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The temperature dependence of rotational tunnelling, modelled with a harmonic substitute system

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Abstract. In 1990, Hüller modelled the temperature dependence of the inelastic lines of the tunnelling spectrum of methyl groups, measured by neutron scattering, using a harmonic substitution system as a replacement for the methyl group. The results obtained there are based on a cumulant expansion that has been restricted to the first two cumulants for a simplified version of the solution of the equation of motion for the σ^+ operator, lacking time ordering. In order to verify the results, we perform the cumulant expansion up to second order including time ordering, and also compute the third and fourth cumulants, but without considering time ordering. Using simple crystal models, we show that the time-ordering symbol may in fact be neglected and that higher cumulants become important only when the density of states is sharply peaked. With the Debye density of states it turns out that for very low temperatures the shift of the inelastic lines is proportional to T^4, whereas the width increases proportionally to T^7. Finally, we present results for the quasielastic line and discuss the mechanism that causes the shift and broadening of the inelastic lines.

1. Introduction

In this paper we are concerned with the rotational tunnelling of methyl groups that are embedded in a solid crystal. A methyl group has three indistinguishable protons. Hence, in principle, its quantum state should be completely antisymmetrized. However at the temperatures we are interested in ($T < 50\,\mathrm{K}$), the excitation energies for the axial and tangential vibrations of these protons are much higher than the temperature. The protons are extremely localized at the end of their valence bonds with the carbon of the CH_3 molecule. Further, we can safely neglect the overlap of the spatial part of the wavefunctions of the three protons, i.e. the only effect of antisymmetrization that needs to be included in this limit is the (very small) tunnelling splitting. Therefore we may consider the group to be rigid. As the barrier for a collective rotation of the three protons is rather low with respect to the temperature range of interest, the rigid group is not entirely fixed in position, but has a single degree of freedom, the rotation angle ϕ. The potential barrier V of rotation is necessarily $\frac{2}{3}\pi$-periodic in ϕ. Taking only the lowest Fourier component of V leads to a $\cos 3\phi$ potential and thus to the Mathieu problem [1].

The inelastic lines of the tunnelling spectrum of methyl groups, measured by means of neutron scattering [2] or NMR spectroscopy, originate from transitions between the A- and E-symmetric states of the methyl group, which differ slightly in energy. As the methyl group is always part of a solid crystal, the measured energy spectra reflect the properties of the full system rather than those of an isolated (single) methyl group.

In this paper we restrict the discussion to model crystals which contain no impurities such as paramagnetic ions, and which show no other kind of excitation than lattice vibrations

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(phonons). In this case the eigenstates of the composite system have a definite (either A or E) symmetry. Therefore, the symmetry of the actual state of the system can only be changed by some external agent, such as neutrons. In neutron scattering experiments the change of energy that is connected with the transition to a state of different symmetry is transferred to the neutron and measured by some spectrometer. It has been observed [2] that at almost zero temperature the spectrum consists of two sharp inelastic lines at $-\omega$ and $+\omega$, where we call ω the zero-temperature tunnel frequency, and another sharp line at zero energy, called the quasielastic line. When the temperature is raised, the inelastic lines shift towards zero energy and become broader. The quasielastic line does not shift, but also becomes broader. In general, the inelastic lines are broader than the quasielastic line.

In this paper we consider the temperature dependence of the inelastic lines and the quasielastic line separately, using different models. In both cases the methyl group is not treated as a Mathieu problem [1], but is substituted by a harmonic system, which is then coupled to a harmonic crystal.

These models are not new [3, 4], but here we treat them in more detail. In particular, we look for an interpretation of the shift and broadening of the inelastic tunnel lines within our model description.

2. The model for the inelastic lines

Due to the C_3 symmetry of the methyl group, its eigenstates can be characterized by a C_3 symmetry label (A, E^a, E^b) and a discrete index n [1]. The $E^{a,b}$ states are degenerate. The actual symmetry of the eigenstate of the isolated methyl group is a time-independent quantity that can only be changed by the influence of some external agents such as neutrons. The substitute shall share these properties. It is constructed to be a composed system consisting of a pseudospin and a harmonic oscillator with pseudospin-dependent frequency. The pseudospin states are taken to be analogous to the A- and E-symmetric states, but in the model no distinction is made analogous to E^a and E^b. The Hamiltonian is given by

$$\begin{aligned} H_0 &\equiv \frac{p_0^2}{2m} + \frac{m}{2}\Omega_0^2 q_0^2 + (\sigma_z - \tfrac{1}{2})V \\ V &\equiv -\Delta + \epsilon\frac{p_0^2}{2m} \end{aligned} \tag{2.1}$$

where p_0 and q_0 denote the momentum and position operators of the oscillator which is substituted for the methyl group, and σ_z is the operator of the pseudospin z-component with eigenvalues $\pm 1/2$. The eigenenergies of H_0 are

$$\begin{aligned} E(n,\uparrow) &= \Omega_0(n+\tfrac{1}{2}) \\ E(n,\downarrow) &= \Delta + \sqrt{(1-\epsilon)}\,\Omega_0(n+\tfrac{1}{2}) \qquad \Omega_0 > 0 \end{aligned} \tag{2.2}$$

where we have set $\hbar \equiv 1$. We define 'tunnel frequencies' by

$$\begin{aligned} \omega_0^* &\equiv E(0,\downarrow) - E(0,\uparrow) = \Delta + \tfrac{1}{2}\Omega_0(\sqrt{(1-\epsilon)} - 1) \\ \omega_1^* &\equiv E(1,\downarrow) - E(1,\uparrow) = \Delta + \tfrac{3}{2}\Omega_0(\sqrt{(1-\epsilon)} - 1) \end{aligned} \tag{2.3}$$

and adjust ω_0^*, ω_1^* and the 'libration frequency' Ω_0 of the model to the values of the corresponding lowest two tunnel frequencies and the libration frequency of the original methyl group, respectively. All model parameters (Δ, Ω_0, ϵ) are thereby uniquely determined. As for methyl groups, ω_0^* is greater than ω_1^*, and ϵ is a positive quantity.

