Dynamics of liquid silane

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Abstract. Neutron scattering of cold neutrons from liquid silane at 137°K
98°K is explained on the basis of a simple model. The rotational diffusion
constant, $D_r$, and the delay time, $\tau_0$, after which rotational diffusion may be said
to occur are derived on the basis of this model. At 137°K we get
$D_r = 0.22 \times 10^{13} \text{ sec}^{-1}$ and $\tau_0 = 0.68 \times 10^{-13} \text{ sec}$. At 98°K $D_r = 0.06 \times 10^{13} \text{ sec}^{-1}$ is down
by a factor of more than three but $\tau_0 = (0.54 \times 10^{-13} \text{ sec})$ shows only a small change.
By comparison with data on liquid CH$_4$ it is concluded that the law of corresponding states is not applicable for describing rotational dynamics of CH$_4$ and SiH$_4$.
Rotational motions in SiH$_4$ are more hindered than in CH$_4$ at the same reduced temperature.

Keywords. Liquid silane; rotational correlation; neutron scattering; law of corresponding states.

1. Introduction

In an earlier paper (Dasannacharya et al 1972), we had shown that it was possible
to understand the spectra of neutron scattered from liquid NH$_3$ on the basis of
a simple model, described therein. One could, therefore, derive the first order
rotational correlation function, $F_1(t)$, from neutron data if a proper correction
was applied for multiple scattering.

This paper summarises our efforts towards understanding the spectra of cold
neutrons scattered from liquid silane. The experiments with which we compare
our calculations were performed by Hautecler and Vorderwisch (1972) at C.E.N.
Mol. They consisted of measuring the time-of-flight distribution of 4.15 Å
neutrons scattered from a 0.7 mm thick sample of silane at 98°K, 123°K and
137°K, at scattering angles of 14°, 45.3° and 90.3° at each temperature. Our
calculations are confined to 98°K and 137°K, at scattering angles of 45.3°K
and 90.3°K.

In the original paper of Hautecler and Vorderwisch, it was shown that one cannot
reproduce the spectra of SiH$_4$ by the use of the law of corresponding states
as applied to CH$_4$. These calculations, however, were not corrected for multiple
scattering. In view of this and also considering the fact that a rotational model
used by us earlier gave good description of neutron scattering spectra from liquid
NH$_3$, we decided to do detailed calculations for liquid SiH$_4$ also.
2. Model

We use the Langevin diffusion model to describe the translational part and a model described earlier (Dasannacharya et al. 1972, Thaper and Dasannacharya 1974) for the rotational part. The rotational model involves a delay time, $\tau_0$, before which the relaxation function, describing the neutron scattering in the Gaussian approximation, has a free gas behaviour for a spherical top. After $\tau_0$ the same relaxation function is described by a rotational diffusion constant $D_r = 1/\lambda$. In this model, under the Gaussian approximation, the double differential cross section [for details and earlier references see Dasannacharya et al. (1972) and Thaper et al. (1974)] is,

$$
\frac{d^2\sigma}{d\Omega d\omega} = \frac{a_{\text{ne}}^2 k_\omega^2}{2\pi k_\omega} \exp \left( -\frac{\hbar \omega}{2k_B T} \right) \exp \left( -\frac{\hbar^2 Q^2}{8Mk_B T} G(T) \right) \\
\times \int_{-\infty}^{\infty} \exp \left[ -Q^2 \left( \rho_T(t) + \rho_R(t) \right) \right] \cos \omega t \, dt
$$

(1)

where the various symbols have the same meaning as given in Thaper et al. (1974). $\rho_T(t)$ and $\rho_R(t)$ are the translational and rotational width functions. In our calculations we take

$$
\rho_T(t) = D \left[ t - \frac{1}{\eta} \exp \left( -\eta t \right) \right]
$$

(2)

with $\eta = k_B T/M$, as given by Langevin diffusion model. For the rotational part

$$
\rho_R(t) = \frac{1}{3} b^2 \left[ 1 - F_1(t) \right]
$$

(3)

where $b$ is the distance between the hydrogen and the centre of mass of the molecule and $F_1(t)$ is the first order rotational correlation function. As in our earlier work we assume that

$$
F_1(t) = \frac{1}{3} \left[ 1 + 2 \left\{ 1 - \frac{k_B T}{I} t^2 \right\} \exp \left( -\frac{k_B T}{2I} t^2 \right) \right] \text{ for } t < \tau_0
$$

(4)

and

$$
F_1(t) = F_1(\tau_0) \exp \left[ -D_r (t - \tau_0) \right] \text{ for } t \geq \tau_0.
$$

(5)

Multiple scattering calculations were performed exactly similar to those described earlier (Thaper et al. 1974).

3. Results of calculations and discussion

(a) Multiple scattering

Figure 1a shows multiple scattering spectra for the two different values of parameter $\tau_0*$ and $\lambda*$ shown therein. One finds that the difference in the two amounts to 13% at $\sim 600 \mu \text{sec/m}$. Since the multiple scattering in these regions is about 60% of total scattering, the 13% difference in multiple scattering amounts to 8% change in the observed spectrum. In view of this we have not performed multiple scattering calculations for different value of $\tau_0*$ and $\lambda*$. This conclusion was also reached earlier in the case of liquid NH$_3$ (Thaper et al. 1974).
Figure 1 (a) Doubly-scattered neutron time-of-flight spectra from liquid silane for two different values of the parameter $\lambda^* (= 1/D^*_r)$. 

