<Original> An Analysis of Inelastic Neutron Scattering
by Liquid Methane

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Abstract

The incoherent neutron scattering cross section of molecular liquids is analyzed using a damping function model for correlation functions of molecular translations and rotations. The present approach is different from recent works in that the scattering function is evaluated directly, not through the intermediate scattering function. The damping fuction is determined from a simple relation between its long-wavelength limit and the generalized frequency distribution function, and translation-rotation couplings are assumed to be neglected. A physical model is used for the translational motions of center-of-mass of a molecule, including properly its short-time and long-time behaviors. A simple model for the rotational motions is suggested which relates the damping function to the Fourier transform of the dipole correlation function, or equivalently, the infrared vibrational absorption spectrum. Theoretical absolute scattering intensities are computed for liquid methane and shown to be in satisfactory agreement with both thermal and cold neutron measurements.

요   약

분자의 병진운동과 회전운동의 상관함수에 대한 감쇠함수 모델을 사용하여 분자액체의 비간섭중성자 산란단면적을 분석하였다. 이러한 방법은 직접적으로 산란함수를 구한다는 점에서 중간함수를 거치는 종래의 방법과는 판연히 다르다. 감쇠함수는 그 장파장극한과 일반진동수 분포함수간의 간단한 관계에서 결정하였고 병진운동과 회전운동의 결합관계는 무시된다고 가정하였다. 분자질량중심의 병진운동은 그 짧은 시간과 장시간에서의 행위를 적절히 기술하는 물리적 모델을 사용하였고 회전운동은 쌍극상관함수 또는 적외선진동 흡수스펙트럼의 푸리어 변환으로 된 감쇠함수에 관계된다고 가정하였다. 액체메탄에 대한 이론적 절대 산란강도를 계산하였으며 이는 열 및 냉중성자 측정치와 만족할만한 일치를 보여주고 있다.

1. Introduction

The inelastic neutron scattering experiment is one of most powerful techniques which can provide information about atomic and molecular processes in liquids, especially when the neutron energy is comparable to the energy levels of the system. Many of these processes can be discussed in terms of time correlation functions, whose basic properties are by now well known in the literature[1,2]. The time correlation functions in classical simple liquids have been quite extensively studied by analyzing inelastic neutron scattering and computer molecular-dynamics experiments[3,4]. Although the formal theory of neutron scattering by molecular liquids and solids is well developed[5,6], practical calculation methods for the scattering cross sections are still rather limited. Recent theoretical studies of neutron scattering by molecular liquids have been based on an indirect approach in which the scattering function is evaluated after the intermediate scattering function is calculated by using mostly the information contained in the frequency distribution function[7-9].

The purpose of this paper is to present a direct method for a detailed analysis of the double differential incoherent cross section of molecular liquids. The calculations are based on the correlation function formalism developed by Martin and Kadanoff[1], which was successfully applied to the analysis of the correlation functions obtained by computer experiments and inelastic neutron scattering by a simple liquid[3]. The method involves specific assumptions which are necessary to obtain numerical results. The validity of these assumptions will be examined quantitatively for liquid methane using the available thermal[10] and cold[11,12] neutron data.

In the present work the main problem is to determine a frequency and wavelength depen-

dent damping function, which should be appropriate to describe the rotational motions as well as the translational motions of a liquid molecule. Through the use of dispersion relation for the self correlation function one obtains sum-rule conditions on the damping function[1,3]. Moreover, the damping function is constrained to give the proper self-diffusion coefficient in the low-frequency and long-wavelength limit. The central approximation for determining the rotational contribution of the damping function will be made from the relation between the translational contribution and the Fourier transform of the velocity autocorrelation function of a simple liquid in the long-wavelength limit[3,6,13]. The advantage of this approach will be seen in that even simple assumptions regarding the damping function, so long as its known proterties are not violated, one can obtain diretly quite reasonable results for the incoherent scattering function. As we will see later, our approach will make use of the rotational correlation function and leads to satisfactory results as comparable as those of Agrawal and Yip[7] and of Sears[8], whose methods are indirect.

In Section 2 we will present a brief summary of Martin's formalism for the self correlation function and discuss the constraints on the damping function. In the next section we will introduce a simple model description for the damping function of a molecular liquid and make specific assumptions about the frequency dependence of the damping function and other assumptions inherent in the present work. In Section 4 we will carry out specific calculations for liquid methane and compare with both thermal and cold neutron scattering data. The overall results are then discussed in the final section where we will examine in some detail the validity of our assumptions with several concluding remarks.

2. Correlation Function Formalism

The method we will use to evaluate the self correlation function is essentially based on the linear response theory of Martin and Kadanoff[1] in which one writes a dispersion relation for a complex susceptibility $x(\kappa, \omega)$.

$$z^2[1-x(\kappa, o)/x((\kappa, z)]^{-1}=iz\kappa^2 D(\kappa, z). \quad (1)$$

where z is a complex variable which will become real by taking the limit of $z=\omega+i\varepsilon$ as ε goes to zero, and $D(\kappa, z)$ is called a complex damping function. In Eq. (1) we have omitted the $z=0$ limit of the left hand side, since we know that it is zero for the self correlation function[3]. We also know that the $z=0$ limit of the susceptibility of the self correlation function is the inverse of the system temperature[3].

The susceptibility function is defined by

$$x(\kappa, z)=\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\ \frac{x''(\kappa, \omega')}{\omega'-z} \quad (2)$$

where

$$x''(\kappa, \omega)=\int_{-\infty}^{\infty}dt e^{i\omega t}\frac{i}{2}<[e^{i\vec{\kappa}\cdot\vec{r}(t)},$$

$$e^{-i\vec{\kappa}\cdot\vec{r}(0)}]_{PB}> \quad (3)$$

represents the response function for the self correlation function. In Eq. (3) $\vec{r}(t)$ is the position of the molecule at time t, the bracket $<X>$ indicates the average of X over an equilibrium distribution function, and the bracket $[,]_{PB}$ denotes the Poisson bracket.