Having substituted the methyl group by an appropriate model based on the harmonic oscillator, we can now easily build the substitute into a lattice of harmonically bound particles without internal degrees of freedom. The harmonic substitute will be considered as a lattice particle itself (with coordinates q_0 and p_0), but with a mass that depends on the pseudospin state. The corresponding Hamiltonian is given by

$$H \equiv \sum_{\mu=0}^{N} \frac{p_\mu^2}{2m_\mu} + \frac{1}{2}\sum_{\mu=0}^{N}\sum_{\nu=0}^{N} \Phi_{\mu\nu} q_\mu q_\nu + (\sigma_z - \tfrac{1}{2})V$$
$$V \equiv -\Delta + \epsilon \frac{p_0^2}{2m_0}. \tag{2.4}$$

The mass of the zeroth particle is m_0 for all spin-up states (A-state analogues) and $m_0/(1-\epsilon)$ for all spin-down states (E-state analogues). As V depends only on the momentum p_0 of the zeroth particle, this model is translation-invariant if we require $\sum_\mu \Phi_{\mu\nu} = 0$ for the symmetric matrix Φ. The inclusion of a term $\delta q_0^2/2m_0$, which means the introduction of a spatially fixed potential, would destroy the translational invariance and lead to an unphysical frequency dependence of the phonon coupling.

The Hilbert space on which H_0 acts is the tensor product of the infinite-dimensional harmonic oscillator space and the two-dimensional spin space. In the following we use the normal coordinates

$$P_\mu \equiv \sum_{\nu=0}^{N} (S^{-1})_{\mu\nu} \frac{p_\nu}{\sqrt{m_\nu}} \qquad Q_\mu \equiv \sum_{\nu=0}^{N} (S^{-1})_{\mu\nu} \sqrt{m_\nu} q_\nu \tag{2.5}$$

where the orthogonal transformation matrix $S_{\mu\nu}$ diagonalizes the matrix $\Phi_{\mu\nu}/\sqrt{m_\mu m_\nu}$. With the raising and lowering operators

$$a_\mu^+ \equiv \sqrt{\frac{\omega_\mu}{2}}\left(Q_\mu - \mathrm{i}\frac{P_\mu}{\omega_\mu}\right) \qquad a_\mu \equiv \sqrt{\frac{\omega_\mu}{2}}\left(Q_\mu + \mathrm{i}\frac{P_\mu}{\omega_\mu}\right) \tag{2.6}$$

the transformed Hamiltonian is

$$H = H_L + (\sigma_z - \tfrac{1}{2})V \qquad H_L \equiv \sum_{\mu=0}^{N} \omega_\mu (a_\mu^+ a_\mu + \tfrac{1}{2}) \tag{2.7}$$
$$V = -\Delta + \frac{\epsilon}{4}\sum_{\mu=0}^{N} \omega_\mu S_{0\mu}^2 + \frac{\epsilon}{4}\sum_{\mu=0}^{N}\sum_{\nu=0}^{N} \sqrt{\omega_\mu \omega_\nu} S_{0\mu} S_{0\nu} (2a_\mu^+ a_\nu - a_\mu^+ a_\nu^+ - a_\mu a_\nu).$$

3. The correlation function

In the pseudospin formalism the spin-dependent part of the neutron scattering operator, which induces transitions between A- and E-states of the methyl group, is replaced by the

raising and lowering operators of the pseudospin. Therefore the neutron scattering spectrum is the Fourier transform of the correlation function

$$C(t) \equiv \frac{\langle \sigma_+(t)\sigma_-(0)\rangle}{\langle \sigma_+(0)\sigma_-(0)\rangle} = \frac{\mathrm{Tr_H}\{\sigma_+(t)\sigma_-(0)\mathrm{e}^{-\beta H}\}}{\mathrm{Tr_H}\{\sigma_+(0)\sigma_-(0)\mathrm{e}^{-\beta H}\}} \tag{3.1}$$

with

$$\sigma_+(t) \equiv \mathrm{e}^{\mathrm{i}Ht}\sigma_+(0)\mathrm{e}^{-\mathrm{i}Ht} \tag{3.2}$$

where σ_+ and σ_- are the spin raising and lowering operators, respectively. The trace $\mathrm{Tr_H}$ in (3.1) is taken over the Hilbert space of H, which is the product space of the lattice space and the pseudospin space.

