Microscopic model for the neutron dynamic structure factor of solid methane in phase II

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\begin{abstract}
We have constructed a microscopic model for the neutron dynamic structure factor $S(Q,\omega)$ of solid methane in phase II. We expect this model to apply for neutron energies below 1 eV at pressures near 1 bar and temperatures below 20 K where methane possesses both free rotation and hindered rotation modes of the tetrahedral molecules in the unit cell. The model treats the motions of molecular translations, intra-molecular vibrations and the free and hindered rotations of methane molecule as independent. Total scattering cross-sections calculated from the model agree with the cross-section measurements for incident neutron energies of 0.5 meV–1 eV. The effective density of states is extracted from the model. We also present the quantitative calculation of the separate contributions of the two different rotational modes to the inelastic cross-section for different methane temperatures in phase II.
\end{abstract}

1. Introduction

The investigation of neutron phase space cooling forms a small but interesting subfield of research which can be seen as a particular example of phase space compression of particle beams. Since the statistical accuracy of a scattering experiment involving incoherent beams, in which one typically restricts the initial and final states of the particles in the beam in the course of preparing the required states of interest, is directly proportional to the phase space density of the particles in the beam, the investigation of methods for phase space compression of ensembles of particles is of general interest \cite{1}. Furthermore, since the motion of the particles before and after encountering the target typically needs to be free of energy dissipation in any scattering experiment in order to interpret the measurement directly in terms of a scattering cross-section, Liouville's theorem applies to this portion of the motion. In this case, the statistical accuracy of the measurement is proportional to the initial phase space density in the source that provides the beam. A wide variety of techniques for phase space compression have been developed for several different types of particle beams in various areas of physics, from stochastic and electron cooling in high energy charged particle accelerators to laser cooling of neutral atoms to form Bose–Einstein condensates.

Seen in this context, the phase space compression of slow neutral particles such as neutrons is especially challenging. Since the neutrons of interest exist in an energy range (meV–eV) in which the neutron does not ionize condensed matter, the usual mechanisms of phase space compression for charged particles are unavailable. The only efficient way at present to increase neutron phase space density is through inelastic collisions in a cold medium. In this case, we must resolve a contradiction: when we cool the medium to the very low temperatures for which a neutron ensemble in equilibrium possesses a energy spectrum in the meV range, the degrees of freedom which can interact elastically with slow neutrons tend to freeze.

In addition, the neutron wavelength becomes larger than the separation of scatterers in the medium and so the total cross-section is dominated by elastic processes and several collisions in the medium are needed to cool the neutrons. Furthermore, it is known that the cross-sections for neutron cooling through phonon creation suffer from shrinking accessible phase space for lower energy neutrons, and therefore one cannot simply stick slow neutrons in an arbitrary cold solid medium and expect the neutrons to efficiently cool to the temperature of the medium.

We also must take into account the increased importance of neutron absorption for slow neutrons: since neutron absorption increases for slower neutrons of velocity $v$ as $1/v$. It should be clear from these considerations that the search for a medium in which the neutron energy is reduced in the smallest number of collisions possible is a worthy subject for research.

Neutron scattering from solid methane has special importance in cold neutron moderation for a number of reasons. First of all, solid CH$_4$ possesses a high number density of hydrogen atoms, and since the isolated hydrogen atoms have large scattering cross-sections, the neutron mean free path is small and the neutron brightness emitted from such a source can be high. Second, the
high symmetry of the CH₄ molecule leaves a significant fraction of the methane molecules free to rotate in the solid phase even temperature close to $T \approx 0$ K [2]. The resulting inelastic rotational excitation modes are more efficient than phonons and are responsible for the experimental observation that solid methane is one of the best-known cold neutron moderating media [3].

The purpose of this paper is to present a description of the dynamics of neutron scattering of solid methane in phase II, construct the dynamic structure factor $S(Q,\omega)$, and use it to investigate the separate contributions from the different excitation modes. In this phase, 1/4 of the methane molecules in the solid are free rotors, but the remaining molecules become trapped in orientational potential in which they librate and among which they can tunnel. The complete dynamics of the crystal include inter-molecular vibrations, intra-molecular vibrations and intra-molecular rotations. For methane molecules in the solid state, these excitation modes are sufficiently decoupled to treat them as independent modes.

Such an analytical treatment is very useful to gain physical insight into the dependence of cold neutron brightness upon the individual dynamic modes of solid methane. Many authors have speculated that the cold neutron brightness from a methane moderator might be enhanced if the motion of solid CH₄ can be modified in some way to free all the rotational modes, since the free rotation mode has a relatively large inelastic component to its neutron scattering cross-section. However, the librational and tunneling motions in methane also introduce new energy levels into the excitation spectrum, some of which are at lower energy than those of the free rotor states. Since these modes cannot be neglected in a complete description of phase II solid methane, it has never been clear what the relative importance of the two rotational modes is for neutron cooling.