By introducing a damping function which is real and defined by

$$D(\kappa, z)=\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\ \frac{D'(\kappa, \omega')}{\omega'-z} \quad (4)$$

into Eq. (1) and the incoherent scattering function $S(\kappa, \omega)$[3],

$$S(\kappa, \omega)=x''(\kappa, \omega)/(\pi\beta\omega), \quad (5)$$

which is established through the fluctuation-dissipation theorem[14], we obtain the following relation between $S(\kappa, \omega)$ and $D'(\kappa, \omega)$:

$$S(\kappa, \omega)=D'(\kappa, \omega)\kappa^2\Big\{\Big[\omega+\kappa^2\omega p\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}$$

$$\frac{D'(\kappa, \omega')}{\omega'^2-\omega^2}\Big]^2+[D'(\kappa, \omega)\kappa^3]^2\Big\}^{-1}/\pi, \quad (6)$$

where p denotes the principal value integral. In Eq. (5) β is the inverse of the temperature in energy units.

If one can determine an appropriate damping function which satisfies as many constraints as possible, one can evaluate directly the scattering function. In other words, our problem is by now to impose the necessary contraints on the damping function using all the information available. This method is different from the usual procedure[5-8] which is basically concerned with the intermediate scattering function instead of the scattering function itself.

The first class of constraints on $D'(\kappa, \omega)$ is obtained by making a large z expansion of Eq. (1). This leads to relations between the frequency moments of x'' and D' among which the first two relations are

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}D'(\kappa, \omega)=\frac{1}{\kappa^2}\int_{-\infty}^{\infty}S(\kappa, \omega)\omega^2 d\omega$$

$$\equiv C^2_{\infty}(\kappa) \quad (7)$$

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\omega^2 D'(\kappa, \omega)=[C^2_{\infty}(\kappa)\kappa^2]^2/\kappa^2$$

$$-\frac{1}{\kappa^2}\int_{-\infty}^{\infty}\omega^4 S(\kappa, \omega)d\omega. \quad (8)$$

As another constraint $D'(\kappa, \omega)$ has to satisfy the hydrodynamic limit[1,15]

$$\pi\lim_{\omega\to 0}\lim_{\kappa\to 0}[\omega^2 S(\kappa, \omega)/k^2]=D'(0, 0)=D \quad (9)$$

where D is the self-diffusion coefficient. We also know that

$$\lim_{\kappa\to 0}[\omega^2 S(\kappa, \omega)/\kappa^2=f(\omega)/2\beta M \quad (10)$$

where M is the mass of the molecule, and $f(\omega)$ is the frequency distribution function. For a monatomic classical liquid $f(\omega)$ is the Fourier transform of the velocity autocorrelation function[6,13].

In the incoherent approximation and for classical calculations the double differential scattering cross section of a hydrogenous substance per molecule is given by[7,16]

$$\frac{d^2\sigma}{d\Omega d\omega}=\frac{n\sigma_b}{4\pi}\left(\frac{\kappa_f}{\kappa_i}\right)e^{-\hbar\beta\omega/2}$$

$$e^{-\beta\hbar^2\kappa^2 G(\beta)/8M}\,S(\kappa,\omega),\qquad(11)$$

where n is the number of hydrogen atoms per molecule, $\sigma_b=81$ barns is the bound proton cross section, κ_i and κ_f are the incident and scattered neutron wave numbers, $\hbar\vec{\kappa}=\hbar(\vec{\kappa_f}-\vec{\kappa_i})$ and $\hbar\omega=\hbar(\omega_f-\omega_i)$ are neutron momentum and energy gains, We will assume that the scattering contributions from other atoms in the molecule are either negligible or can be easily added[16]. The first exponential in Eq. (11) represents the detailed balance factor and the second one is the generalized recoil factor which is given by

$$G(\beta)=2\int_0^\infty d\omega f(\omega)[\cosh(\hbar\beta\omega/2)-1]$$

$$/\left(\frac{\hbar\beta\omega}{2}\right)\sinh\left(\frac{\hbar\beta\omega}{2}\right).\qquad(12)$$

For monatomic systems $G(\beta)$ is usually very close to unity but for molecular systems it can be quite different from unity. For high temperatures the integrand of Eq. (13) reduces to $f(\omega)$, which means that $G(\beta)$ is just the zeroth moment of $f(\omega)$. This moment will be seen later to determine the normalization condition for the generalized frequency distribution function $f(\omega)$. In classical calculations $S(\kappa,\omega)$ is even in frequencies, and also even in wavenumbers due to translational and rotational invariance in a liquid.

3 Damping Function Model

The correlation function formalism using the damping function which is constructed to satisfy various constraints connected with measurable or calculatable quantities has been successful in analyzing the correlation functions in a simple liquid. In this section we will attempt to extend the same approach to a molecular liquid by considering a phenomenological model for the damping function which contains the information about rotational motions in addition to translational motions

It is reasonable to assume that translational motions in a molecular liquid are the same as the atomic motions in a simple liquid[17,18]. We have seen from the analysis of the self correlation function in a simple liquid that the damping function does not show a strong wavelength dependence as compared with the damping function associated with the density correlation function. In other words, a generalized self-diffusion coefficient, which is the damping function for the self correlation function, exhibits smaller variations with the wavenumber in comparison with a generalized viscosity coefficient[3,4]. For the moment we will assume that the translational damping function associated with the translational motions has no wavenumber dependence. From Eq. (6) and Eq. (10) we have

$$D'(0,\omega)=\pi f(\omega)/2\beta M=D'(\kappa,\omega)\qquad(13)$$

where the second equality is the result of our assumption. As a specific example of the damping function without any wavenumber dependence, the translational damping function given by

$$D_t'(\kappa,\omega)=D[(\omega^2-\omega_t^2)^2+(\omega/\tau_t)^2]^{-1}\qquad(14)$$

$$D=\omega_t^2/\beta M\tau_t\qquad(15)$$

and its corresponding frequency distribution function

$$f_t(\omega)=\frac{2}{\pi}\frac{\omega_t^2}{\tau_t}[(\omega^2-\omega_t^2)^2+)\omega/\tau_t)^2]^{-1}\qquad(16)$$

are found to describe satisfactorily the frequency spetrum obtained from the computer molecular-dynamics experiments and the incoherent scattering function for a simple liquid[3,19-21].