We obtain $C(t)$ through the Heisenberg equation of motion for $\sigma_+(t)$:

$$\dot{\sigma}_+(t) = (1/\mathrm{i})[\sigma_+(t), H] = \mathrm{i}V(t)\sigma_+(t) \tag{3.3}$$

with $V(t) \equiv \mathrm{e}^{\mathrm{i}Ht}V\mathrm{e}^{-\mathrm{i}Ht}$. It has the solution

$$\sigma_+(t) = T\exp\left(\mathrm{i}\int_0^t \mathrm{d}\tau V(\tau)\right)\sigma_+(0) \tag{3.4}$$

where T denotes Dyson's time-ordering symbol. As H does not flip the spin component of any product state, we may remove the spin-flip operators by inserting (3.4) into (3.1) and obtain

$$C(t) = \left\langle T\exp\left(\mathrm{i}\int_0^t \mathrm{d}\tau V(\tau)\right)\right\rangle_{\mathrm{L}} \tag{3.5}$$

with

$$\langle\cdot\rangle_{\mathrm{L}} \equiv \frac{\mathrm{Tr_L}\{\,\cdot\,\mathrm{e}^{-\beta H_{\mathrm{L}}}\}}{\mathrm{Tr_L}\{\mathrm{e}^{-\beta H_{\mathrm{L}}}\}} \tag{3.6}$$

the trace being taken only over the lattice states. In the following we omit the subscript L. Noting that the a^+a^+ and aa terms in (2.7) only lead to oscillating contributions, we may approximate (3.5) by

$$C(t) = \exp\left[\mathrm{i}\left(-\Delta + \frac{\epsilon}{4}\sum_{\mu=0}^{N}\omega_\mu S_{0\mu}^2\right)t\right]\left\langle T\exp\left(\int_0^t \mathrm{d}\tau V_1(\tau)\right)\right\rangle \tag{3.7}$$

with

$$V_1(t) \equiv \mathrm{i}\sum_{\mu,\nu=0}^{N} S_\mu S_\nu a_\mu^+(t)a_\nu(t) \tag{3.8}$$

where

$$S_\mu \equiv \sqrt{\frac{\epsilon\omega_\mu}{2}}S_{0\mu} \tag{3.9}$$

and

$$a_\mu(t) \equiv a_\mu e^{-i\omega_\mu t} \tag{3.10}$$

have been used. We solve (3.7) using a cumulant expansion, defined by

$$\left\langle T\exp\left(\int_0^t d\tau\, V_1(\tau)\right)\right\rangle = \exp\left(\sum_{n=1}^{\infty} C_n(t)\right). \tag{3.11}$$

The evaluation of the C_n goes as follows. The average

$$(1/n!)\left\langle T\left(\int_0^t \sum S_\mu S_\nu a_\mu^+(\tau)a_\nu(\tau)\,d\tau\right)^n\right\rangle$$

which is the nth term in the series expansion of the left-hand side of (3.11), consists of all sums of products of two-operator contractions of the creation and destruction operators, where the contraction of two operators $\alpha_1(t_1)$ and $\alpha_2(t_2)$, α_i being either a creation or destruction operator, is just the time-ordered average $\langle T\alpha_1(t_1)\alpha_2(t_2)\rangle$. This follows from Wick's theorem [5, 6]. Now to obtain C_n we drop all terms that contain two different time variables t_i, t_j that are not 'connected' by a contraction $\langle T\alpha_\mu(t_i)\alpha_\nu(t_j)\rangle$. For example, a term of the form

$$\langle T\alpha_1(t_1)\alpha_3(t_2)\rangle\langle T\alpha_2(t_1)\alpha_4(t_2)\rangle$$

contributes to the second cumulant C_2, whereas the term

$$\langle T\alpha_1(t_1)\alpha_2(t_1)\rangle\langle T\alpha_3(t_2)\alpha_4(t_2)\rangle$$

does not. For a more detailed description in terms of connected graphs see [6]. Fortunately only very few terms withstand this elimination procedure, which greatly simplifies the evaluation of higher cumulants.

The first cumulant is given by

$$C_1(t) = i\int_0^t d\tau \sum_{\mu,\nu=0}^{N} S_\mu S_\nu \langle a_\mu^+(\tau)a_\nu(\tau)\rangle = it\sum_{\mu=0}^{N} S_\mu^2 \bar{n}_\mu \tag{3.12}$$

with

$$\bar{n}_\mu \equiv \langle a_\mu^+ a_\mu\rangle = \frac{1}{e^{\omega_\mu/T}-1}. \tag{3.13}$$

For a periodic crystal we can use the fact that the modes μ are completely characterized by a branch index $\zeta = 1, \ldots, k$ and a wavevector q from the first Brillouin zone. As the function $\omega_\zeta(q)$, which relates the wavevector q to the mode frequency ω for a given branch index ζ, approaches a continuous function for a macroscopic crystal, we may approximate the sums over q by integrals over ω. To this end we introduce the density of states $g_\zeta(\omega)$ and write $S_{0\zeta}(\omega)$ instead of $S_{0\mu}$. Inserting (3.9) into (3.12) we obtain

$$C_1(t) = it\frac{\epsilon}{2}\int d\omega\, g(\omega)S_0^2(\omega)\omega\bar{n}(\omega) \tag{3.14}$$

where for notational convenience we take account only of a single phonon branch.