Even though there was an interesting approximate analysis by Utsuro [4] of this issue, the relative importance of the rotational modes to the effectiveness of neutron moderation at temperatures below 20K was not established. For the first time, we have constructed a model which is accurate enough to be able to answer this question quantitatively with the dynamic structure factor $S(Q,\omega)$. The direct relationship of two separate rotational modes to the neutron brightness will be present in separate paper.

The rest of the paper is organized as follows. Section 2 briefly reviews the relationship between the phase space density and the dynamic structure factor $S(Q,\omega)$. Section 3 discusses the structure of solid methane in phase II and summarizes relevant past work on both theoretical descriptions of the states of the system and key experimental results that are important for our calculation. Section 4 discusses our neutron scattering model of solid methane. We present the results including neutron cross-section and spectral intensity in Section 5. We conclude and suggest further work in Section 6.

2. Neutron phase space density and $S(Q,\omega)$

The fundamental object of interest in neutron phase space compression or moderation is the phase space distribution function $f(r,v,t)$, where $f(r,v,t)drdv$ is the average number of neutrons in the phase space element $drdv$ at time $t$. Since neutron–neutron interactions can be neglected for practical moderators, the moderation of neutrons in a medium is described by a Boltzmann equation of the form

$$\left(\frac{\partial f}{\partial t} + v \cdot \nabla f\right)f(r,v,t) = -\rho v \sigma_d(v)f(r,v,t)$$

$$+ \int \rho v \sigma_s(v_0,v)f(r,v_0,t)dv_0 - \int \rho v \sigma_s(v,v_0)f(r,v,t)dv_0$$  \hspace{1cm} (1)

where $v = |v|$ is the neutron speed, $\rho$ is the density of the medium, $\sigma_d(v)$ is the neutron absorption cross-section, and $\sigma_s(v_0,v)$ is the scattering kernel. The first term integral term in Eq. (1) can be understood to represent “downscattering” of the neutron of velocity $v_0$ to velocity $v$ and the second integral term can be understood to represent “upscattering” of the neutron of velocity $v$ to velocity $v_0$.

In terms of the double differential scattering cross-section $d^2\sigma$, defined as the average number of incident particles with velocity $v_0$ scattered into the volume element $dv$ per atom per unit time per unit incident flux, the scattering kernel is defined by

$$d^2\sigma = \sigma_s(v_0,v)dv$$

which is expressed in spherical coordinates in terms of the scattered neutron energy $E = \frac{1}{2}mv^2$.

If $(\theta,\phi)$ are the polar coordinate of $v$ with respect to $v_0$ as polar axis, then $dv = v^2 dv \sin \theta \, d\theta \, d\phi = \frac{1}{2} \, d\Omega \, dE$. The double differential scattering cross-section becomes

$$\frac{d^2\sigma}{d\Omega \, dE} = \frac{v}{m} \sigma_s(v_0,v).$$  \hspace{1cm} (3)

On the other hand, the usual expression for the double differential scattering cross-section is

$$\frac{d^2\sigma}{d\Omega \, dE} = \left(\frac{\sigma_s}{4\pi\hbar}\right) \frac{v}{v_0} S(Q,\omega)$$

where $S(Q,\omega)$ is the dynamic structure factor [6], $\sigma_s$ is the bound scattering cross-section per atom, and $Q$ and $\omega$ are the momentum and energy transfers from the neutron to the medium. Comparing Eqs. (3) and (4), one can see that the scattering kernel is directly proportional to the dynamic structure factor,

$$\sigma_s(v_0,v) = \left(\frac{m \sigma_s}{4\pi\hbar v_0}\right) S(Q,\omega)$$

and that the rate of neutron moderation per collision is proportional to the neutron dynamic structure factor $S(Q,\omega)$ in the medium.

The theory of neutron moderation has been developed for nuclear engineering and related applications in the energy regime between the typical energy which neutrons possess upon liberation from nuclei (MeV) to the kinetic energies of atoms in matter at room temperature ($\sim$ 25 MeV). In this regime $S(Q,\omega)$ can be calculated analytically and the answer is discussed in nuclear engineering textbooks [7]. For neutron with energy below the energies of motion of the moderating medium, however, the situation is qualitatively different. In this case, the neutron wavelength is larger than the separation between atoms in the medium, and the scattering exhibits strong interference effects which depend on the details of the structure and modes of motion of the medium. The problem of neutron phase space cooling then reduces to the calculation of $S(Q,\omega)$.

3. Solid methane in phase II

Methane at low temperatures has two distinct solid phases. The detailed phase diagram is shown in Fig.1. At equilibrium vapor pressure, phase I appears from the triple point temperature (90.6 K) to the transition temperature (20.4 K) into phase II. In phase I, methane has a face-centered cubic (fcc) structure with four orientationally disordered molecules per unit cell [8].

The phase change is associated with an incomplete orientational order and the introduction of sites with point group symmetry of D₂h and O₁h in phase II.¹ The center of mass of each

¹ Strictly speaking the point symmetry of the high-symmetry sites is O, but the crystal field at these sites has symmetry O₁h.
molecule is located on the site of the fcc lattice in phase II. Fig. 2 shows the partially ordered structure of phase II. The unit cell of phase II contains 32 molecules. Three-fourths of the molecules are hindered rotors which librate in the minima of a strong orientational potential of D_{2d} symmetry. The other 1/4 of the molecules are free rotors.

