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Dynamics of liquid silane

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Abstract. Neutron scattering of cold neutrons from liquid silane at 137° K and 98° K is explained on the basis of a simple model. The rotational diffusion constant, D_r, and the delay time, τ_0, after which rotational diffusion may be said to occur are derived on the basis of this model. At 137° K we get $D_r = 0{\cdot}22 \times 10^{13}$ sec^{-1} and $\tau_0 = 0{\cdot}68 \times 10^{-13}$ sec. At 98° K D_r ($= 0{\cdot}06 \times 10^{13}$ sec^{-1}) is down by a factor of more than three but τ_0 ($= 0{\cdot}54 \times 10^{-13}$ 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, τ_0, before which the relaxation function, describing the neutron scattering in the Gaussian approximation, has a free gas behaviour for a spherical top. After τ_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,

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{a_{\text{inc}}^2}{2\pi}\frac{k_2}{k_0}\exp\left(-\frac{\hbar\omega}{2k_BT}\right)\exp\left(-\frac{\hbar^2Q^2}{8Mk_BT}G(T)\right)$$

$$\times\int_{-\infty}^{\infty}\exp\left[-Q^2\{\rho_T(t)+\rho_R(t)\}\right]\cos\omega t\,dt \qquad (1)$$

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

$$\rho_T(t) = D\left[t - \frac{1-\exp(-\eta t)}{\eta}\right] \qquad (2)$$

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

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

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

$$F_1(t) = \frac{1}{3}\left[1+2\left\{1-\frac{k_BT}{I}t^2\right\}\exp\left(-\frac{k_BT}{2I}t^2\right)\right] \text{ for } t \leqslant \tau_0 \qquad (4)$$

and

$$F_1(t) = F_1(\tau_0)\exp[-D_r(t-\tau_0)] \text{ for } t \geqslant \tau_0. \qquad (5)$$

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 1 *a* shows multiple scattering spectra for the two different values of parameter τ_0^* and λ^* shown therein. One finds that the difference in the two amounts to 13% at $\sim 600\,\mu$ 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 τ_0^* and λ^*. This conclusion was also reached earlier in the case of liquid NH_3 (Thaper *et al* 1974).