The second cumulant is given by

$$C_2(t) = \frac{\mathrm{i}^2}{2}\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \sum_{\mu\nu}\sum_{\rho\sigma} S_\mu S_\nu S_\rho S_\sigma \langle T a_\mu^+(t_1) a_\sigma(t_2)\rangle \langle T a_\nu(t_1) a_\rho^+(t_2)\rangle. \tag{3.15}$$

With the identity

$$\langle T a_\mu^+(t_1) a_\sigma(t_2)\rangle = [\bar{n}_\mu + \Theta(t_2 - t_1)]\delta_{\mu\sigma} \mathrm{e}^{\mathrm{i}\omega_\mu(t_1 - t_2)} \tag{3.16}$$

equation (3.15) becomes

$$\begin{aligned} C_2(t) = &-\frac{1}{2}\sum_{\mu\nu} S_\mu^2 S_\nu^2 \bar{n}_\mu \bar{n}_\nu \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, \mathrm{e}^{\mathrm{i}(\omega_\mu - \omega_\nu)(t_1 - t_2)} \\ &- \sum_{\mu\nu} S_\mu^2 S_\nu^2 \bar{n}_\mu \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\, \mathrm{e}^{\mathrm{i}(\omega_\mu - \omega_\nu)(t_1 - t_2)}. \end{aligned} \tag{3.17}$$

Since we are interested in $C(t)$ for long times only, we may write for the time integrals

$$\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, \mathrm{e}^{\mathrm{i}\omega(t_1 - t_2)} = \frac{4}{\omega^2}\sin^2\frac{\omega t}{2} \simeq 2\pi|t|\delta(\omega)$$

and

$$\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\, \mathrm{e}^{\mathrm{i}\omega(t_1 - t_2)} = \frac{2}{\omega^2}\sin^2\frac{\omega t}{2} + \frac{\mathrm{i}}{\omega^2}[\omega t - \sin(\omega t)] \simeq \pi|t|\delta(\omega) + \mathrm{i}\frac{t}{\omega}.$$

Inserting these approximations into the continuum version of (3.17), this yields

$$\begin{aligned} C_2(t) = &-\frac{\pi}{4}\epsilon^2|t| \int \mathrm{d}\omega\, g^2(\omega) S_0^4(\omega)\omega^2 [\bar{n}^2(\omega) + \bar{n}(\omega)] \\ &- \tfrac{1}{4}\epsilon^2 t \int \mathrm{d}\omega_1 \int \mathrm{d}\omega_2\, g(\omega_1) g(\omega_2) S_0^2(\omega_1) S_0^2(\omega_2) \omega_1 \omega_2 \bar{n}(\omega_1) \frac{1}{\omega_1 - \omega_2}. \end{aligned} \tag{3.18}$$

The third and fourth cumulant are computed in a similar fashion, but in order to avoid technical complications we neglect Dyson's time-ordering symbol in (3.4). The resulting approximate expressions are

$$\begin{aligned} C_3(t) &= -\frac{\epsilon^3\pi^2}{12} t \int \mathrm{d}\omega\, g^3(\omega) S_0^6(\omega)\omega^3 [2\bar{n}^3(\omega) + 3\bar{n}^2(\omega) + \bar{n}(\omega)] \\ C_4(t) &= \frac{\epsilon^4\pi^3}{48}|t| \int \mathrm{d}\omega\, g^4(\omega) S_0^8(\omega)\omega^4 [6\bar{n}^4(\omega) + 12\bar{n}^3(\omega) + 7\bar{n}^2(\omega) + \bar{n}(\omega)]\,. \end{aligned} \tag{3.19}$$

With these results the correlation function (3.5) becomes

$$\begin{aligned} &C(t) = \tfrac{1}{2}\mathrm{e}^{-\mathrm{i}\overline{\omega}t}\mathrm{e}^{-\overline{\gamma}|t|/2} \\ &\overline{\gamma} \equiv \overline{\gamma}_2 - \overline{\gamma}_4 \\ &\overline{\omega} \equiv \omega_0 + \overline{\omega}_1 + \overline{\omega}_2 + \overline{\omega}_3 \end{aligned} \tag{3.20}$$

with

$$\begin{aligned}
\overline{\omega}_0 &\equiv \Delta - \frac{\epsilon}{4}\int \mathrm{d}\omega\, g(\omega)S_0^2(\omega)\omega \\
\overline{\omega}_1 &\equiv -\frac{\epsilon}{2}\int \mathrm{d}\omega\, g(\omega)S_0^2(\omega)\omega\overline{n}(\omega) \\
\overline{\omega}_2 &\equiv \frac{1}{4}\epsilon^2\int \mathrm{d}\omega_1 \int \mathrm{d}\omega_2\, g(\omega_1)g(\omega_2)S_0^2(\omega_1)S_0^2(\omega_2)\omega_1\omega_2\overline{n}(\omega_1)\frac{1}{\omega_1-\omega_2} \\
\overline{\omega}_3 &\equiv \frac{\epsilon^3\pi^2}{12}\int \mathrm{d}\omega\, g^3(\omega)S_0^6(\omega)\omega^3[2\overline{n}^3(\omega)+3\overline{n}^2(\omega)+\overline{n}(\omega)]
\end{aligned} \tag{3.21}$$

and

$$\begin{aligned}
\overline{\gamma}_2 &\equiv \frac{\pi}{2}\epsilon^2\int \mathrm{d}\omega\, g^2(\omega)S_0^4(\omega)\omega^2[\overline{n}^2(\omega)+\overline{n}(\omega)] \\
\overline{\gamma}_4 &\equiv \frac{\epsilon^4\pi^3}{24}\int \mathrm{d}\omega\, g^4(\omega)S_0^8(\omega)\omega^4[6\overline{n}^4(\omega)+12\overline{n}^3(\omega)+7\overline{n}^2(\omega)+\overline{n}(\omega)].
\end{aligned} \tag{3.22}$$

The Fourier transform of the correlation function (3.20) is a Lorentzian of width $\overline{\gamma}$ centred at $\overline{\omega}$. In (3.21) $\overline{\omega}_0$ is the zero-temperature tunnel frequency. The quantities $\overline{\omega}_1$, $\overline{\omega}_2$ and $\overline{\omega}_3$ represent the temperature-dependent contributions of the first, second and third cumulant, respectively, to the shift of the tunnel line. The term $\overline{\omega}_2$ is not present in [3], because Dyson's time-ordering symbol had been neglected there. The contributions of the second and fourth cumulant to the tunnel width are given by $\overline{\gamma}_2$ and $\overline{\gamma}_4$, respectively.