This structure was predicted by James and Keenan on the basis of electrostatic octopole–octopole interactions [10]. The structure of phase II was experimentally determined by Press [11] through neutron diffraction on CD_{4}.

In solid CH_{4}, phase II is stable in the temperature range 22 K \leq T \leq 27 K. Although the structure of CH_{4} was not possible to determine directly using neutron scattering because of the high incoherent neutron cross-section of protons, Press assumed that the experimentally measured symmetry of CD_{4} implies the same orientational structure for CH_{4}. The effect of spin correlation on the neutron scattering dynamics has been described for CH_{4} [12] and also in the similar cases of NH_{3} [13] and CH_{3} [14].

3.1. Rotational excitation of free rotor: O_{h} symmetry

In phase II, the methane crystal has the same fcc translational structure as in phase I but with eight sublattices. The eight sublattice structure consists of six ordered sites with point group symmetry D_{2d} and two disordered sites with point group symmetry O_{h}. The site of O_{h} symmetry feels only a weak crystalline field and no molecular field. Therefore, the methane molecules on this site are almost free quantum rotors [2].

The Hamiltonian of the Extended James–Keenan (EJK) model for molecule i in a crystal field V_{c} is

\[ \hat{H}_{i} = K_{i} + f_{c} \sum_{l=4}^{6} V_{c}(\omega_{l}^{j}) = K_{i} + f_{c}(\beta_{4}(\omega_{4}^{j}) + \beta_{6}(\omega_{6}^{j})) \]

using the notation of Yamamoto et al. [5]. The numerical values of \beta_{4} and \beta_{6} are listed in Table I of Yamamoto et al. [5]. \( K_{i} \) is the operator for the rotational kinetic energy. The parameter \( f_{c} = 1.25 \) was determined from experiment by fitting the strength of the observed crystalline field [5]. The rotational wave function is given by the standard Wigner D functions \( D_{l,k,m}^{j}(\omega) \) [16]. The rotational states of a tetrahedral rotor with potential parameters determined for CH_{4} are shown in column B of Fig. 3.

The energy levels are classified through the symmetry \( T^{f} \) of the corresponding wave function. The label \( T^{f} \) denotes the 25 irreducible representations of the direct product group \( \mathbf{O} \times \mathbf{O} \) which describes the symmetry with reference to the crystal-fixed frame (\( f \)) and with reference to the molecular fixed frame (\( T \)). The total wave function of a CH_{4} molecule is the product of a rotational wave function and a spin wave function. Since protons are spin 1/2 particles, the total wave function must be antisymmetric under a permutation of any two protons. Therefore, each state is related to a representation \( A, T \) and \( E \) corresponding to the total nuclear spin \( I = 2 \) (ortho), \( I = 1 \) (meta) and \( I = 0 \) (para), respectively. By conservation of angular momentum in s-wave
scattering, the state $E_E$ cannot be reached by neutron interactions from the ground state $A_A$ [2].

A simple description in terms of the energy levels of CH$_4$ beginning with $J=0$ (A symmetry, $l=2$) for the ground state has been given by Ozaki et al. [17]. As may be seen in column A and B of Fig. 3, the $J=1$ (T symmetry, $l=1$) level is lowered from the free rotor value by 25% due to crystal field effects. The $J=2$ (E symmetry, $l=0$) level is split by the reduced local crystal field into four energy levels. The energies of the transitions between rotational energy levels are 1.09 meV for the $J=0\rightarrow J=1$ transition, 1.56 meV for the $J=1\rightarrow J=2$ transition and 2.65 meV for the $J=0\rightarrow J=2$ transition.

3.2 The rotational tunneling in molecular field: $D_{2d}$ symmetry

The molecule on the orientationally ordered lattice points of CH$_4$ not only librates in the minima of the orientational potential but also tunnels between each of the indistinguishable equilibria in the rotational motions of the CH$_4$ molecule. The rotational tunneling is accessible from various librational states of the molecule. Since the rotating axes are indistinguishable [18], this tunneling leads to a splitting between the states. The calculation of eigenstates for the orientational motion using free rotational wave functions was performed in the framework of EJK model by Yamamoto et al. [5]. These procedures required a diagonalization of an infinite dimensional Hamiltonian matrix. Although the procedure converged quickly because of the weak orientational potential, the wave functions of these tunneling levels are only slightly different from those of the completely free rotor.

An alternative approach was developed by H"uller and Kroll using a “pocket state” to treat the rotational and tunneling excitations in molecular crystals [19,20]. A systematic representation is shown in column C of Fig. 3. A rotational potential with $n$ minima on two or three dimensional unit sphere was considered. These minima have a symmetric relation to each other. A set of minima on two or three dimensional unit sphere was considered.

