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COUPLING OF TUNNELING AND HOPPING TRANSPORT INTERACTIONS IN NEUTRON SCATTERING LINESHAPES

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Abstract—The results of a recently presented formalism for neutron scattering lineshape calculations are used to characterize the observable consequences of the coupling of tunneling and hopping interactions of atoms moving in solids and are compared with those of another development, which treats the two interactions but neglects the coupling.

1. INTRODUCTION

In a number of physical systems ranging from metal hydrides and solid electrolytes to molecular crystals, the transport of microscopic (quasi) particles fails to conform to traditional models for highly coherent or highly incoherent motion. In some of these systems, in particular, metal hydrides, the motion of the mobile particles, e.g. hydrogen nuclei, may be directly probed through the application of neutron spectroscopy. In a recent article [1] (hereafter referred to as KB) the present authors have presented an evaluation of the neutron scattering lineshape based on the stochastic Liouville equation. The emphasis of KB was placed on the behavior of the lineshape as a function of the degree of transport coherence and on the dependence of lineshape detail on temperature. The usual motional narrowing behavior was shown to result: small degrees of incoherence broaden the coherent lineshape due to band motion, while large degrees of incoherence narrow the line toward an asymptotically Lorentzian form.

In this study we wish to examine more closely the broadening contributions of hopping processes when they need to be considered as an *additional* channel for the motion. We first consider a development proposed recently [2] which, although incorporating both tunneling and hopping processes, neglects correlations between the two channels. We then consider the consequences of coupling the two channels by using a stochastic Liouville equation and following the development of KB. This will allow, through a direct comparison, an examination of the extent of the validity of the uncoupled development. Debye–Waller factors are neglected throughout both developments, for simplicity.

The central role is played by the scattering auto-correlation function

$$I(k, t) = \mathrm{Tr}\, \rho e^{-ikx} e^{ikx(t)}, \qquad (1)$$

from which the scattering function is obtained by Fourier transformation in the time variable [3]. In (1), ρ is the equilibrium density matrix, x is the position operator of the scatterer and k is the momentum transferred to the target; x and k are generally vectors, and kx is their dot product.

If one neglects, as in [2], the coupling of tunneling and hopping motions by writing (1) as a product of the correlation functions due to the individual processes,

$$I(k, t) = I_b(k, t) I_h(k, t), \qquad (2)$$

the combined lineshape is a convolution of the lineshapes derived from the tunneling and hopping processes separately:

$$S(k, \omega) = \int_{-\infty}^{\infty} d\omega'\, S_b(k, \omega - \omega') S_h(k, \omega'), \qquad (3)$$

the functions $S_b(k, \omega)$ and $S_h(k, \omega)$ being the respective time-Fourier transforms of $I_b(k, t)$ and $I_h(k, t)$.

If the hopping process may be represented by a master equation with translationally invariant rates,

$$\dot{P}_m(t) = 2 \sum_r [\gamma_{mr} P_r(t) - \gamma_{rm} P_m(t)], \qquad (4)$$

the correlation function due to the hopping process is a simple exponential, and the resulting scattering function for the hopping channel alone is a Lorentzian

$$S_h(k, \omega) = \pi^{-1}\left[\frac{2(\gamma^0 - \gamma^k)}{\omega^2 + 4(\gamma^0 - \gamma^k)^2}\right], \qquad (5)$$

wherein k superscripts indicate discrete Fourier transforms in the site index.

If, as in KB, one denotes the Laplace transform of the band channel correlation function $I_b(k,t)$ by $\tilde{\eta}^k(\epsilon)$, where ϵ is the Laplace variable, one obtains

$$S(k, \omega) = \pi^{-1}\, \mathrm{Re}\{\tilde{\eta}^k(i\omega + 2(\gamma^0 - \gamma^k))\} \qquad (6)$$

from a conjunction of (3) and (5).