4. Crystal models

In this section we wish to calculate the frequency and width of the inelastic tunnel line as given by (3.21) and (3.22) for two simple crystal models. We start with the density of states of the Debye model for a three-dimensional crystal

$$g(\omega) \equiv \frac{3N}{\omega_{\mathrm{D}}^3}\omega^2 \tag{4.1}$$

where ω_{D} is the cut-off frequency and N is the number of crystal atoms. We identify the cut-off frequency ω_{D} with the 'libration' frequency Ω_0 of the harmonic model that mimics the methyl group, i.e. we set $\Omega_0 = \omega_{\mathrm{D}}$. We also assume that all modes couple to the zeroth particle with the same strength:

$$S_0(\omega) \equiv \frac{1}{\sqrt{N}}. \tag{4.2}$$

Inserting this in (3.21), we obtain

$$\overline{\omega}_0 = \Delta - \tfrac{3}{16}\epsilon\omega_{\mathrm{D}} \tag{4.3}$$

and

$$\overline{\omega}_1 = -\tfrac{3}{2}\epsilon\frac{T^4}{\omega_{\mathrm{D}}^3}g_{4,1}(\omega_{\mathrm{D}}/T) \simeq -\tfrac{3}{2}\epsilon\frac{T^4}{\omega_{\mathrm{D}}^3}\Gamma(4)\zeta(4) = -\epsilon\frac{\pi^4}{10}\frac{T^4}{\omega_{\mathrm{D}}^3} \tag{4.4}$$

where we have introduced the function

$$g_{m,n}(x) \equiv \int_0^x \mathrm{d}y \, \frac{y^{m-1}}{(\mathrm{e}^y - 1)^n}. \tag{4.5}$$

The approximation in (4.4) is valid for temperatures well below the cut-off frequency ω_D. In an analogous manner we compute $\overline{\omega}_2$, $\overline{\omega}_3$:

$$\overline{\omega}_2 = -\epsilon^2\left(\frac{3}{4}\frac{T^4}{\omega_D^3}g_{4,1}(\omega_D/T) + \frac{9}{8}\frac{T^5}{\omega_D^4}g_{5,1}(\omega_D/T) + \frac{9}{4}\frac{T^6}{\omega_D^5}g_{6,1}(\omega_D/T) + \frac{9}{4}\frac{T^7}{\omega_D^6}\int_0^{\omega_D/T}\mathrm{d}x\,\frac{x^6}{\mathrm{e}^x - 1}\ln\frac{\omega_D - xT}{xT}\right) \tag{4.6}$$

$$\overline{\omega}_3 = \tfrac{9}{4}\epsilon^3\pi^2\frac{T^{10}}{\omega_D^9}[2g_{10,3}(\omega_D/T) + 3g_{10,2}(\omega_D/T) + g_{10,1}(\omega_D/T)] \tag{4.7}$$

and the widths $\overline{\gamma}_2$ and $\overline{\gamma}_4$:

$$\overline{\gamma}_2 = \tfrac{9}{2}\pi\epsilon^2\frac{T^7}{\omega_D^6}[g_{7,2}(\omega_D/T) + g_{7,1}(\omega_D/T)] \simeq \tfrac{72}{21}\pi^7\epsilon^2\frac{T^7}{\omega_D^6} \tag{4.8}$$

$$\overline{\gamma}_4 = \tfrac{27}{8}\epsilon^4\pi^3\frac{T^{13}}{\omega_D^{12}}[6g_{13,4}(\omega_D/T) + 12g_{13,3}(\omega_D/T) + 7g_{13,2}(\omega_D/T) + g_{13,1}(\omega_D/T)] \tag{4.9}$$

with the approximation in (4.8) being valid for temperatures well below ω_D.

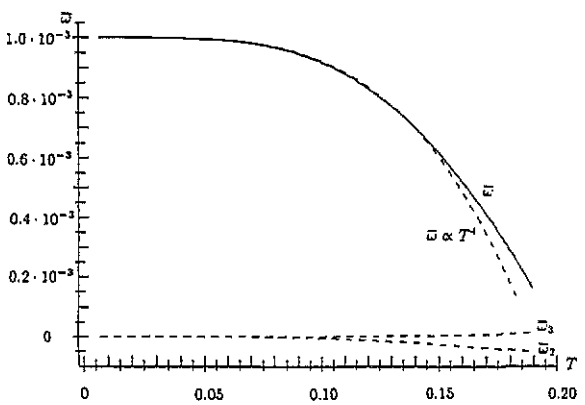

Figure 1. The tunnel frequency as a function of temperature. The full curve shows the tunnel frequency $\overline{\omega}$, including all contributions. The dotted curves display the contributions $\overline{\omega}_2$ and $\overline{\omega}_3$ from the second and third cumulant, respectively, and the approximation of the shift by a T^4 law.