The whole molecule oscillates in the crystal lattice. Finally, the protons vibrate around their equilibrium positions within the molecule.

The total neutron scattering cross-section is evaluated from the usual expression

$$\frac{d^2\sigma}{d\Omega dE} = b^2 \left( \frac{k_i}{k_f} \right) S(Q,\omega)$$

where $b$ denotes the scattering amplitude and $k_i$ and $k_f$ the momentum of the neutron before and after the scattering. By integrating $S(Q,\omega)$ over the solid angle $\Omega$ and the neutron energy transfer $\omega$, the total cross-section $\sigma_{nr}$ can be obtained.

The scattering function $S(Q,\omega)$ depends on the complete set of modes of the methane molecule; intra-molecular rotations of tetrahedron about the center, center, inter-molecular transitions of the center of mass and intra-molecular vibrations. Then $S(Q,\omega)$ may be written as a convolution of the dynamic structure factors for the different dynamic modes of the motion:

$$S(Q,\omega) = S_{rot}(Q,\omega) \otimes S_{trans}(Q,\omega) \otimes S_{vib}(Q,\omega).$$

Each dynamic mode in Eq. (9) is characterized by a definite spectrum $\rho_i(\omega)$ of the excitation in each mode. To determine the total excitation energy of the solid methane which occur in neutron scattering, we must know the excitation spectra of all of the modes and the statistics obeyed by the quanta belonging to each mode. In the first approximation, the total excitation energy of the solid system can be represented as

$$E_{total} = \int \int dE \rho(\omega) dE = \sum \int dE \rho_i(\omega) dE$$

where $d[E]$ is the distribution function. We assume that the coupling among the different dynamic modes can be ignored. In our case, this means that the total excitation spectrum is the sum of contribution from rotations, translations and vibrations. Denoting each contribution by $\rho_{rot}(\omega)$, $\rho_{trans}(\omega)$ and $\rho_{vib}(\omega)$ respectively, the total excitation spectrum $\rho(\omega)$ is

$$\rho(\omega) = \rho_{rot}(\omega) + \rho_{trans}(\omega) + \rho_{vib}(\omega).$$

$E_{rot}=6.5$ meV. Transitions between levels of different symmetry cannot be induced by phonon interaction alone, but are mediated by the weak dipole–dipole interaction among protons. As a consequence, the spin system shows slow thermal relaxation after a change of the lattice temperature [22].

Theoretical and experimental works have been performed on the temperature dependence of $D_{2d}$ energy levels below $T=4K$. Yamamoto et al. [5] predicted the temperature dependence of the tunneling levels based on the EJK model. Their theoretical prediction was made for an equilibrium mixture of spin species. The tunneling level spacings at 0K were about 10% larger than those at 4K in their study. Some experiments indicated the temperature dependence of tunneling states of CH$_4$ both in decreasing temperature [23] and in approaching phase transition temperature [24]. By contrast, the rotational levels of $O_h$ molecules were predicted to be independent of temperature. Press et al. [12] measured this level spacing of disordered rotational system of methane at $T=5K$ and $T=0.1K$ with inelastic neutron scattering. It showed that $J=1$ energy level at $T=0.1K$ remains unchanged at $T=5K$. In this paper, we assume that the energy levels of both ordered and disordered molecules are unchanged over the temperature range from $0K < T < 20.4K$. 

4. Neutron cross-section model of solid methane

A methane molecule in a crystal shows three different dynamic modes depending on incident neutron energy $E_n$. The rigid $H_4$ tetrahedron rotates about the central carbon atom. The whole molecule oscillates in the crystal lattice. Finally, the protons vibrate around their equilibrium positions within the molecule.
Egelstaff and Schofield [25] developed a relationship between \( \rho(\omega) \) and \( S(Q,\omega) \) in the incoherent approximation. In this approximation, the total excitation spectrum \( \rho(\omega) \) is related to \( S(Q,\omega) \) by

\[
\left( \frac{S_{\text{inc}}(Q,\omega)}{Q^2} \right)_{Q=0} = \frac{\hbar}{2M} \frac{\rho(\omega) \exp\left( \frac{\hbar \omega}{2k_B T} \right)}{2\omega \sinh(\hbar \omega/2k_B T)}.
\]

(12)

The detailed description of the Eq. (12) will be in Section 4.3. From the Eqs. (11) and (12), the incoherent scattering function \( S(Q,\omega) \) in Eq. (9) can be easily approximated as

\[
S(O,\omega) \approx S_{\text{rot}}(Q,\omega) + S_{\text{trans}}(Q,\omega).
\]

(13)

In addition, each dynamic mode of solid methane actually dominates in different incident neutron energy regimes \( E_n \). For \( E_n \leq 6.5 \text{ meV} \), the protons in solid CH\(_4\) behave like bound particles. Only the lowest few orientational energy levels are thermally populated in the solid at low temperatures, while the molecules are in their translational and vibrational ground states [9]. Therefore, the scattering function \( S(Q,\omega) \) in this energy region can be approximated as

\[
S(Q,\omega) \approx S_{\text{rot}}(Q,\omega).
\]