Equation (6) is the result of the scheme prescribed in [2]. The contributions of the tunneling process are reflected in the nature of η^k whereas those of the hopping processes are in the γ's, and the correlations between the two processes are neglected as a result of the decoupling approximation (2). To examine the extent of validity of the decoupling approximation, we use the exact analysis of KB. That analysis takes as its point of departure a well-known evolution equation for the matrix elements of the density matrix ρ of the moving particle in the representation of the site states m, n

$$\dot{\rho}_{mn} = -i[H, \rho]_{mn} - 2\Gamma(1 - \delta_{mn})\rho_{mn} + 2\delta_{mn} \sum_r (\gamma_{mr}\rho_{rr} - \gamma_{rm}\rho_{mm}). \quad (7)$$

This equation is called the stochastic Liouville equation (SLE) [4] and contains two kinds of fluctuation parameters: nonlocal ($m \neq r$) fluctuation strengths γ_{mr} and local fluctuation strengths γ_{mm}. Both types of fluctuation serve to scatter a particle whose coherent evolution is otherwise determined by a Hamiltonian H; however, the nonlocal fluctuations contribute to the transport of the particle independently of H, and hence constitute a distinct transport channel. The parameter Γ may be defined through the relation $\Gamma = \Sigma_r \Gamma_{mm+r}$, which results from derivations of (7) based on a stochastic Hamiltonian [4, 5]. An evaluation of the scattering function from an exact solution of (7) is given by KB. It takes the form

$$S(k, \omega) = \pi^{-1}\,\mathrm{Re}\left[\frac{\tilde{\eta}^k(i\omega + 2\Gamma)}{1 - 2[\Gamma - (\gamma^0 - \gamma^k)]\tilde{\psi}^k(i\omega + 2\Gamma)}\right], \quad (8)$$

where the quantity $\tilde{\eta}^k(i\omega + 2\Gamma)$ is the Laplace transform of the function

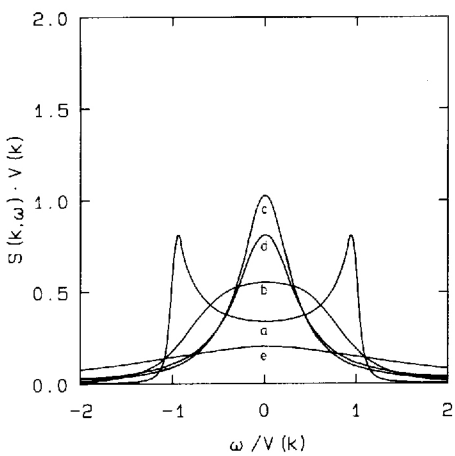

Fig. 1. Neutron scattering lineshape $S(k, \omega)$ calculated from the SLE incorporating both tunneling and hopping interactions. Parameter values: (a) $\gamma^0/2V = 0.01$, (b) $\gamma^0/2V = 0.1$, (c) $\gamma^0/2V = 0.5$, (d) $\gamma^0/2V = 1.0$, (e) $\gamma^0/2V = 5.0$; for all curves $ka = \pi/10$.

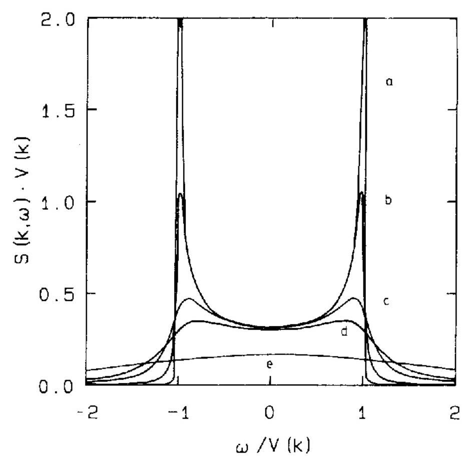

Fig. 2. Neutron scattering lineshape $S(k, \omega)$ calculated using the same tunneling and hopping interactions as are incorporated in the SLE, but neglecting their correlation. Parameter values: (a) $\gamma^0/2V = 0.01$, (b) $\gamma^0/2V = 0.1$, (c) $\gamma^0/2V = 0.5$, (d) $\gamma^0/2V = 1.0$, (e) $\gamma^0/2V = 5.0$; for all curves, $ka = \pi/10$.

$$I_b(k, t) = Z^{-1} \sum_{mrs} (e^{-iHt})_{mr} (e^{-\beta H} e^{-ikx})_{rs} (e^{iHt})_{sm} e^{ikm}, \quad (9)$$

evaluated at the value ($i\omega + 2\Gamma$) of the Laplace variable, and ψ^k is the infinite temperature limit of η^k. In (9), Z is the partition function and β^{-1} is the product of the Boltzmann constant and the absolute temperature.