For the purpose of a plot we set $\Omega_0 = 1$ and take a methyl group which has the tunnel frequencies [3]

$$\omega_0^* = 0.001 \qquad \omega_1^* = -0.029\,. \tag{4.10}$$

With these values we get the model parameter $\Delta = 0.016$ from (2.3). In order to obtain ω_0^* as the tunnel frequency at zero temperature, we do not use (2.3) to evaluate ϵ. Instead, we use (4.3) which accounts for the zero point energy of the lattice and obtain $\epsilon = 0.08$. Figures 1 and 2 show the tunnel frequency $\overline{\omega}$ and the tunnel width $\overline{\gamma}$. The contributions $\overline{\omega}_2$,

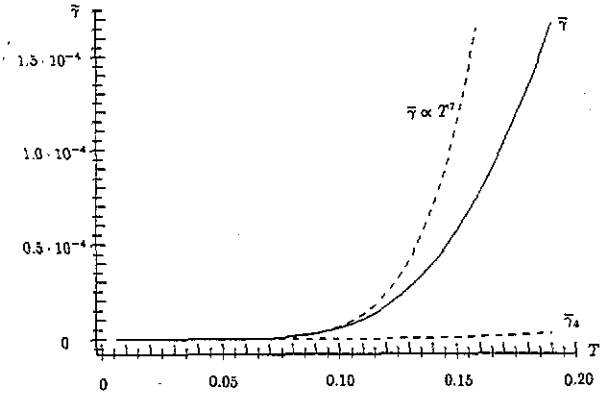

Figure 2. The tunnel width as a function of temperature. The full curve shows the tunnel width $\overline{\gamma}$, including all contributions. The dotted curves display the contribution $\overline{\gamma}_4$ from the fourth cumulant and the approximation of the shift by a T^7 law.

$\overline{\omega}_3$ and $\overline{\gamma}_4$ are also displayed in order to demonstrate that their influence can be neglected. It can be seen that the approximation $\overline{\omega}_1 \propto T^4$ is quite good over the whole temperature range where the tunnel frequency is non-negative, whereas the width $\overline{\gamma}$ increases as T^7 only for temperatures up to 0.1. From the figures it follows that neither the inclusion of time ordering in the calculation of the second cumulant nor the third and fourth cumulant have a significant impact on the results when the density of states of the Debye model is used.

A somewhat different situation arises when a sharply peaked density of states is inserted in (3.21) and (3.22). A peaked density of states does not affect $\overline{\omega}_0$, $\overline{\omega}_1$ and $\overline{\omega}_2$ very much, but $\overline{\omega}_3$, $\overline{\gamma}_2$ and $\overline{\gamma}_4$ will yield much higher values than those that are obtained from the Debye model. This is due to the fact that the density of states is taken to a power greater than unity in the formulae for these latter quantities.

We estimate the minimum acceptable width of the phonon band by using the density of states

$$g(\omega) = \frac{N}{\alpha\Omega_0}\left[\Theta\left(\omega - \Omega_0(1 - \tfrac{1}{2}\alpha)\right) - \Theta\left(\omega - \Omega_0(1 + \tfrac{1}{2}\alpha)\right)\right] \tag{4.11}$$

which is constant in the range $\Omega_0(1 \mp \frac{1}{2}\alpha)$ and zero elsewhere, where α is the relative width of the phonon band. For a small bandwidth α we insert (4.11) into (3.21) and (3.22) to obtain

$$\begin{aligned} \overline{\omega}_0 &= \Delta - \frac{\epsilon}{4}\Omega_0 \\ \overline{\omega}_1 &= -\frac{\epsilon}{2}\Omega_0 \overline{n}(\Omega_0) \\ \overline{\gamma}_2 &= \tfrac{1}{2}\pi\epsilon^2\alpha^{-1}\Omega_0\left[\overline{n}^2(\Omega_0) + \overline{n}(\Omega_0)\right]. \end{aligned} \tag{4.12}$$

For temperatures well below the libration frequency Ω_0 we may approximate the shift and width of the tunnel line by an Arrhenius law with common activation energy Ω_0:

$$\overline{\omega}_1 = -\tfrac{1}{2}\epsilon\Omega_0 e^{-\Omega_0/T} \qquad \overline{\gamma}_2 = \tfrac{1}{2}\pi\epsilon^2\alpha^{-1}\Omega_0 e^{-\Omega_0/T}. \tag{4.13}$$

From (4.12) it follows that the maximum occupation number $\overline{n}(\Omega_0)$ for which the tunnel frequency is non-negative is given by

$$\overline{n}(\Omega_0) = \frac{2\Delta}{\epsilon\Omega_0} - \frac{1}{2}. \tag{4.14}$$

The relative contribution of the third cumulant to the shift of the tunnel line is given by

$$\left|\frac{\overline{\omega}_3}{\overline{\omega}_1}\right| = \tfrac{1}{6}\pi^2\epsilon^2\alpha^{-2}[2\overline{n}^2(\Omega_0) + 3\overline{n}(\Omega_0) + 1] \tag{4.15}$$

and the relative contribution of the fourth cumulant to the width is expressed by

$$\left|\frac{\overline{\gamma}_4}{\overline{\gamma}_2}\right| = \tfrac{1}{12}\pi^2\epsilon^2\alpha^{-2}\frac{6\overline{n}^3(\Omega_0) + 12\overline{n}^2(\Omega_0) + 7\overline{n}(\Omega_0) + 1}{1 + \overline{n}(\Omega_0)}. \tag{4.16}$$

With the methyl group tunnel frequencies (4.10) the minimum phonon bandwidth for which the above ratios (4.15) and (4.16) are less than 20% over the whole temperature range that leads to positive tunnel frequencies turns out to be $\alpha_{\min} \simeq 0.2$. The tunnel frequency is zero at $T \simeq 0.3$.