(14)

For \( 6.5 \text{ meV} \leq E_n \leq 165 \text{ meV} \), the \( H_4 \) tetrahedron reaches its rotational “free” state and the librational degrees of freedom are active. The cross-section for excitation of rotational degrees of freedom significantly decreases, and the cross-section for molecular oscillations in the crystal lattice appears,

\[
S(Q,\omega) \approx S_{\text{rot}}(Q,\omega) + S_{\text{trans}}(Q,\omega).
\]

(15)

Finally, when neutrons reach the energy \( E_n \approx 165 \text{ meV} \), the protons start to behave like individual free particles. The neutron scattering is then dominated not only by multiple inelastic scattering, but also by vibration of the tetrahedrons,

\[
S(Q,\omega) \approx S_{\text{trans}}(Q,\omega) + S_{\text{vib}}(Q,\omega).
\]

(16)

4.1. Rotational excitation

The rotational excitations of solid methane in phase II were taken from Ozaki’s work [17,26] which has more complete description of rotational excitation of methane. The double differential cross-section for rotational motion can be divided into two parts:

\[
\frac{d^2\sigma}{d\Omega d\omega} = \left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{spin–ind}} + \left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{spin–dep}}.
\]

(17)

Each term of Eq. (17) represents coherent and incoherent scattering in the rotational system as

\[
\left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{spin–ind}} = b_{\text{inc}} \frac{k_f}{k_i} p_i(T) g_i g_f \sum_{l=0}^{\infty} (2l+1) j_l^2 (kr) \times f_{ij}^l \delta(h\omega + E_f - E_i) \times e^{-\gamma_{\text{rot}}Q^2}
\]

\[
\left( \frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{spin–dep}} = b_{\text{inc}} \frac{k_f}{k_i} p_i(T) g_i g_f \sum_{l=0}^{\infty} (2l+1) j_l^2 (kr) \times G_{ij}^l \delta(h\omega + E_f - E_i) \times e^{-\gamma_{\text{rot}}Q^2},
\]

(18)

in which the coherent scattering corresponds to the spin-independent part and the incoherent part to the spin-dependent part. \( p_i(T) \) are the usual occupation probabilities for the initial states in thermal equilibrium

\[
p_i(T) = \exp\left(-E_i/k_BT\right)/\sum_i \exp(-E_i/k_BT).
\]

From Eq. (18), the scattering functions for molecular rotations in each rotational state are

\[
S_{\text{rot}}(Q,\omega)_{ij} = p_i(T) g_i g_f \sum_{l=0}^{\infty} (2l+1) j_l^2 (kr) \times f_{ij}^l \delta(h\omega + E_f - E_i) \times e^{-\gamma_{\text{rot}}Q^2}
\]

\[
S_{\text{rot}}(Q,\omega)_{ij} = p_i(T) g_i g_f \sum_{l=0}^{\infty} (2l+1) j_l^2 (kr) \times G_{ij}^l \delta(h\omega + E_f - E_i) \times e^{-\gamma_{\text{rot}}Q^2}.
\]

(19)

Here \( g_i \) and \( g_f \) denote the degeneracy of the initial and final states and \( F_{ij}^l \) and \( G_{ij}^l \) are overlap integrals between the initial and final states which were calculated in Ozaki’s work [17,26]. \( S_{\text{rot}}(Q,\omega) \) and \( S_{\text{rot}}(Q,\omega) \) represent coherent and incoherent scattering from the rotational mode. \( j_l(kr) \) is the spherical Bessel function. The \( \mathbf{r} \) stands for C–H distance within a methane molecule (\( r=1.093 \text{Å} \)) and \( \gamma_{\text{rot}} = 2.15 \times 10^{-4} \text{nm}^2 \) represents an effective Debye–Waller factor, whose value we take from previous work by Grier et al. [9].

After summing over all initial and final states, the complete expression for the scattering function for molecular rotations in solid methane including coherent and incoherent parts is

\[
S_{\text{rot}}(Q,\omega) = \sum_l (S_{\text{rot}}(Q,\omega)_{ij} + S_{\text{rot}}(Q,\omega)_{ij}).
\]

(20)

4.2. Intermolecular vibrations: multi-phonon excitations

The incoherent scattering from a Bravais lattice due to one-phonon processes is

\[
\frac{d^2\sigma}{d\Omega d\omega} = b_{\text{inc}} \sum_{q} \frac{k_f}{k_i} \delta(h\omega + hf) (\mathbf{Q} \cdot \mathbf{V})^2 \times \frac{\hbar \left( \frac{n+1}{2} + \frac{1}{2} \right)}{2Mf} \times e^{-\gamma_{\text{rot}}Q^2},
\]

(21)

where \( \mathbf{Q} \) denotes momentum transfer and \( \mathbf{V} \) is the polarization vector for each phonon mode [27]. The model parameter is \( \gamma_{\text{rot}} = 2.08 \times 10^{-4} \text{nm}^2 \) which was found from fitting the experimental neutron scattering cross-section data across 10 meV over all temperatures.