In a similar way we will assume that the rotational damping function $D_r'(\kappa,\omega)$ associated with the rotational motions be obtained from the rotational contribution of the generalized frequency distribution function through the relation.

$$D_r'(\kappa,\omega)=\pi f_r(\omega)/2\beta M.\qquad(17)$$
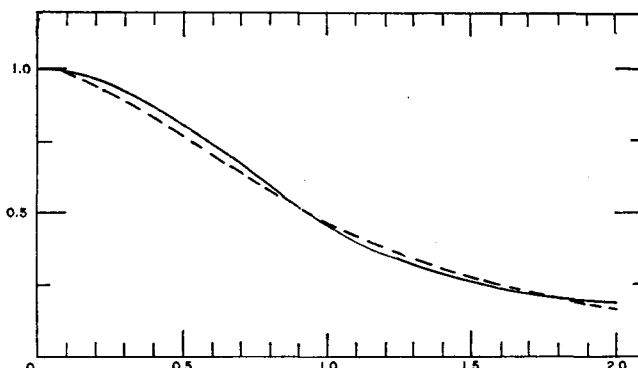
We may introduce a wavenumber dependence

Fig. 1. Rotational correlation functions for liquid methane at $98°K$, transform of infrared absorption band (solid) and result of the model given by Eq. (30) and (31) (dashed). Dimensionless time is defined as $t^*=\sqrt{1/I\beta t}$.

into the model parameters in the damping function, if possible, as done for $D_i'(\kappa, \omega)$ later in Sec. 4.

At this stage we will assume that the couplings between the different degrees of freedom can be ignored[7]. This means that the frequency distribution function is additive, being the sum of contributions from translations, rotations, and vibrations. Denoting each contribution by $f_t(\omega)$, $f_r(\omega)$, and $f_v(\omega)$ respectively, we have

$$f(\omega)=f_t(\omega)+f_r(\omega)+f_v(\omega). \qquad (18)$$

We will also ignore the vibrational motions, since thermal neutrons cannot excite the intramolecular vibrations. Then using Eq. (13) and (18), we obtain

$$D'(\kappa, \omega)=D_i'(\kappa, \omega)+D_r'(\kappa, \omega). \qquad (19)$$

The rotational frequency distribution function $f_r(\omega)$ can be shown to be related to the dipole correlation function $F_1(t)$ according to[7, 13, 16, 22]

$$f_r(\omega)=\frac{2}{3}b^2M\beta\frac{\omega}{\pi}\int_0^\infty dt\cos\omega t F_1(t) \qquad (20)$$

where b is the interatomic bond. Notice that $f_r(\omega)$ is determined solely by $F_1(t)$, not by higher order rotational correlation functions. This is the direct consequence of the Gaussian approximation[17, 22, 23] of the rotational width function occuring in the intermediate scatte-

ring function. For isotropic rotations one has

$$F_1(t)=\langle\vec{b}(t)\cdot\vec{b}(0)\rangle/b^2 \qquad (21)$$

where $\vec{b}(t)$ changes its direction but its magnitude b remains constant, as the molecule rotates, because we ignore the intramolecular vibrational effects. Then the dipole correlation function is entirely determined by the molecular reorientational motions. This function can be calculated using various phenomenological models[22, 26] Gordon[24] has shown that $F_1(t)$ can be obtained from the Fourier transform of a vibrational absorption band, using a time-dependent formulation of infrared absorption. Ignoring the coupling of internal vibrations of different molecules, one can show that

$$F_1(t)=\langle\vec{\mu}(t)\cdot\vec{\mu}(0)\rangle=\int_{band}d\omega\cos\omega t\hat{I}(\omega) \qquad (22)$$

where $\vec{\mu}(t)$ is the dipole moment of the molecule at time t, and $\hat{I}(\omega)$ is the normalized spectrum centered about the vibration frequency. Thus from Eq. (20) and Eq. (22) we have

$$f_r(\omega)=\frac{2}{3}b^2M\beta\omega^2\hat{I}(\omega). \qquad (23)$$

Now we will examine the normalization condition for $D'(\kappa, \omega)$. Agrawal and Yip[7] has shown that the normalization for $f(\omega)$ in a hydrogenous substance is
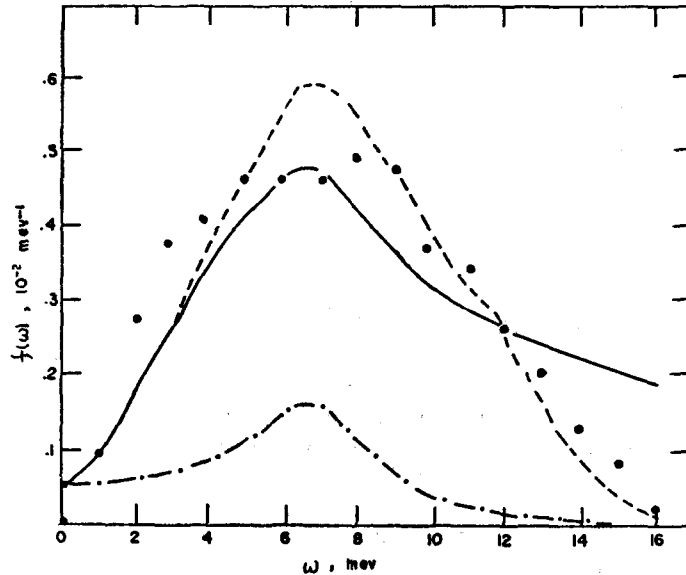
Fig. 2. Comparision of the frequency distribution function of liquid methane, the result of Agrawal and Yip (dashed) and the present model calculated using Eqs. (16) and (32) (dashed) at 98°K in absolute scales, and the result extracted from measurements on solid methane at 22°K, normalized to an area of 5 (circles). The broken line represents the translational contribution

$$\int_0^{\infty} d\omega f(\omega) = M/m_p,\qquad (24)$$

where m_p is the proton mass, by considering the short time behavior of the complex width function of the intermediate scattering function. They have also derived the normalization condition for each contribution of $f(\omega)$ as

$$M/m_p = 1 + \frac{M}{M_r} + \frac{M}{M_v} = \int_0^{\infty} d\omega f_t(\omega)$$

$$+ \int_0^{\infty} d\omega f_r(\omega) + \int_0^{\infty} d\omega f_v(\omega). \qquad (25)$$

In Eq. (25) M_r is the effective rotational mass, which is $3I/2b^2$ with I being the moment of inertia, for a spherical molecule like methane, and M_v is the effective vibrational mass. By ignoring the vibrational effects and using Eq. (17) the normaliozation condition for the damping function becomes

$$\int_{-\infty}^{\infty} \frac{d\omega}{\pi} [D_t{}'(\kappa, \omega) + D_r{}'(\kappa, \omega)]$$

$$= \left(1 + \frac{M}{M_r}\right)/\beta M. \qquad (26)$$

Notice that by neglecting the vibrational effects our damping function will not be adequate at high energies.