5. The quasielastic line

A harmonic model for the quasielastic line is presented in [4]. It is based on transitions between E^a- and E^b-state analogues. We use the result [4]

$$H'_{\mathrm{SL}} = \sum_{j=1}^{N} g_j(\cos\alpha_j m\omega q_0 + 2\sigma_z \sin\alpha_j p_0)q_j.$$

The tunnelling width is computed in the same way as for the inelastic line, via a cumulant expansion. The first and third cumulants are zero. The width resulting from the second cumulant is

$$\overline{\Gamma}_2 \equiv 4\pi \int \mathrm{d}\omega\, g^2(\omega)S_0^2(\omega)H^2(\omega)n(\omega)[1 + n(\omega)] \tag{5.1}$$

and the fourth cumulant contributes

$$\overline{\Gamma}_4 \equiv -\tfrac{4}{3}\pi^3 \int \mathrm{d}\omega\, g^4(\omega)S_0^4(\omega)H^4(\omega)[6n^4(\omega) + 12n^3(\omega) + 7n^2(\omega) + n(\omega)] \tag{5.2}$$

where we use the definition

$$H(\omega) \equiv C_{01} \sum_{j=1}^{N} g_j^{\mathrm{c}} S_j(\omega). \tag{5.3}$$

Here g_j^{c} are the coupling strengths of the methyl group to the lattice and C_{01} is the cosine matrix element defined in [4]. The $\overline{\Gamma}_i$ have the same meaning as the $\overline{\gamma}_i$ of (3.22). $S_i(\omega)$ is the continuum version of the lattice transformation matrix $S_{i\mu}$.

With the assumption $S_j(\omega) = 1/\sqrt{N}$ and the definition

$$g \equiv \Omega_0^{-1} \sum_{j=1}^{N} g_j^{\mathrm{c}}$$

the constant density of states (4.11) leads to the width

$$\overline{\Gamma}_2 \simeq 4\pi\Omega_0\alpha^{-1}(gC_{01})^2[\overline{n}^2+\overline{n}] \simeq 4\pi\Omega_0\alpha^{-1}(gC_{01})^2 e^{-\Omega_0/T} \tag{5.4}$$

where the approximations hold for low bandwidth α and temperatures well below Ω_0. The ratio of the quasielastic width to the inelastic width (4.12) then becomes

$$\frac{\overline{\Gamma}_2}{\overline{\gamma}_2} = 8\left(\frac{gC_{01}}{\epsilon}\right)^2. \tag{5.5}$$

For a methyl group with tunnel frequencies (4.10) we have approximately $C_{01} = 1/80$ and $\epsilon = 0.06$, from which we obtain

$$\frac{\overline{\Gamma}_2}{\overline{\gamma}_2} \simeq 0.35g^2.$$

Assuming that the coupling constant g of the rotor–lattice coupling is of the order of the lattice force constant, i.e. assuming $g = 1$, we see that within our model description the quasielastic line is much narrower than the elastic line, which is in accordance with the experimental results [2].

By means of the fourth cumulant (5.2) we find that the truncation of the cumulant series after the second term causes an error of less than 20% for phonon bandwidths greater than $\alpha_{min} \simeq 0.1$ and temperatures below $\Omega_0/2$.

In figure 3 we display the quasielastic width for the Debye density of states (4.1). Comparing the result with the corresponding width of the inelastic line, figure 2, we again obtain the result that the quasielastic line is much narrower than the inelastic line.

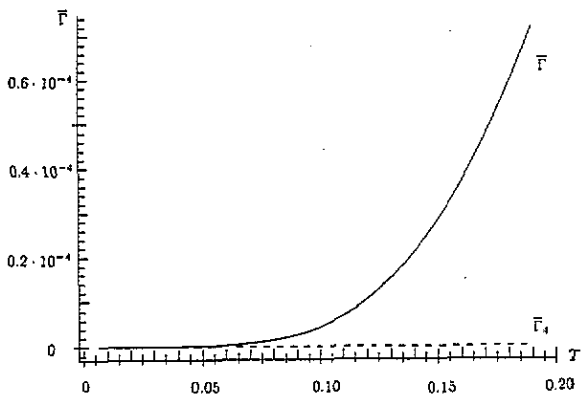

Figure 3. The tunnel width of the quasielastic curve as a function of temperature. The full curve shows the width $\overline{\Gamma}$, including all contributions. The dotted curves display the contribution $\overline{\Gamma}_4$ from the fourth cumulant.

The contribution of the fourth cumulant to the width is negligible.

6. Interpretation of the shift and broadening of the tunnel line

In order to gain physical insight into the reasons for the shift of the tunnel frequency $\overline{\omega}_t \equiv \overline{\omega}_0 + \overline{\omega}_1$ we write it in a form different from (3.21). From (2.7) and (3.21) it follows

that

$$\begin{aligned}\overline{\omega}_t = -\langle V\rangle &= -\mathrm{Tr}\{Ve^{-\beta H_L}\}/\mathrm{Tr}\{e^{-\beta H_L}\} \\ &= -\sum_{n_0=0}^{\infty}\cdots\sum_{n_N=0}^{\infty}\langle n_0,\ldots,n_N|V|n_0,\ldots,n_N\rangle \\ &\quad\times\exp\left(-\beta\sum_{\mu=0}^{N}\omega_\mu(n_\mu+\tfrac{1}{2})\right)(\mathrm{Tr}\{e^{-\beta H_L}\})^{-1}. \qquad (6.1)\end{aligned}$$