If we take an average over constant frequency surface, the incoherent cross-section may be written as

\[
\frac{d^2\sigma}{d\Omega d\omega} = b_{\text{inc}} \int_0^\infty df(zf) k_f \frac{\hbar}{k_i} (\frac{n+1}{2} + \frac{1}{2}) \times e^{-\gamma_{\text{rot}}Q^2} \delta(h\omega + hf),
\]

(22)

where \( z(f) \) is the frequency of the phonon mode and cubic symmetry has been assumed.

Since phonons of different wave vectors are independent in the incoherent approximation, the multi-phonon scattering can be easily generalized for the one phonon case. We considered different phonon modes which change their population by \( \pm 1 \). Thus, the cross-section for neutron scattering is

\[
\frac{d^2\sigma}{d\Omega d\omega} = b_{\text{inc}} N \frac{k_f}{k_i} \prod_{l=1}^{n} \left( \int_{-\infty}^\infty df(zf) \frac{\hbar^2 Q^2 / 2M}{e^{\beta_i/f zf}} \right) \times e^{-\gamma_{\text{rot}}Q^2} \delta \left( h\omega + \sum \hbar f_l \right).
\]

(23)
Using the Debye approximation, it is possible to integrate to obtain the cross-section of $n$-th phonon scattering $\sigma_{\text{trans}}^n$. The total inelastic incoherent cross-section of translational motion (phonon scattering) is then given by

$$\sigma_{\text{trans}}^{\text{inc}} = \sum_{n=1}^\infty \sigma_{\text{trans}}^n.$$  \hfill (24)

The scattering function of translational motion $S_{\text{trans}}(Q,\omega)$ is now written as

$$\frac{d^3\sigma_{\text{trans}}^n}{d^3Q d\omega} = \sum_{n=1}^\infty \frac{1}{n!} \left( \int_{-\infty}^\infty df \frac{2 f_n}{f_n} \right) \frac{\hbar^2 Q^2}{2M} \exp(-\varepsilon f_n) \times e^{-\frac{\omega^2}{2}} \times \delta\left(\hbar \omega + \sum f_n\right).$$  \hfill (25)

In our model, we include the effects of multi-phonon excitation up to $n=5$ since even though one phonon processes are predominant throughout most of the neutron energy range at low temperature, the probability of 2 and 3 phonon processes cannot be neglected above a certain energy near 20 K.

4.3. Intramolecular vibrations

From the simple harmonic oscillator model [6], the scattering function for intramolecular vibration $S_{\text{vib}}(Q,\omega)$ is

$$S_{\text{vib}}(Q,\omega) = \frac{1}{2\pi h} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \times \left\langle \exp(-iQ \cdot \mathbf{r}) \exp(iQ \cdot \mathbf{r}(t)) \right\rangle.$$  \hfill (26)

We simply use the scattering function of the vibrational mode from the book [6] as

$$S_{\text{vib}}(Q,\omega) = \exp\left(-\gamma_{\text{vib}} Q^2 + \frac{1}{2} \omega \hbar \beta\right) \sum_{n=\infty}^\infty I_n(y) \delta(\omega - n\hbar \omega_0).$$  \hfill (27)

where $\omega_0$ is normal vibration frequency. A methane molecule has four normal vibrations with characteristic energies of $\hbar \omega_0 = 168, 172, 376, \text{and } 391 \text{ meV}$ [28]. The model parameter, $\gamma_{\text{vib}} = 0.31 \times 10^{-3} \text{ nm}^2$, was calculated from Eq. (27) using the first two characteristic energies $\hbar \omega_0 = 168, 172 \text{ meV}.$

5. Results and discussion

5.1. Scattering function $S(Q,\omega)$ of solid methane

The total scattering function of solid methane is the convolution of scattering functions of the three different modes. In our model, we treat this total scattering function as the linear combination of each scattering function depending on incident neutron energy as mentioned on Eq. (16). This is an approximation to calculate the total scattering function in which each different scattering mode dominates in different neutron energy regimes. We show the 3D plot of $S(Q,\omega)$ at 20 and 4 K as a function of momentum transfer ($Q = 0-10 \text{ Å}^{-1}$) and energy transfer ($\hbar \omega = 0-20 \text{ meV}$) in Figs. 4(a) and (b). Based on our assumption in Section 2, the scattering function of solid methane at $T=0$ K is also present in Fig. 4(c).

In these figures, the two peaks with lower energy transfer ($0 \leq \hbar \omega \leq 10 \text{ meV}$), labeled as 1 and 2, represent energy and momentum transfers from the rotational modes. The long knoll around $\hbar \omega \approx 12 \text{ meV}$ comes from multi-phonon excitations. For lower temperatures, the overall probability for energy transfer from the rotational mode is increased while the energy transfer from multi-phonon scattering is suppressed as expected.