In the present work we will use Eq. (14) for the translational damping function. The physical meaning of this model can be seen from the translational frequency distribution function, Eq. (16) and its corresponding velocity autocorrelation (See Eq. (28))[7, 20, 21].

In this model a molecule is pictured as moving in a kind of potential cage fromed by its neighbors, thus oscillating initially and then the cage is relaxing in time due to the restoring forces, which causes the molecule to diffuse into a frictional background. Notice that $D_t{}'(\kappa, \omega)$ satisfies the first two sum rules given by Eq. (7) and Eq. (8), when we treat $S(\kappa, \omega)$ as describing only the translational motions of the center-of-mass of a molecule. Furthermore, we can introduce a wavenumber dependence into $D_t{}'(\kappa, \omega)$ using Eq. (8), if the fourth freduency moment of
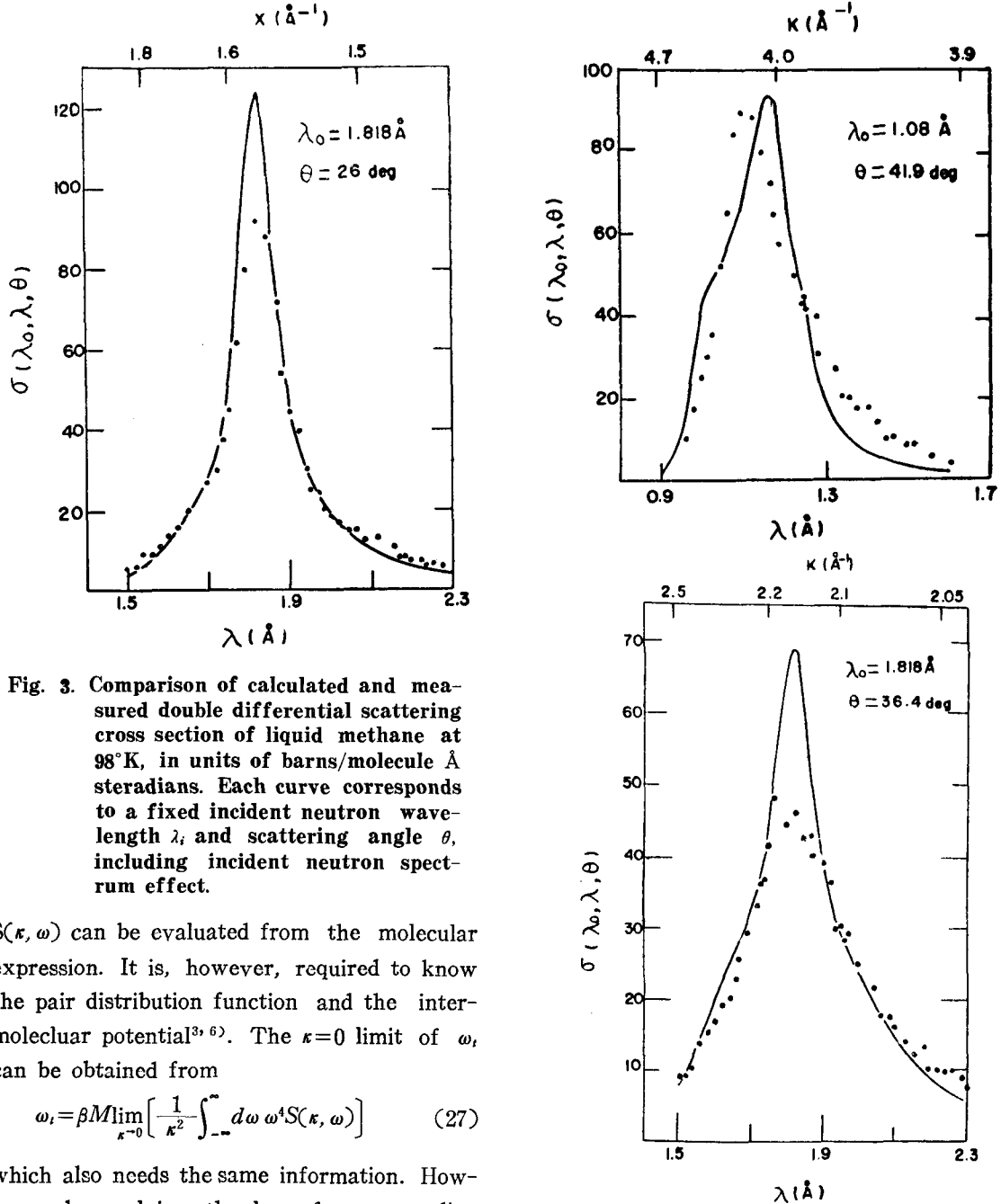
Fig. 3. Comparison of calculated and measured double differential scattering cross section of liquid methane at 98°K, in units of barns/molecule Å steradians. Each curve corresponds to a fixed incident neutron wavelength λ_i and scattering angle θ, including incident neutron spectrum effect.

$S(\kappa, \omega)$ can be evaluated from the molecular expression. It is, however, required to know the pair distribution function and the intermolecluar potential[3, 6]. The $\kappa=0$ limit of ω_t can be obtained from

$$\omega_t=\beta M \lim_{\kappa \to 0}\left[\frac{1}{\kappa^2}\int_{-\infty}^{\infty} d\omega\, \omega^4 S(\kappa, \omega)\right] \qquad (27)$$

which also needs the same information. However, by applying the law of corresponding states to the value for liquid argon[20], we have $\omega_t=1.1\times10^{13}$ sec^{-1} for methane, which will be needed later.