The states $|n_0,\ldots,n_N\rangle$ are the eigenstates of H_L (2.7) with occupation numbers n_μ. Up to first order in perturbation theory the matrix element $\langle n_0,\ldots,n_N|V|n_0,\ldots,n_N\rangle$ is the difference of the eigenenergies of the Hamiltonians H_L (system in the A state) and $H_L - V$ (system in the E state), corresponding to the same occupation numbers. Both H_L and $H_L - V$ are harmonic lattices, which posses eigenfrequencies ω_μ^A and ω_μ^E, respectively. Hence we may write

$$\langle n_0,\ldots,n_N|V|n_0,\ldots,n_N\rangle \simeq -\Delta + \sum_{\mu=0}^{N}(\omega_\mu^A - \omega_\mu^E)(n_\mu+\tfrac{1}{2}). \qquad (6.2)$$

With this inserted in (6.1) we obtain

$$\overline{\omega}_0 = \Delta + \frac{1}{2}\sum_{\mu=0}^{N}(\omega_\mu^E - \omega_\mu^A) \qquad \overline{\omega}_1 = \sum_{\mu=0}^{N}(\omega_\mu^E - \omega_\mu^A)\overline{n}(\omega_\mu^A) \qquad (6.3)$$

with the temperature-dependent average occupation numbers

$$\overline{n}(\omega) \equiv \frac{1}{e^{\beta\omega}-1}. \qquad (6.4)$$

Here $\overline{\omega}_0$ constitutes the location of the tunnel line at zero temperature, whereas $\overline{\omega}_1$ is the temperature-dependent shift of the tunnel line. Now consider the neutron scattering process for which we assume that the system has A symmetry before the scattering event and E symmetry afterwards. Before the scattering our model system is a harmonic lattice with eigenfrequencies ω_μ^A and mean energy

$$\overline{E}^A = \sum_{\mu=0}^{N}\omega_\mu^A\,[\overline{n}(\omega_\mu^A)+\tfrac{1}{2}].$$

When the scattering event occurs in our model, the pseudospin state changes from spin up (A-state analogue) to spin down (E-state analogue). Accordingly, the mass of the zeroth particle, which mimics the methyl group, increases from m_0 to $m_0/(1-\epsilon)$, with ϵ given in (2.6). This in turn reduces the eigenfrequencies of the whole crystal:

$$\omega_\mu^E \leqslant \omega_\mu^A \quad \forall\mu.$$

Keeping the average occupation numbers fixed, this means that the mean energy of the crystal decreases. Equation (6.3) states that this decrease in crystal energy causes the measured shift of the tunnel frequency. As the energy loss due to the modification of the

oscillator frequencies is proportional to the occupation numbers of the state of the system it follows, since the average occupation numbers are increasing functions of temperature, that we always get a stronger shift when the temperature is raised. However, even at $T = 0$ we have a lowering of the tunnel frequency as compared to an isolated methyl group. It is due to the zero-point energy of the lattice, which also decreases when the mass of the zeroth particle increases.

The difference between (6.2) and (6.3) is that (6.2) yields the measured tunnel frequencies, provided that the system is prepared to be in the pure state $|n_0, \ldots, n_N\rangle$, whereas (6.3) refers to the case where the system is in thermal equilibrium with a heat bath at temperature T. In this case the measured tunnel frequency fluctuates from neutron to neutron around the average value given by (6.3). The width of the tunnel line is made of just these fluctuations and may be calculated from (6.2):

$$\overline{\gamma}_t \equiv \sigma^2(\langle n_0, \ldots, n_N | V | n_0, \ldots, n_N \rangle) = \sum_{\mu=0}^{N} (\omega_\mu^E - \omega_\mu^A)^2 \sigma^2(n_\mu)$$

$$= \sum_{\mu=0}^{N} (\omega_\mu^E - \omega_\mu^A)^2 [\overline{n}^2(\omega_\mu^A) + \overline{n}(\omega_\mu^A)] \tag{6.5}$$

where $\sigma^2(\cdot)$ denotes the variance. Noting that up to first-order perturbation theory we have

$$\omega_\mu^E - \omega_\mu^A \simeq -\epsilon \omega_\mu S_{0\mu}^2$$

we see that apart from the constant factor $\pi/2$ the width $\overline{\gamma}_t$ coincides width the width $\overline{\gamma}_2$ in (3.22), which has been obtained through the cumulant expansion. This means that our statistical interpretation given here fits well to the second-order cumulant expansion.

However, it should be noted that the explanation of the shift and the broadening of the tunnel line presented in this section only refers to the harmonic model system. It is not obvious how far it also applies to the original methyl group coupled to a (harmonic) crystal. With methyl groups we have to deal with E- and A-symmetry states, whereas in our model system we have dealt with the change of the mass of a lattice particle. The only connection that has been made between both systems is (2.3), which links the lowest tunnel frequencies of the methyl group to the model parameters of the harmonic system.

7. Conclusions

In this paper we used the cumulant expansion presented in [3] to deal with the harmonic replacement and added to it the third and fourth cumulant. It turns out that for not too narrow phonon bandwidths (strong coupling) the higher cumulants are negligible when compared to the second cumulant. Only for very low bandwidths (low coupling) does the cumulant expansion cease to be valid, where the actual limiting bandwidth depends on the tunnel frequencies of the methyl group.

Within our models we find that the functional dependence of the shift and the width of the tunnel line is determined by the density of states $g(\omega)$ of the crystal. For low temperatures the Debye density of states leads to a potential law, whereas a constant density of states with a low bandwidth leads to an exponential (Arrhenius) law.

The quantitative comparison of the widths of the quasielastic and the inelastic line agrees with the experimental result that the quasielastic line is narrower than the inelastic line.

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