2. COMPARISON

There are obvious differences between (8), which is an exact consequence of the SLE (7), and (6), which is the result of the decoupling approximation (2). For definiteness, we evaluate (6) and (8) at infinite temperature ($\eta = \psi$) for the simple model consisting of a linear chain with nearest neighbor tunneling interactions, viz., $H_{mn} = V(\delta_{m,n+1} + \delta_{m,n-1})$. In order that (7) represent the evolution of the system under the action of tunneling and hopping processes *only*, we neglect local fluctuations γ_{mm}. This consists of replacing Γ by γ^0 in all expressions. The resulting lineshape formula may then be directly compared with (6). It is easily shown [6] that (2) then becomes

$$S(k, \omega) = \pi^{-1}\,\mathrm{Re}(\{[(i\omega + 2\gamma^0)^2 + V(k)^2]^{-1/2} - 2\gamma^k\}^{-1}). \quad (10a)$$

On the other hand (6) takes the form

$$S(k, \omega) = \pi^{-1}\,\mathrm{Re}\{[(i\omega + 2\gamma^0 - 2\gamma^k)^2 + V(k)^2]^{-1/2}\}. \quad (10b)$$

These results are shown in Figs. 1 and 2, respectively.

The narrowing of the lineshape seen in Fig. 1 is related to that discussed in KB—it is the consequence of limited quantum mechanical phase memory and will be caused by either local or nonlocal fluctuations. If only local fluctuations are considered, the lineshape does not rebroaden as is seen here; this rebroadening may be attributed to the dominance of the hopping transport channel.

There exist some limits in which (10a) and (10b) are identical. These occur when the basic band or hopping parameter is allowed to vanish, in the limit of infinite wavelengths ($k = 0$) and for particular k such that $\gamma^k = 0$. The latter, for example, would occur at $ka = \pi/2$ for nearest-neighbor hopping interactions. A useful parameter for clarifying the limiting behavior of lineshapes is the complex ratio $\zeta = V(k)/(i\omega + 2\gamma^0)$. Denoting $(i\omega + 2\gamma^0)$ by ϵ' and reexpressing eqns (10) in these parameters,

$$S(k, \omega) = \pi^{-1} \operatorname{Re}\{[\epsilon'^2 + V(k)^2 + 2\gamma^k(2\gamma^k - 2\epsilon'(1 + \zeta^2)^{1/2})]^{-1/2}\}, \quad (11a)$$

$$S(k, \omega) = \pi^{-1} \operatorname{Re}\{[\epsilon'^2 + V(k)^2 + 2\gamma^k(2\gamma^k - 2\epsilon')]^{-1/2}\}, \quad (11b)$$

it is clear that the two approaches yield identical results when ζ^2 is small enough to be neglected. Thus, the two formulations yield similar results when transport is extremely incoherent, and in any case yield the same behavior in the far tails of the scattering lineshape.

The comparison of the two results (10a) and (10b) may be complemented by considering the corresponding correlation functions in the time domain. The quantity of interest is the intermediate scattering function $I(k, t)$. In the infinite temperature limit this is the Fourier transform of the probability propagator of the particle being probed. The latter quantity has been calculated [7], and for the present model yields

$$I(k, t) = \exp(-4\gamma_1 t) J_0\left(4Vt \sin\left(\frac{ka}{2}\right)\right) + (4\gamma_1 \cos ka) \exp(-4\gamma_1 t) \int_0^t du \exp[(4\gamma_1 \cos ka)u] \times J_0\left(4V \sin\left(\frac{ka}{2}\right)(t^2 - u^2)^{1/2}\right), \quad (12a)$$

wherein we have denoted $\gamma_{m,m+1}$ by γ_1. Equation (12a) is the time domain result corresponding to (11a). The corresponding result which follows from (2) is

$$I(k, t) = \exp[-(4\gamma_1 \cos ka)t] J_0\left(4Vt \sin\left(\frac{ka}{2}\right)\right). \quad (12b)$$