We may interpret $F_1(t)$ as the rotational analog of the velocity autocorrelation function connected with the translational motions of the center-of-mass of the molecule. The velocity autocorrelation function $\psi(t)$ corresponding to the $f_i(\omega)$ of Eq. (16) is given by[20].

$$\psi(t)=e^{-\frac{t}{2\tau_i}}(\cos\Omega_i t+\sin\Omega_i t/2\Omega_i\tau_i) \qquad (28)$$

where

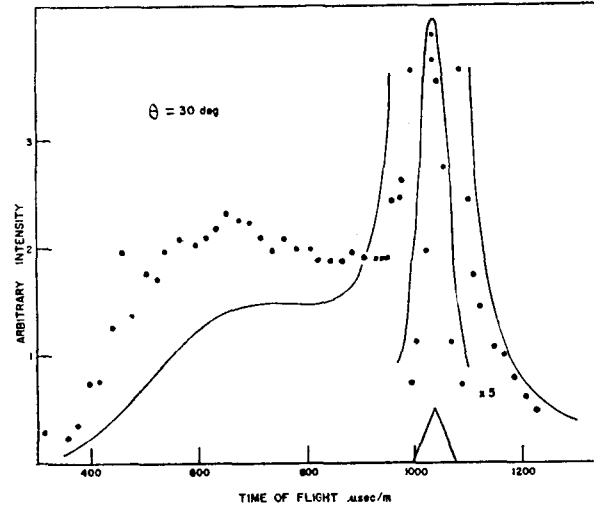$$\Omega_i{}^2=\omega_i{}^2-\frac{1}{4\tau_i{}^2} \qquad (29)$$

Fig. 4. Comparison of calculated and measured double differential scattering cross section of liquid methane at 98°K, in units of barns m/molecule μsec steradians at a fixed scattering angle and the same incident neutron energy of 4.87 MeV. Theoretical results are averaged over the incident neutron spectrum. Dashed curve at θ-90° corresponds to the $\tau_i(0)$ half of the value from Eq. (15). The small triangles indicate the position and width of the incident spectrum.

It is seen that $\psi(t)$ exhibits damped oscillations in time, when $\Omega_r > 0$, whereas $F_1(t)$ for a spherical molecule does not become negative. It can be shown, however, that $\psi(t)$ remains positive, if $\Omega_r{}^2 \leq 0$. The general behavior of $F_1(t)$ from optical line shape data[25] or various models[22, 26] indicates that it decays to zero as $t \to \infty$. Though we can use the $F_1(t)$ obtained from the measurements or the one derived from a realistic model like a Langevin diffusion model[26] in order to calculate $D_r{}'(\kappa, \omega)$, we may consider a simple analytic model for its mathematical simplicity and convenience of physical interpretation. The principal value integral appearing in Eq. (6) can be troublesome, if we use the $F_1(t)$ from the observed spectrum. The Fourier transform of the $F_1(t)$ from the Langevin model also requires a numerical evaluation as well as its principal value integral. A simple exponential form for $F_1(t)$ is good only for long times. Besides, it cannot satisfy the normalization

condition for $D_r{}'(\kappa, \omega)$ in Eq. (26).

We propose a phenomenological model for $F_1(t)$ which can reproduce the general behavior described earlier,

$$F_1(t) = e^{-\frac{t}{2\tau_t}}(\cosh \ \Omega_r t + \sinh \Omega_r t / 2\Omega_r \tau_r)$$
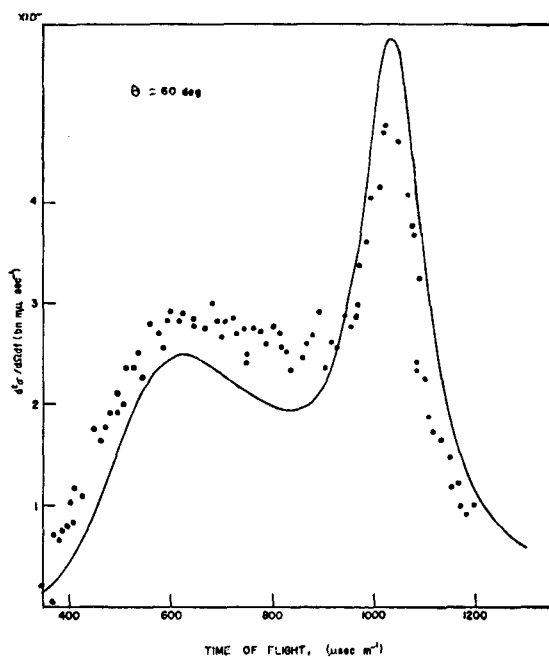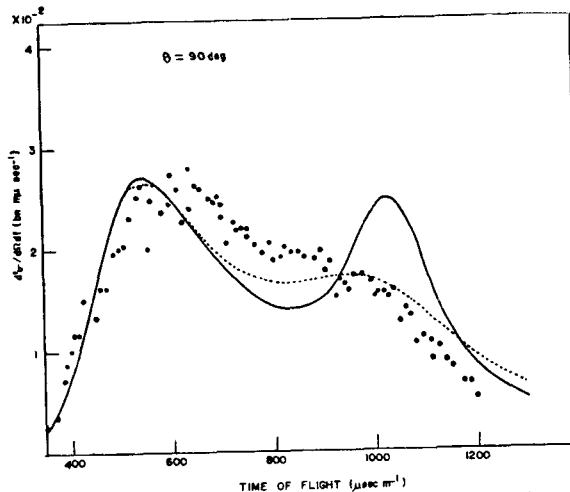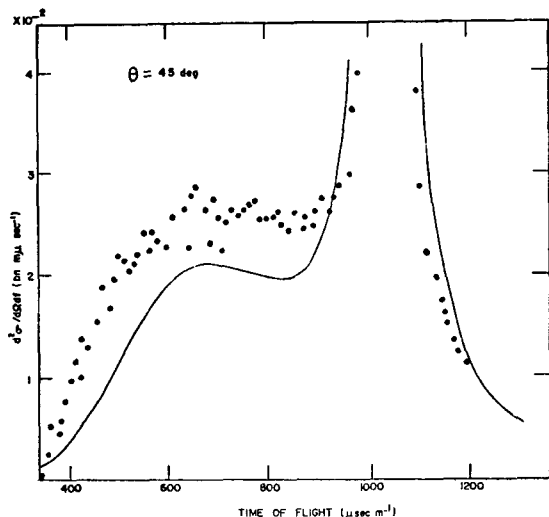
$$(30)$$

