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NEUTRON SCATTERING LINESHAPES FOR NEARLY-INCOHERENT TRANSPORT ON NON-BRAVAIS LATTICES†

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Abstract—A method for recovering results valid near the limit of incoherent transport from corresponding results at the limit of complete incoherence is applied to the calculation of the neutron scattering lineshape. Lineshape formulae due to Kutner and Sosnowska for master equation transport on general non-Bravais lattices are extended by means of this method to include the effects of small degrees of transport coherence. The resulting lineshape is a sum of non-Lortenzian components. The effect of coherence on the width functions of the multicomponent lineshape is illustrated.

Keywords: Neutron scattering, metal hydrides, hydrogen diffusion, non-Bravais lattices, master equation, stochastic Liouville equation.

1. INTRODUCTION

In recent papers [1–3], the authors have studied the effects which varied degrees of transport coherence produce in the lineshapes encountered in quasielastic neutron scattering. The mobile particles of principal interest have been hydrogen nuclei in metal hydrides, and attention has been given to motion in Bravais interstice lattices. The coherence of the motion has been treated in a unified way, and results have been obtained for all degrees of coherence. The problem posed by the non-Bravais interstice lattices of most real metal hydrides is considerably more complex than that heretofore considered. However, we may exploit one simplification of the transport problem in these complex lattices, which is the consequence of experimental conditions: Experiments on α-phase metal hydrides are limited to relatively high temperatures due to the precipitation of the mobile α-hydrogen into ordered phases which occurs at low temperatures. At the high temperatures relevant to such experiments, transport is expected to be nearly incoherent. Strong evidence of coherence is expected at best at temperatures far below those at which the neutron scattering technique ceases to be practical. Thus, it is the neighborhood of the incoherent limit which is most relevant to neutron scattering experiments on hydrogen in the α-phase of real metal hydrides. Rather than pursuing results for the case of extended, three-dimensional non-Bravais lattices affording the same generality as those of Refs. [2] and [3] (which would be of little use because of their complexity, as well as being irrelevant), we wish to develop useful lineshape formulae valid near the incoherent limit, where transport and observables sensitive to transport are only weakly influenced by the residual coherence.

Since the temperatures in the scenarios we consider are high, we will be unconcerned with the detailed balance symmetry of the scattering lineshape, and we will further neglect Debye–Waller factors, for simplicity. Moreover, we need not be concerned with the structure of the full density matrix, since the lineshape contributions of off-diagonal density matrix elements are negligible at sufficiently high temperatures. We need consider only the site-occupation probabilities, and will base our transport analysis on the generalized master equation for these probabilities [4, 5]

$$\dot{P}^i_m(t) = \int_0^t dt' \sum_{j,n} \{\mathcal{W}^{ij}_{mn}(t-t')P^j_n(t') - \mathcal{W}^{ji}_{nm}(t-t')P^i_m(t')\}$$

in which subscript indices m, n label unit cells and superscript indices i, j label inequivalent sites within a unit cell. We shall find it convenient to consider also an alternative memory kernel defined by the relations $\mathcal{A}^{ij}_{mm'} \equiv -\mathcal{W}^{ij}_{mm'}$ $(m \neq m')$ and $\mathcal{A}^{ij}_{mm} \equiv \sum_{m'} \mathcal{W}^{ij}_{m'm}$.

Near the incoherent limit, a formalism based on memory functions simplifies due to the suppression of memory function structure by bath interactions. The coherent structure responsible for maintaining phase relations becomes ineffectual due to smoothing and to increasingly rapid decay. As the incoherent limit is approached, the memory functions become proportional to delta functions in time, reducing the generalized master equation to the simpler Pauli master equation. Kenkre and Wong [6, 7] have approximated such strongly decaying memory functions by taking the Markoffian limit of the memory kernel

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$$\mathcal{W}(t) \rightarrow \left[\int_0^\infty dt' \mathcal{W}(t')\right]\delta(t) \qquad (1.2)$$

and introducing a finite duration of memory by replacing $\delta(t)$ with a normalized exponential decay

$$\mathcal{W}(t) \approx \left[\int_0^\infty dt' \mathcal{W}(t')\right]\alpha \exp[-\alpha t]. \qquad (1.3)$$

In terms of Laplace transforms, denoted below by tildes, this exponential approximation takes the form

$$\tilde{\mathcal{W}}[\epsilon] \approx \frac{\tilde{\mathcal{W}}[0]\alpha}{\epsilon + \alpha}. \qquad (1.4)$$