The mean square displacements for an initially localized condition implicit in the two approaches are easily evaluated from eqns (12). These are, respectively,

$$\langle m^2(t)\rangle \propto \left(2\gamma_1 + \frac{2V^2}{(4\gamma_1)}\right)t - \frac{2V^2}{(4\gamma_1)^2}[1 - \exp(-4\gamma_1 t)], \quad (13a)$$

$$\langle m^2(t)\rangle \propto 2\gamma_1 t + V^2 t^2. \quad (13b)$$

At long times the SLE produces a mean square displacement (13a) which increases linearly in time and yields a two-channel diffusion rate. On the other hand, neglecting correlations between the two channels eliminates the scattering of an otherwise coherently propagating particle which is necessary to produce diffusive motion over macroscopic length scales, with the result that at long times the mean square displacement (13b) increases quadratically in time. At short times, both mean-square displacements increase linearly in time. This feature is directly attributable to the existence of a purely incoherent transport channel in the models considered. Needless to say, when SLE's are used to study motion at short times, the approximation of *completely* incoherent motion via the additional channel of motion represented by the γ's is not made, and the mean square displacement initially displays a quadratic dependence on time, as required.

To examine the subtler behavior of the two lineshapes we have discussed, it is useful to consider the "peak height" $S(k, 0)$ and its reciprocal $S(k, 0)^{-1}$ as functions of the available parameters. Care must be taken that this formally useful device does not lead to misinterpretation of our results. For a Lorentzian lineshape, $\pi S(k, 0)^{-1}$ is identical to the half width at half maximum (HWHM). In general, no simple relation exists between $S(k, 0)$ and the HWHM, particularly for such parameters that $S(k, 0)$ is not a peak. In practice, however, data are commonly fitted incorporating the experimental errors in weighting functions, with the result that fit parameters are most representative of line shapes in their peak regions. Thus, one may sometimes use $S(k, 0)$ to obtain information about *derived* HWHM's. We shall not use $S(k, 0)$ in this way. Rather, we shall use $S(k, 0)$ as a simple formal device for comparing line-shape formulations.

Figures 3 and 4 display $S(k, 0)$ as a function of incoherence and $S(k, 0)^{-1}$ as a function of momentum transfer. The narrowing behavior seen in Fig. 1 appears in Fig. 3 as an increase in $S(k, 0)$ which is initially linear in the incoherence parameter $2\gamma^0/V(k)$, with a slope determined by the value of k. When $\gamma^k/\gamma^0 < 0$, that slope is negative, in which case the line does not narrow before final broadening sets in. The $\gamma^k = 0$ case discussed above, in which the two formulations are identical, is thus seen to be the marginal case demarking regions of k-space in which motional narrowing will and will not be observed. In all cases, however, the dependence of $S(k, 0)$ on the incoherence parameter continues to be linear near the coherent limit. When correlations between the band and hopping channels are neglected, $S(k, 0)$

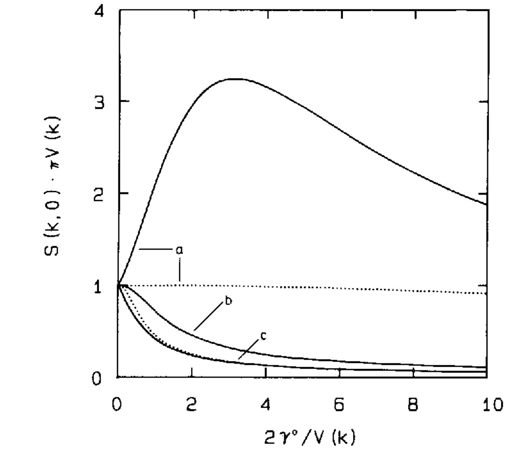

Fig. 3. $S(k, 0)\cdot\pi V(k)$ as a function of the incoherence parameter $2\gamma^0/V(k)$. The solid curves (——) were calculated from the SLE and display the characteristic features of motional narrowing. The dotted curves (·····) were calculated neglecting correlations between tunneling and hopping processes: (a) $ka = \pi/10$, (b) $ka = \pi/2$, solid and dotted curves coincide, (c) $ka = \pi$.

becomes a monotonically decreasing function of incoherence for all values of k, as is seen also in Fig. 3, and no narrowing of the lineshape occurs. The dependence of $S(k, 0)$ on the incoherence parameter is quadratic near the coherent limit. Near the incoherent limit, both formulations yield essentially the same results, attesting to the weakening of correlations between the two channels with increasing incoherence.