where

$$\Omega_r{}^2 = 1/4\tau_r{}^2 - \omega_r{}^2. \qquad (31)$$

The corresponding $f_r(\omega)$ is then given by

$$f_r(\omega) = \frac{2}{3}b^2 M\beta \frac{\omega^2}{\pi} \ \frac{\omega^2/\tau_r}{(\omega^2 - \omega_r{}^2)^2 + (\omega/\tau_r)^2}$$

$$= \frac{2\beta M}{\pi} D_r{}'(\kappa, \omega) \qquad (32)$$

where the second equality holds from Eq. (17). We note that the $F_1(t)$ in Eq. (30) can satisfy Eq. (26), when $M_r = 2m_p$. From the fact that the measured moment of inertia is very close to $8b^2 m_p/3$ for methane, we have $M_r = 4m_p$. We will discuss the implication of this discrepancy later in Sec. 5.

The maximum of the $f_r(\omega)$ in Eq. (32) occurs at ω_r and its gneral features are

TIME OF FLIGHT (μsec m⁻¹)

TIME OF FLIGHT (μsec m⁻¹)

TIME OF FLIGHT (μsec m⁻¹)

τ_r in Eq. (30) is $1/2\omega_r$, when $\Omega_r=0$ corresponding to the fastest decaying $F_1(t)$ with a given ω_r in which case $F_1(t)$ becomes $e^{-t/2}\tau_r$ $(1+t/2\tau_r)$. This function decays faster as τ_r becomes smaller. It is, thus found that in order to fit the $F_1(t)$ derived from the observed infrared spectrum, there should be an upper limit for τ_r. This means a low limit for ω_r. and we find that to reproduce the observed $F_1(t)$ the low limit of ω_r is $2/\sqrt{\beta I}$ which complies with Eq. (33). Moreover, the observed $f_r(\omega)$ shows a maximum near $\omega=2/\sqrt{\beta I}$ (See Fig. 1.). Therefore, we will choose

$$\omega_r=2/\sqrt{\beta I}. \tag{34}$$

For the value of τ_r we can use the $\omega=0$ limit of $\widehat{I}(\omega)$ combined with Eqs. (23), (32), and (34), the result being

$$\tau_r=\frac{\beta I}{4}\left[\int_0^\infty F_1(t)\,dt\right]^{-1}\simeq 0.21\sqrt{\beta I}, \tag{35}$$

Which is also found to give the best fit to the observed $F_1(t)$. In Eq. (35) we use the $F_1(t)$ obtained by Gordon, assuming an expoential extrapolation for long times beyond the data points.

4. Numerical Results in Comparison with Experiments

In this section we will compute the double differential scattering cross section of liquid

very similar to the $f_r(\omega)$ derived from solid and liquid methane measurements. (See Fig. 2.) In Eq. (31) Ω_r should not be less than zero in order to avoid negative values of oscillations of $F_1(t)$. This requires

$$2\omega_r\tau_r=1. \tag{33}$$

From the $\widehat{I}(\omega)$ derived for the freely rotating sphelrical molecule[22]. it can be easily shown that the maximum of the corresponding $f_r(\omega)$ occurs at $\omega=2/\sqrt{\beta I}$. The maximum allowable
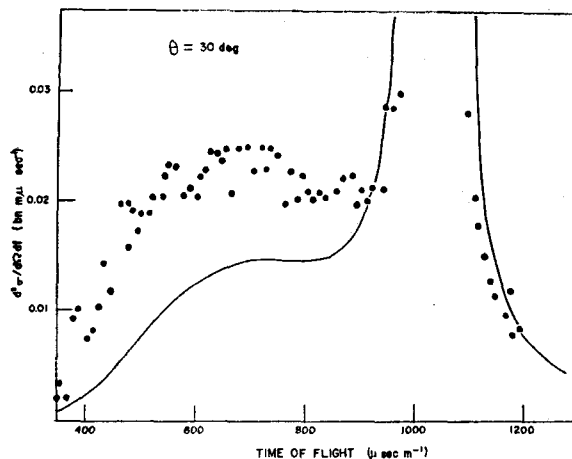
Fig. 5. Same as in Fig. 4, except that measured cross section is normalized to the result of the present calculations.

methane at 98K, and the results will be compared with the thermal neutron data of Harker and Brugger[10] and with the cold neutron measurements of Venkataraman[11] and of Dasannacharya and Venkataraman[12]. The double differential cross section in Eq. (11) is computed using Eq. (6) with $D'(\kappa,\omega)$ in Eq. (19) where $D_t'(\kappa,\omega)$ is given by Eq. (14) and $D_r'(\kappa,\omega)$ by Eq. (32).

In Fig. 1 the rotational correlation function $F_1(t)$ used in our calculation is shown in comparison with the results of Gordon[24]. We have computed the frequency distribution function for our model which consists of Eqs. (16) and (32) and compared in Fig. 2 with the results of Agrawal and Yip who used the $F_1(t)$ from Gordon and those of Harker and Brugger[27] as obtained from their solid methane measurements at 22.1°K. Our results are in absolute scales and the others are normalized to an area of 5. Notice that the $f(0)$ values in our results and those of Agrawal and Yip are matched. Since the translational contribution is the same in both cases, this matching means that the results of Agrawal and Yip are also in absolute scales. We note that the area of our results is 9, which

can be seen from the normalization condition in Eq. (32), the ratio of the translational contribution to the rotational one being 8 with $M_r=2m_p$. Our model overestimates $f(\omega)$ at high frequencies, which is expected from the comparison of $F_1(t)$ at short times as shown in Fig. 1.