(b) Change in the doubly scattered spectra when only the temperature is changed without any change in the parameters $\lambda^*$ and $\tau_0^*$. 

It has also been checked again that the multiple scattering spectrum can be taken to be isotropic for the present calculations, a conclusion similar to that for liquid NH$_3$.

Figure 1 b shows the change in multiple scattering for the same $\tau_0^*$ and $\lambda^*$ when temperature is changed from 137°K to 98°K. This is clearly an important effect and has been taken into account.

(b) Total scattering

As mentioned earlier single scattering spectra are calculated using a Langevin diffusion model for translational and a two parameter model for rotational motions (Dasannacharya et al 1972). These two parameters are the delay time, $\tau_0$ and the rotational diffusion constant $D_r = 1/\lambda$. For convenience the parameters are defined in reduced units, $\tau_0^* = \tau_0 \left( \frac{k_B T}{I} \right)^{1/2}$ and $\lambda^* = \lambda \left( \frac{k_B T}{I} \right)^{1/2}$ where $T$ is the temperature and $I$ the moment of inertia of the molecule. In our analysis we have fixed the value of the effective translational self diffusion constant $D$ and calculated the spectra for different values of $\tau_0^*$ and $\lambda^*$. The value of $D$ has been determined from the experimental quasielastic width at the two smaller scattering
angles, assuming that the observed width is a convolution of a Gaussian resolution function and a Lorentzian function due to true translational width. A value of 25 \(\mu\) sec has been assumed for the instrumental time resolution at the elastic peak at both the scattering angles. The values obtained in this manner at 137° K and 98° K are 4.7 \(\times\) 10^{-5} cm^2/sec and 1.5 \(\times\) 10^{-5} cm^2/sec respectively. These are very different from values 2.04 \(\times\) 10^{-5} and 0.35 \(\times\) 10^{-5} cm^2/sec derived from macroscopic diffusion coefficient of liquid methane using the law of corresponding states (Hautecler and Vorderwisch 1972).

Figure 2 shows the experimental data of Hautecler and Vorderwisch at 137° K at scattering angles of 45.3° and 90.3°. The calculated spectra which give a good fit at both the angles are obtained for \(\tau_0^* = 0.3\) and \(\lambda^* = 2.0\), and are shown in the same figure. The calculated spectra are corrected for instrumental resolution and multiple scattering and are area normalized to the experimental areas. With the present analysis it is found that at 137° K the rotational correlation function \(F_1(t)\) can be described by \(\tau_0^* = 0.3 \pm 0.1\) and \(\lambda^* = 2.0 \pm 1.0 - 0.5\).

The values of these parameters at this temperature derived from the \(F_1(t)\) of liquid methane using law of corresponding states turn out to be 0.8 and 1.47 respectively. This shows that the free gas behaviour for the rotational correlation function continues for much longer reduced time for liquid methane than for liquid silane. The collision effects are visible for SiH₄ earlier. Also the reduced rotational diffusion constant \((D_r^* = 1/\lambda^*)\) is somewhat smaller for liquid silane.

The effect of lowering the temperature is shown in figure 3. The experimental data and the calculations for \(\tau_0^* = 0.2\) and \(\lambda^* = 6.0\) are shown. Also shown, with dashed line, are spectra which would be expected if the parameters in the rotational model had not changed with temperature between 137° K and 98° K. This is included merely to show the sensitivity of the spectra to these parameters. The agreement between the calculation and theory is not as good as at 137° K, but certain features are easily noticeable. As may be expected the \(\lambda^*\) increases,

![Figure 2. Calculated and measured neutron time-of-flight spectra for liquid silane at \(T = 137° K\). \(\tau_0^* = 0.3; \lambda^* = 2.0\).](image-url)
Dynamics of liquid silane

Figure 3. Calculated and measured neutron time-of-flight spectra for liquid silane at 98°K, for parameter values shown: The dashed curves corresponding to rotational parameters which fit the data at 137°K.

giving a much smaller rotational diffusion constant. The change in the $\tau_0^*$ is not so dramatic. It seems to have slightly decreased which is not surprising.

The discrepancy between the experiment and the model calculations seem to arise mainly from a lack of proper description of the translational part. It may be argued that for SiH$_4$ one may have to use a more "solid-like" model which would give a narrowing of the quasi-elastic peak. This may improve the agreement. However, in view of the various other uncertainties we did not think it worthwhile introducing a more sophisticated model at this stage.

4. Summary

The law of corresponding states cannot be applied between CH$_4$ and SiH$_4$ for describing rotational dynamics. The rotations in SiH$_4$, at the same reduced temperature, are more hindered than in liquid CH$_4$. The delay time and the rotational diffusion constant, which have been derived here for SiH$_4$ at 137°K and 98°K bear this out. The situation seems to be similar with respect to the translational motions also.

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