The "reciprocal peak height" $S(k, 0)^{-1}$, which has some of the properties of the HWHM, is displayed in Fig. 4 as a function of momentum transfer. The most significant feature of this comparison is that the SLE (7) results in a quadratic dependence on k in the long-wavelength limit ($ka \ll 1$), with a coefficient given by the two-channel macroscopic diffusion rate

$$\pi S(k, 0)^{-1} \propto \left(\gamma^0 + \frac{V^2}{\gamma^0}\right)(ka)^2, \tag{14}$$

reflecting the usual diffusive behavior as seen in the mean square displacement (13a). This result remains valid when V^2/γ^0 is replaced by V^2/Γ. Neglecting correlations between channels results in a linear dependence on k in the same limit, with a coefficient given by the rms velocity of an unscattered particle in the coherent channel,

$$\pi S(k, 0)^{-1} \propto 2Vka, \tag{15}$$

reflecting the behavior of the mean-square displacement (13b).

3. CONCLUSION

The techniques of neutron scattering lineshape theory are well developed for addressing microscopic motion which is completely coherent (as for a particle in an energy band) or completely incoherent (as for a random walker). It is also possible (as in KB) to treat the intermediate case of an arbitrary degree of coherence. The coupling of a particle's translational motion and its local vibrational motion can be treated in various ways, depending on the nature of its environment (e.g. solid or liquid) and the strength with which the two kinds of motion are coupled. For an atom moving among the sites of a crystal, the local and translational motions may usually be taken to be uncorrelated, resulting in the familiar Debye–Waller factors as coefficients of quasielastic scattering intensities. The proven usefulness of this approach for separating the scattering contributions of local and translational motion has suggested that a similar separation might be used to advantage when the translational motion is the consequence of the combined action of tunneling and hopping processes [2].

Our calculation of the neutron scattering lineshape using a transport equation which embodies the coupling of tunneling and hopping processes has allowed us to isolate lineshape features attributable to that coupling by contrasting an exact analysis of the stochastic Liouville equation [1] with its correspondent for which the coupling of the two channels of motion was specifically neglected [2]. It has been shown that motional narrowing of the scattering line shape is the normal behavior near the coherent limit, even in the presence of an additional hopping channel, and the conditions under which narrowing would not occur have been determined. It has been found, on the other hand, that, when correlations between the two channels are neglected, the lineshape does not narrow. Importantly, it was seen that neglecting correlations between the two channels of motion results in unphysical lineshape features for small momentum transfers. Specifically, both a direct evaluation of the

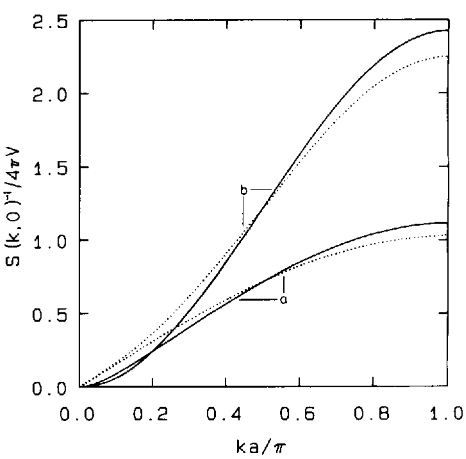

Fig. 4. $S(k, 0)^{-1}/(4\pi V)$ as a function of momentum transfer. The solid curves (——) were calculated from the SLE, while the dotted curves (·····) were calculated neglecting correlations between tunneling and hopping processes: (a) $\gamma_1/V = 0.1$, (b) $\gamma_1/V = 1.0$. The differences between the two treatments are particularly acute at long wavelengths.

relevant mean square displacement and the behavior of the peak height as a function of momentum transfer has revealed that the assumptions underlying such a lineshape calculation are inconsistent with diffusive behavior on a macroscopic scale.

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