The principal value integral in Eq. (6) can be carried out analytically as

$$P\int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{D'(\kappa,\omega')}{\omega'^2-\omega^2} = -(\omega^2-\omega_t^2+1/\tau_t^2)$$
$$[(\omega^2-\omega_t^2)^2+(\omega/\tau_t)^2]^{-1}/\beta M$$
$$-b^2\omega_r^2(\omega^2-\omega_r^2)[(\omega^2-\omega_r^2)^2+(\omega/\tau_r)^2]^{-1}/3.$$

In the previous calculations of $S(\kappa,\omega)$ for liquid argon, we have introduced a wavelength-dependent ω_t into the D_t' (κ,ω) of Eq. (14). This is not possible in the present work, because we do not know the pair distribution function and the intermolecular potential for methane. In the case of using a wavelength-independent ω_t, however, we can make τ_t be wavelength-dependent by interpolating limiting values of the relaxation time. The $\kappa=0$ limit of τ_t is given by Eq. (15). At the opposite limit of short wavelengths one knows that the self correlation function decay

$$\exp[-\omega^2/(\kappa v_0)^2], \text{ where } v_0=(2/\beta M)^{1/2}$$

like is the thermal speed of the particles. Thus qualitatively we expect $\tau_t(\kappa)$ to behave like $(\kappa v_0)^{-1}$ at large κ. Aside from the limiting behavior, not much is known about $\tau_t(\kappa)$. When we use a simple interpolation scheme for $\tau_t(\kappa)$ given by

$$\tau_t(\kappa)^{-1}=\tau_t(0)^{-1}+\kappa v_0 \qquad (36)$$

it is found that the theoretical scattering intensities around quasi-elastic peaks show a better agreement with the data.

For the rotational damping function we use $b=1.0929\text{Å}$, the experimental interatomic bond distance[28], $D_r'(\kappa,\omega)$ given by Eq. (32) with ω_r in Eq. (34) and τ_r in Eq. (35), and any wavelength dependence cannot be introduced,
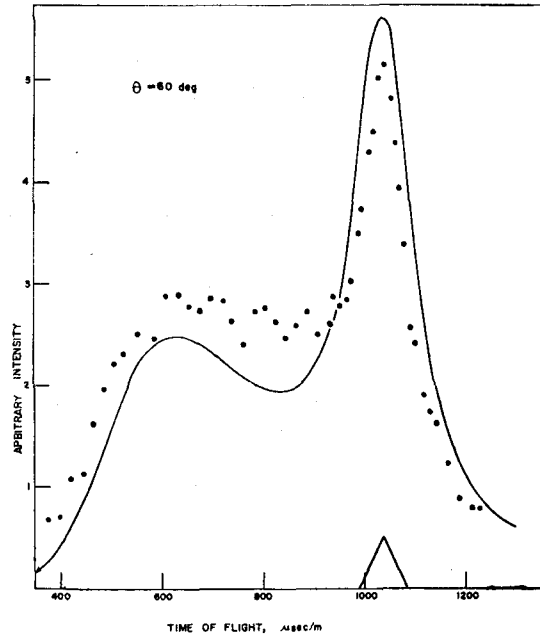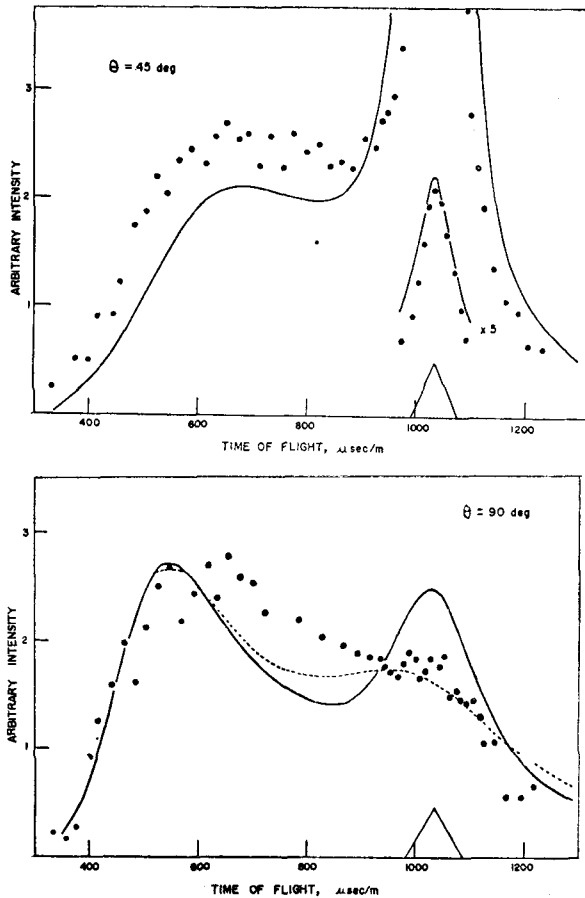
$$\frac{d^2\sigma}{d\Omega d\tau} = \frac{m_n}{\hbar \tau_f{}^3} \frac{d^2\sigma}{d\Omega d\omega} \qquad (38)$$

where τ_f is the time-of-flight of scattered neutrons. The average incident neutron energy is taken to be 4.87 meV and the theoretical results are averaged over the incident neutron spectrum. In Fig. 3 the comparison is shown in the absolute scale, while in Fig. 4 the observed intensiti∘s are normalized to the area of theoretical results, because in the latter case only relative measurements were carried out.

The theoretical intensities of Fig. 3 are obtained by making $M_r = 4m_p$, or equivalently, deviding the $D_r'(\kappa, \omega)$ in Eq. (32) by a factor of 2, while for the time-of-flight spectra we used Eq. (32). This difficulty can be explained by examining the comparison of $f(\omega)$ in Fig. 2. Our model $f(\omega)$ covering the frequency range of the cold neutron data is in good agreement with the $f(\omega)$ obtained from the observed $F_1(t)$, but it deviates considerably from the latter at the higher frequency region of the thermal neutron data. By making $M_r = 4m_p$ we force the higher fre-

because of the lack of information available for any parameter in $D_r'(\kappa, \omega)$.

In Fig. 3 we show the comparison of absolute scattering intensities with the thermal neutron experiments at fixed incident neutron wavelength λ_i and scattering angle θ. The cross sections are given in wavelength length, the conversion from the frequency scale being

$$\frac{d^2\sigma}{d\Omega d\lambda} = \frac{4\pi^2 \hbar}{m_n \lambda_f{}^3} \frac{d^2\sigma}{d\Omega d\omega} \qquad (37)$$

where m_n is the neutron mass and $\lambda_f = 2\pi/\kappa_f$ is the scattered neutron wavelength. The theoretical results include the broadening due to incident neutron spectrum, which is assumed to be a normal distribution.