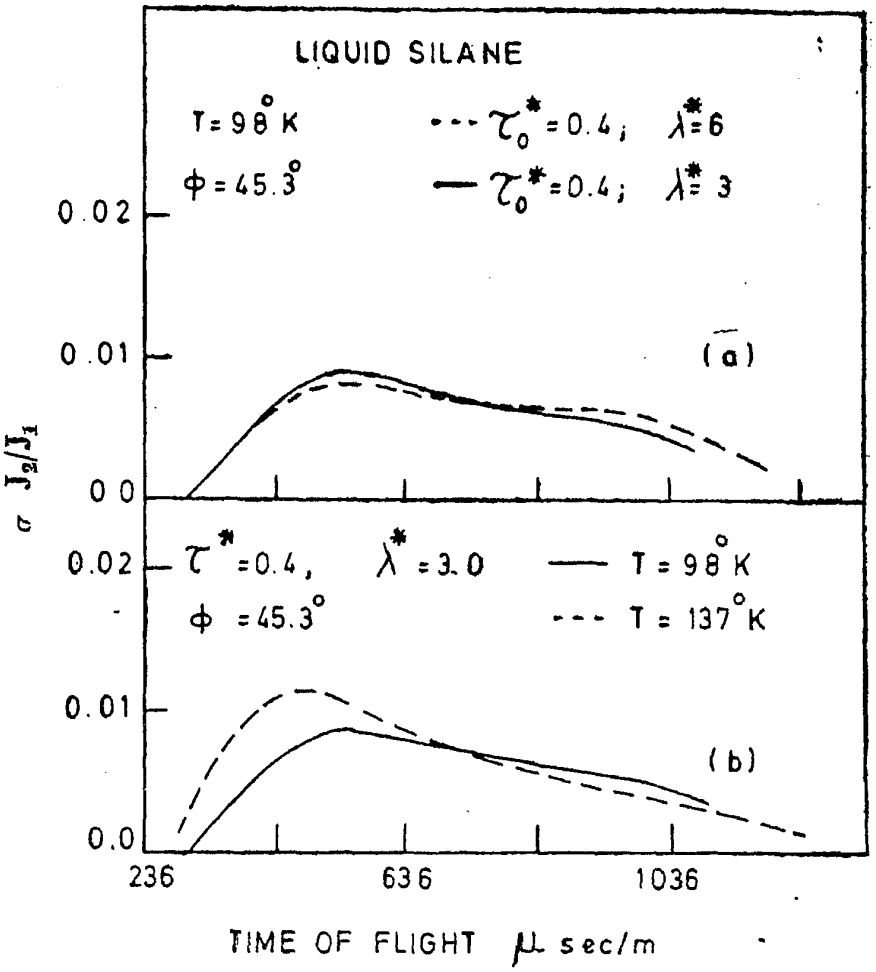

Figure 1 (*a*) Doubly-scattered neutron time-of-flight spectra from liquid silane for two different values of the parameter $\lambda^* (= 1/D_r^*)$.

(*b*) Change in the doubly scattered spectra when only the temperature is changed without any change in the parameters λ^* and τ_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 τ_0^* and λ^* 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, τ_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 τ_0^* and λ^*. The value of D has been determined from the experimental quasi elastic 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 28 μ 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 $4{\cdot}7 \times 10^{-5}$ and $1{\cdot}5 \times 10^{-5}$ cm²/sec respectively. These are very different from values $2{\cdot}04 \times 10^{-5}$ and $0{\cdot}35 \times 10^{-5}$ cm²/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 $\tau_0^* = 0{\cdot}3$ and $\lambda^* = 2{\cdot}0$, 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 $\tau_0^* = 0{\cdot}3 \pm 0{\cdot}1$ and $\lambda^* = 2{\cdot}0\ ^{+1{\cdot}0}_{-0{\cdot}5}$ 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 SiH_4 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 $\tau_0^* = 0{\cdot}2$ and $\lambda^* = 6{\cdot}0$ 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 λ^* increases,

