is unaltered; appreciable deviations occur only in the wings in such a way that we can conclude that multiple scattering does not affect significantly our diffusion coefficient measurements.

On the other hand, it has been shown [1, 15] that in order to safely ignore the rotational contribution to the quasielastic profile, it is necessary for the following situations to exist:

i) \( Qd < 1 \), which makes \( j_2(Qd) \) the predominant term in the Bessel expansion (3). The mean radius of gyration for cyclopropane is 1.7 Å [16], and the highest \( Q \) value investigated is 0.39 Å\(^{-1}\). This leads to \((Qd)_{\text{max}} = 0.68\).

ii) \( DQ^2 < D_{\text{rot}} \) is the condition for less broadening by translational than by rotational motion. If we consider the more unfavourable case corresponding to the tumbling of the threefold axis of the molecule, \( D_{\text{rot}} = 0.22 \times 10^{12} \text{ s}^{-1} [3] \), we find at 251 K the maximum \( DQ^2 \) equal to \( 0.092 \times 10^{12} \text{ s}^{-1} \) (tables I and II).

iii) The amount of broadening has to exceed one-fifth of the resolution in order to minimize the error in the convolution process. This situation was generally realized in our measurements.

The above remarks confirm the reliability of our Q.N.S. results. As a consequence, the agreement with the N.M.R. macroscopic results can be considered meaningful. It shows that in the \( Q \) range considered, the conditions for a hydrodynamic regime are satisfied.

In order to compare our results for cyclopropane with those available in the literature for other molecular liquids, we have used the method proposed by Douglass and McCall [17] which consists in plotting \( \log D \text{ versus } T_c/T \) where \( T_c \) is the critical temperature.

This comparison on a reduced temperature scale (Fig. 6) shows that the cyclopropane data lie fairly well in the region delimited by the other liquids. The agreement is especially good with the data for cyclopentene which have been obtained recently both by N.M.R. spin-echo and Q.N.S. measurements [18].

4.2 THEORETICAL INTERPRETATION OF THE SELF-DIFFUSION COEFFICIENT. — Numerous theories, both qualitative and semi-quantitative, have been proposed for the interpretation of transport properties in liquids. An excellent review, which includes comparison with experiment is given in reference [22]. One of the major goal of these theories is to relate microscopic quantities like the self-diffusion coefficient to macroscopic...
ones like the viscosity. In this context, one of the most successful theories has been developed by Longuet-Higgins and Pople [23] for a hard-sphere fluid with no attractive forces. They derived an explicit expression for the self-diffusion coefficient

\[ D = \frac{a}{2} \left( \frac{\pi RT}{M} \right)^{1/2} \left( \frac{PV}{RT} - 1 \right)^{-1} \]

where \( a \) is the hard sphere radius, \( M \) the molecular mass, \( V \) the molar volume and \( P \) the pressure. This theory also gives a relationship between \( D \) and the viscosity \( \eta \):

\[ D = \frac{3 kTf}{10 \pi a} \]

where \( f \) is the packing fraction of the fluid.

Unfortunately, we cannot test this relationship for cyclopropane since there is no direct measurement of the viscosity. The published data [24] are only estimated from the density, through an empirical formula. MacCall et al. [25], in developing the original ideas of Longuet-Higgins and Pople, proposed replacing the hard-sphere pressure \( P \), by the cohesive energy \( E_c/V \), where \( E_c \) is the energy of vaporization. The basic idea is that the hard-sphere repulsive pressure has to be balanced by an attractive Van der Waals term. One then obtains the expression for \( D \):

\[ D = \left( \frac{\pi RT}{M} \right)^{1/2} \left( \frac{E_c}{RT} - 1 \right)^{-1} \]  

(10)

The hard-sphere radius \( a \) is calculated for example by assuming hexagonal close-packing of spheres:

\[ \frac{4}{3} \pi a^3 = 0.74 \frac{M}{Nd} \]

(11)

where \( M \) is the molecular weight, \( d \) the density and \( N \) the Avogadro number.

One thus can relate the self-diffusion coefficient to the density and the latent heat of vaporization [24]. Of course one cannot expect an agreement over an extended range of temperature since the hard sphere liquid-diffusion is not an activated process and does not follow an Arrhenius behaviour of the type we have found experimentally (Fig. 4). Nevertheless the agreement is quite good at high temperature (above the boiling point at normal pressure). This is shown in table III.

### TABLE III

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( D_{exp} ) ( 10^{-5} \text{ cm}^2 \text{s}^{-1} )</th>
<th>( D_{cal} ) ( 10^{-5} \text{ cm}^2 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>5.0</td>
<td>5.6</td>
</tr>
<tr>
<td>297</td>
<td>9.2</td>
<td>9.9</td>
</tr>
</tbody>
</table>

We do not want to push too far the interpretation of the present self-diffusion data. In our opinion it represents only the first essential step for the understanding of molecular motions in liquid cyclopropane as seen by neutron scattering in a more extended \((Q, \omega)\) space [26].

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### References