The comparison of our results with the cold neutron is shown in Fig. 3 and 4. The data were reported in the form of time-of-flight distributions, the conversion being

quency portion of our $f(\omega)$ to be in better agreement with the observed $f(\omega)$. In this regard we feel that if we use the measured $F_1(t)$ instead of the present model, though we have to evaluate the principal value integral numerically, the theoretical intensities will be in better agreement than shown here.

In all the theoretical results we do not include instrumental resolution and multiple scattering contaminations. The latter is expected to appreciably in inelastic scattering region at the smaller scattering angles.

5. Discussions

In this work we have attempted to extend to extend the time correlation function formalism of Martin and Kadanoff, which was successfully applied to the analysis of correlation functions in a simple liquid, to the evaluation of the self correlation fanction of a molecular liquid. The method used in the pressent work is basically the same as for a simple liquid in that the most important part of the procedure is to determine a damping function which satisfies sum rules and hydrodynamic limits. Though the method can be, in principle, useful in evaluating other correlation functions by determining their corresponding damping functions, in the present work the damping function for the incoherent scattering function has been related to the generalized frequency distribution function. This damping function is in general dependent on both frequency and wavelength, and can be exactly related to the frequency distribution function only at the $\kappa=0$ limit. Since we do not know any method to introduce wavelength dependence into the damping function associated with rotational motions of a molecule, we have assumed that there is no wavelength dependence. However, we have found that a wavelength-dependent relaxation time interpolated between the $\kappa=0$ limit and large κ behavior in

the damping function of translational motions gives better results. From the rather satisfactory comparison of our theoretical absolute intensities with the thermal and cold neutron scattering measurements, we conclude that our direct method of calculating the incoherent scattering function is as useful as the indirect method in which the intermediate scattering function is first evaluated.

We have introduced the assumptions of the incoherent approximation, the neglect of translation-rotation coupling effects, and the classical calculation which were discussed in detail by Agrawal and Yip, and hence we will not discuss them here any further. The other assumption that the rotational contribution of damping function is determined solely by the dipole correlation function $F_1(t)$ is the direct result of the Gaussian approximation of the intermediate scattering function. Our procedure does not involve the evaluation of the intermediate scattering function, though we have used the $f_r(\omega)$ based on this assumption. We have also made the assumption about the relation between the damping function and the rotational freqency distribution function. Therefore, we cannot make any conclusion on non-Gaussians correction as done by Agrawal and Yip[7]. In this regard we note that the works of Sears[13] and Rao et al[9], which utilized higher order rotational correlation functions gave the results similar to those of Agrawal Yip in which $F_1(t)$ was mainly responsible for the scattering intensities. For the rotational frequency distribution function we have used a model for the dipole correlation function which reproduces the general behavior of the $F_1(t)$ obtained by Gordon from the observed infrared absorption line data. Our model $F_1(t)$ contains the rexation time and a characteristic frequency of rotational motions which are determined by considering the known quantities such as

the position of the maxima of the observed $f_r(\omega)$ and the $f_r(\omega)$ for a freely rotating spherical molecule, and the $\kappa=0$ limit of the observed infrared absorption spectrum. This $F_1(t)$ gives the correct behavior at long times, but reduces to $1-(4/\beta I)t^2$, in contrast to the free-rotation limit of $1-(1/\beta I)t^2$ at short times. This discrepancy shown in the comprison of $F_1(t)$ at short times is also seen in the comparison of the frequency distribution function, especially in the high frequency region. We feel that this difficulty is not very serious in two regards. First, the comparison of $f(\omega)$ is meaningful only at the $\kappa=0$ limit, because at finite wavelenghs our model includes a wavelength dependence. Secondly, by forcing the effective roational mass in our model to be $4m_p$, as done for the comparison of the thermal neutron scattering intensities, we can have better agreement of $f(\omega)$ at higher frequencies. This broblem can be avoided by using the $f_r(\omega)$ obtained from the measured $F_1(t)$. The roason we used a model for $F_1(t)$ is mainly to see whether a direct evaluation of the scattering function for a molecular liquid is feasible with a simple model for the damping function. It would be interesting to recalculate the scattering intensities using the rotational damping function obtained from the observed $F_1(t)$.

By considering the relative contributions of the translational and rotational damping funcction s in our model, we expect that the contribution to the scattering intensities will be dominated by the rotational motions. It is, however, found that cross sections near quasielstic peaks are very sensitive to the translational damping function. This may be expected from the fact that at the $\omega=o$ limit the rotational damping function does not contribute at all to the total damping function. This sensitivity is shown in the comparison of the cold neutron data at the scattering

angle $\theta=90°$, where we had better agreement using the $\tau_t(0)$ half of the value obtained from the observed self-diffusion coefficient. This means that we used a self-diffusion coefficient larger by a factor of 2 compared to the obsered value. However, we note that we used a wavelength-dependemt relaxation time $\tau_t(\kappa)$. Therefore, this comparison should be interpreted as that considerable wavelengh dependence is to be brought into the relaxation time in a single relaxation time approximation for the correlation function. This point was also raised in the analysis of correlation function in a simple liquid[3, 4]. The reason that we did not make the rotational relaxation time be wavelength-dependent is simply because we do not have any information about its wavelength dependence.

It is interesting to note that our damping function approach to the direct evaluation method makes use of the information contained in the generalized frequency distribution function which plays a key role in the indirect method using the intermediate scattering function. We feel that in order to give a better insight into the molecular motions our method reqires a better knowledge of spatial correlations contained in the quanties such as frequency moments of the scattering function, while the indirect method will need a better description for determining time correlations included in the quantities such as width functions of the intermediate function. This contrast may be one of inherent difficulties in each method.

By making a simple assumption about the frequency dependence of the rotational damping function using the relation between the frequency distribution function and the damping function, and a simple interpolation prescription for the wavelength-dependent relaxation times $\tau_t(\kappa)$, we have been able to obtain the absolute neutron scattering intensities for

liquid methane. The results are at least in semiquantitative agreement with experiments. It would be interesting to see if the present approach can be extended to estimating the coherent scattering function in a moleular liquid arising from molecular motions of different molecules. It would be also useful for the analysis of recent computer studies of molecular dynamics in molecular liquids[30].

Acknowledgement

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