The main difference of $S(Q,\omega)$ at 0 K from 20 and 4 K is the scattering probability in the low $Q,\omega$ region labeled as peak 1. It increases by 40% at 0 K from 4 and 20 K. On the other hand, the intensity of peak 2 reduces by 20% and peak 3 changes less. The reason is that, as the temperature lowered below 4 K, the spin conversion begins to occur among the tunneling levels of different symmetry and the ground state with A ($I=2, \ J=0$) symmetry becomes increasingly populated. Consequently, this makes the $A \rightarrow T$ transition more intense [5].

5.2. Generalized frequency spectrum

The dynamics of a given system can be described by establishing the corresponding space-time correlation functions $G(r,\tau)$. If the system includes a large number of particles, one can use the statistical independence of widely separated particles and assume that if the particle B is far distant from particle A, the influence from particle B on particle A can be neglected.

For small $r$ and $\tau$, it is expected on general grounds that the important part of the scattering law for neutron thermalization is the self-term $G(r,\tau)$ defined as the Van-Hove self-correlation function.
function
\[ G_\text{r}(r, \tau) = \frac{1}{N} \sum_r \int \frac{dr'}{4\pi} \delta(r + r_0(0) - r') \delta(t' - r_0(\tau)) \]  
(28)

which gives rise to the scattering function
\[ S(Q, \omega) = \frac{1}{2\pi} \int e^{iQ \cdot r - \omega t} G_\text{r}(r, \tau) \, dr \, dt. \]  
(29)

Eq. (28) is the velocity–velocity correlation function for the motion of an atom in the medium [29]. The correlation function has a very simple interpretation in classical limit. However, it is still possible to describe the dynamics of a quantum mechanical system with a connection between the real and imaginary parts of correlation functions [30]. The interpretation of this function as a generalized frequency spectrum is as follows: one imagines that the velocity of an atom is measured at certain time \( t_1 \). Then its velocity is remeasured at a later time \( t_2 \). The product of these two velocity measurements is taken and averaged over all values of the velocity which may be generated by thermal excitation of the system to define the function \( P(\omega) \) [31].

\[ \left( \frac{\omega^2 \exp \left( -\frac{i\omega}{2k_B T} S(Q, \omega) \right)}{Q^2} \right) q \rightarrow 0 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle v_Q(0)v_Q(t) \rangle e^{\omega t} \, dt = \frac{k_B T}{2M} \rho(\omega). \]  
(30)

The function \( P(\omega) \) defined in this way is a complex function and its real and imaginary parts are related to the \( P(\omega) \) as

\[ \text{Im} \langle v_Q(0)v_Q(t) \rangle = \frac{\hbar}{2M} \int_0^{\infty} \omega \rho(\omega) \sin(\omega t) \, d\omega \]
\[ \text{Re} \langle v_Q(0)v_Q(t) \rangle = \frac{k_B T}{2M} \int_0^{\infty} P(\omega) \frac{\cos(\omega t)}{\cosh(h\omega/2k_B T)} \, d\omega \]  
(31)

where \( \rho(\omega) = P(\omega) \sinh(h\omega/2k_B T)/h\omega/2k_B T \) is the generalized frequency spectrum, with normalization condition \( \int_0^{\infty} \rho(\omega) \, d\omega = 1 \). For a solid, the function \( \rho(\omega) \) is the same as the frequency distribution. In solid methane, the frequency spectrum represents all characteristics of the rotational, translational and vibrational behaviors of a molecule [29]. The total excitation spectrum is additive as shown in Eq. (11).

Fig. 5 shows the frequency spectra of solid methane at three temperatures in phase II, 20, 4 and 0 K from our model. We plotted these spectra up to \( E \approx 22 \text{ meV} \) which means this plot includes only rotational and phonon modes. The red dotted line is the frequency spectrum at 20 K, the blue short-dashed line is at 4 K, and the light blue long dashed line is at 0 K. The first peak around 2 meV in the frequency spectrum at 20, 4 and 0 K represents the linear superposition of the energy excitations from ground and the first excited rotational energy states to higher states in \( \text{O}_\text{h} \) molecules and the tunneling among ground state multiplets (three lowest states) in \( \text{D}_{2\text{d}} \) molecules. The second peak comes from the linear superposition of energy excitations to the higher rotational states in \( \text{O}_\text{h} \) molecules and the librational states in \( \text{D}_{2\text{d}} \) molecules. The final peak around 12.9 meV is a multi-phonon mode corresponding to the Debye temperature of solid methane \( (T_D = 145 \text{ K}) \) [32]. The multi-phonon scattering and higher excitations in orientational modes are suppressed at low temperature, but the transition probabilities from ground state in the free rotor state and the tunneling among ground state multiplets in hindered rotor increase.

### 5.3. Total neutron scattering cross-section

We compared our model with the measured total cross-section for methane in phase II as a function of neutron energy. In the low neutron energy limit, the total cross-section is mainly due to elastic scattering from free and hindered rotors. We calculated the elastic coherent and incoherent scattering of hydrogen from Ozaki [17,26]. For \( 10 \text{ meV} \leq E_n \leq 100 \text{ meV} \), \( \sigma_{\text{tot}} \) mainly depends on translational excitation. In the higher energy region, the vibrational excitation becomes more important than the rotational and translational scattering.