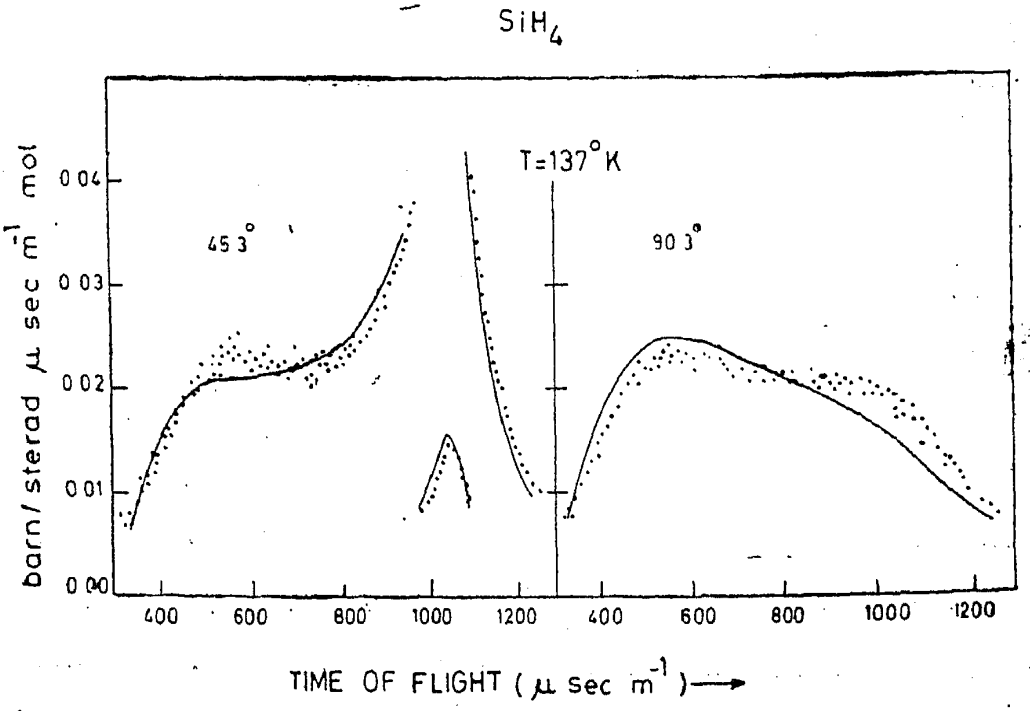

Figure 2. Calculated and measured neutron time-of-flight spectra for liquid silane at $T = 137°$ K. $\tau_0^* = 0{\cdot}3$; $\lambda^* = 2{\cdot}0$.

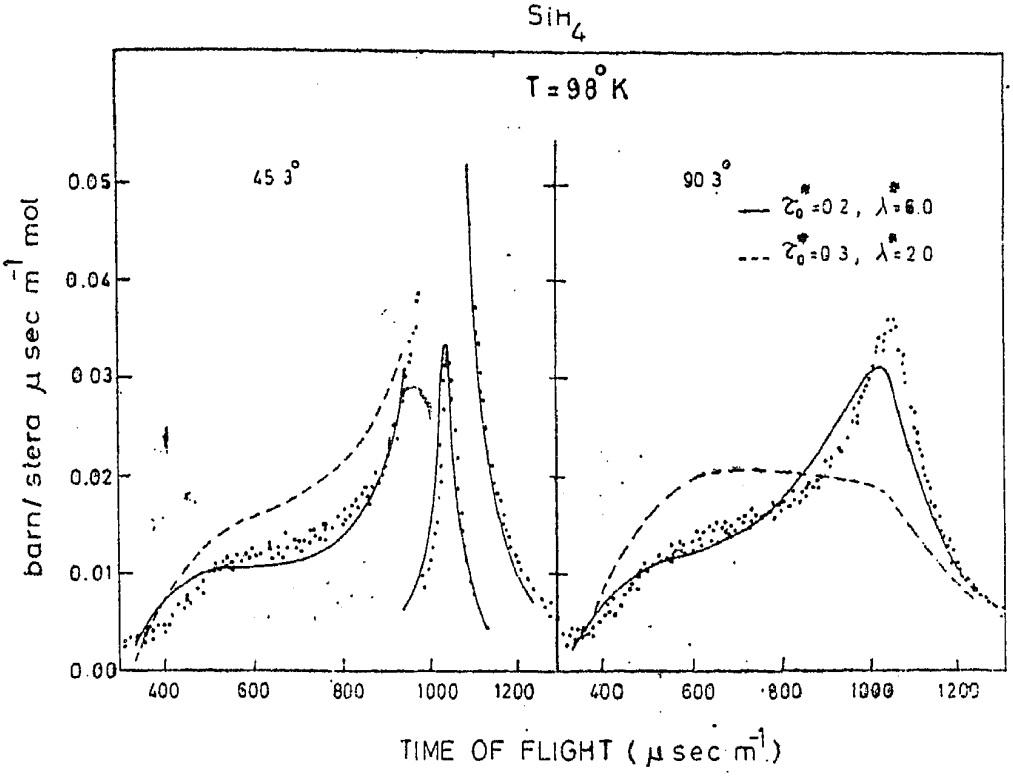

Figure 3. Calculated and measured neutron time-of-flight spectra for liquid silane at 98° K, for parameter values shown: The dashed curves corresponding to rotational parameters which fit the data at 137° K.

giving a much smaller rotational diffusion constant. The change in the τ_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.

Acknowledgement

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