Fig. 6 shows the total neutron scattering cross-section per molecule at 20, 7, 4 and 2.6 K. The theoretical calculations are compared to the measured data at 20, 7 and 2.6 K [33]. Around \( E_n = 10 \text{ meV} \), the total cross-section is almost temperature independent. For lower neutron energies, the total cross-section depends strongly on temperature. The increase of the cross-section from \( E_n = 10 \text{ meV} \) down to \( E_n = 0.1 \text{ meV} \) is about 150 barns at 20 K and 300 barns at 2.6 K. Independent of temperature, above \( E_n = 10 \text{ meV} \), the cross-section decreases from 200 barns to 100 barns around \( E_n = 100 \text{ meV} \) and then converges to 80 barns, which is the single free hydrogen scattering cross-section, for large \( E_n \).

### 5.4. Contribution of the two rotational modes to \( S(Q, \omega) \)

Our model allows us to study the contributions to \( S(Q, \omega) \) from the free and hindered rotors. We assumed that one of the two types of rotational modes in phase II of \( \text{CH}_4 \) can be turned off in
our model so that the rotational degrees of freedom are either a completely free mode or a completely hindered mode. The phonon and vibrational scattering are not included in this analysis since they are assumed to be same in both cases.

Figs. 7 and 8 show the scattering functions at 20 and 4 K for the free rotation and the hindered rotation case, respectively. The hindered rotation mode produces two separate contributions to the scattering function corresponding to the rotational tunneling at low energies and the librations in the high energy region. From these plots of $S(Q,\omega)$, one can see immediately the much greater spectral weight present at low energy transfers in the free rotor spectrum compared to the hindered rotation spectrum.

These features are also present in the frequency spectrum plot in Fig. 9. The spectral weight in the free rotation mode is roughly twice that in the hindered rotation mode in the low Q limit. The weight from librations of the hindered rotors is relatively small. We also note from Figs. 7 and 8 that the scattering probability for the free rotation and tunneling modes increases with decreasing temperature while that of the librations falls considerably from 20 to 4 K. Therefore, it is clear from our studies that the small number of free rotors in phase II of solid methane are in fact much more important to the cold neutron moderation properties of methane below 20 K than are the librations and tunneling modes contributed by the hindered rotor sites.

In fact, inelastic neutron scattering studies have shown that alloying methane with krypton or argon can suppress the transition between the phase I and phase II structures of methane, and therefore the methane molecules in these system remain free rotors even well below the 20 K phase transition temperature of pure methane [34,35]. From our calculations we conclude that the higher inelastic cross-section for the free rotor modes in such a system strongly justify its investigation as a possible improved slow neutron moderator medium.

6. Conclusions

Theoretical studies of the neutron scattering cross-section model of solid methane in phase II were performed. Based on the model, we evaluated the scattering function $S(Q,\omega)$, the frequency spectrum $\rho(\omega)$ and the total scattering cross-section for solid methane at 20, 4 and 0 K. The model also implicitly uses experimental input from neutron scattering, light scattering and thermodynamic measurements which determine the energy spectra and other properties for the different modes in solid methane. The total scattering cross-sections are shown to be consistently explained in our model. Moreover, the relative contributions of the free and hindered rotational modes in the scattering function, frequency spectrum and scattering cross-section have also been calculated using the model. We conclude that the inelastic cross-section from the free rotor modes is so much larger than that from the hindered modes that any medium which can increase the fraction of the methane molecules able to rotate freely is likely to outperform phase II solid methane for neutron phase space cooling. Methane mixtures with krypton and

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**Fig. 7.** The $S(Q,\omega)$ of free rotation and hindered rotation at 20 K. Each peak from left to right corresponds to the excitation energies of free rotation and hindered rotation described in Figs. 3 and 4(c). The $S_{\text{trans}}(Q,\omega)$ is not included in this plot: (a) 20 K free rotation; (b) 20 K hindered rotation.

**Fig. 8.** The $S(Q,\omega)$ of free rotation and hindered rotation at 4 K. Each peak from left to right corresponds to the energy excitations of free rotation and hindered rotation described in Figs. 3 and 4(c). The $S_{\text{trans}}(Q,\omega)$ is not included in this plot: (a) 4 K free rotation; (b) 4 K hindered rotation.
argon is one known example of such a system, and we recommend that this medium be investigated experimentally.

In a separate paper, we will present a comparison of the Monte-Carlo calculation of the neutron spectrum using the our frequency spectrum based scattering kernels with the measured one from the Low Energy Neutron Source (LENS) operating with a solid methane moderator in phase II [36].

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Fig. 9. The frequency spectra of solid methane in free rotation and hindered rotation at 20 K (a), 4 K (b). The intensity of tunneling mode in hindered rotation increase in lower temperature limit. For free rotation, the higher excitations (5 meV < \(h\omega\) < 10 meV) was vanished but lower excitations has increased in lower temperature limit.