Caution must be used in applying the exponential memory [6–10] which results, since the generalized master equation with such a memory is closely related to the telegrapher's equation: The latter contains an admixture of the wave equation, and so admits "probabilities" which may exhibit negative excursions [11, 12]. Let us consider the scattering functions which follow from such memories. Let us first consider the case of the Pauli master equation for which $\tilde{\mathcal{W}}_{mn}[0] = F_{mn}$. For a Bravais lattice, the scattering function so obtained is

$$S(\mathbf{k}, \omega) = \frac{1}{\pi} \mathrm{Re}\left\{\frac{1}{i\omega + \{F(0) - F(\mathbf{k})\}}\right\} \qquad (1.5)$$

where $F(\mathbf{k})$ is the spatial Fourier transform of the hopping rates F_{mn}. The exponential memory generalization may be introduced as above by substituting $\{F(0) - F(\mathbf{k})\}\alpha(i\omega + \alpha)^{-1}$ for $\{F(0) - F(\mathbf{k})\}$

$$S(\mathbf{k}, \omega) \rightarrow \frac{1}{\pi} \mathrm{Re}\left\{\frac{(i\omega + \alpha)}{\alpha\{F(0) - F(\mathbf{k})\} + i\omega(i\omega + \alpha)}\right\}$$

$$= \frac{1}{\pi} \frac{\{F(0) - F(\mathbf{k})\}\alpha^2}{[\alpha\{F(0) - F(\mathbf{k})\} - \omega^2]^2 + \omega^2\alpha^2}. \qquad (1.6)$$

This result is identical to its correspondent obtained near the incoherent limit directly from the stochastic Liouville equation calculation for a linear chain presented in Ref. [2]. The equivalence is established through the identification of $2\alpha\{F(0) - F(\mathbf{k})\}$ with $V(\mathbf{k})^2$.

The memory function obtained exactly from the stochastic Liouville equation can be approximated near its incoherent limit in a direct and particularly simple way (see, e.g., Refs. [11] and [13]). Since the structure of the coherent memory function occurs on the time scale of V^{-1} while the exponential envelope decays on the time scale α^{-1}, the memory function is completely dominated by the exponential envelope when $\alpha/V \gg 1$. In this nearly incoherent limit we may write

$$\exp[-\alpha t]\mathcal{A}^c(\mathbf{k}, t) \approx \exp[-\alpha t]\mathcal{A}^c(\mathbf{k}, 0) \qquad (1.7)$$

with the result for the scattering function (again for a Bravais lattice)

$$S(\mathbf{k}, \omega) = \frac{1}{\pi}\left\{\frac{\mathcal{A}^c(\mathbf{k}, 0)\alpha}{(\mathcal{A}^c(\mathbf{k}, 0) - \omega^2)^2 + \omega^2\alpha^2}\right\}. \qquad (1.8)$$

We therefore find, comparing (1.8) and (1.6), that the results which are valid in the neighborhood of the incoherent limit can be recovered from solutions of the master equation, i.e. from results which describe the totally incoherent limit.

2. NON-BRAVAIS LATTICES

Kutner and Sosnowska [14, 15] have obtained formulae for neutron scattering lineshapes for particles in general non-Bravais lattices when transport is governed by the master equation. The lineshapes consist of a number of commonly centered Lorentzians, the number at a general point in the Brillouin zone being the same as the number p of inequivalent sites in a primitive cell. Since we have neglected Debye-Waller factors and are considering high temperatures, their result may be expressed

$$S(\mathbf{k}, \omega) = \frac{1}{\pi}\sum_{i=1}^{p} c_i\left\{\frac{\mu_i(\mathbf{k})}{\omega^2 + \mu_i^2(\mathbf{k})}\right\} \qquad (2.1)$$

in which $\mu_i(\mathbf{k})$ is the ith eigenvalue of the jump matrix $J(\mathbf{k})$ and c_i is the equilibrium population of the ith sublattice. The elements of the jump matrix are

$$J_{ij}(\mathbf{k}) = \begin{cases} \sum_m F^{ij}_{mn}\exp[-i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n + \mathbf{R}_i - \mathbf{R}_j) & i \neq j \\ \sum_m F^{ii}_{mn}\exp[-i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n) - \sum_m F^{ii}_{mn} & i = j \end{cases} \qquad (2.2)$$

where F^{ij}_{mn} is the master equation hopping rate from the jth site in the nth cell to the ith site in the mth cell. The corresponding result for a generalized master equation is immediate:

$$\tilde{\mathcal{J}}_{ij}(\mathbf{k}, \epsilon) = \begin{cases} \sum_m \tilde{\mathcal{W}}^{ij}_{mn}[\epsilon]\exp[-i\mathbf{k}\cdot(\mathbf{r}_m - \mathbf{r}_n + \mathbf{R}_i - \mathbf{R}_j) & i \neq j \\ \sum_m \tilde{\mathcal{W}}^{ii}_{mn}[\epsilon]\exp[-i\mathbf{k}\cdot(\mathbf{r}_m - \mathbf{r}_n) - \sum_m \tilde{\mathcal{W}}^{ii}_{mn}[\epsilon] & i = j. \end{cases} \qquad (2.3)$$

The general case is intractable since the memory functions are known only for simple "jump" geometries in systems of low dimensionality. However, the approximate memory (1.4) belongs to the class of separable memories, viz., memories such that

$$\mathcal{W}^{ij}_{mn}(t) = \phi(t)F^{ij}_{mn}. \tag{2.4}$$

A separable memory results in a time dependent "jump matrix" which is also separable, and equal to $\phi(t)J(\mathbf{k})$. The separability of the jump matrix allows an exact generalization of the master equation scattering function to be obtained:

$$S(\mathbf{k}, \omega) \to \frac{1}{\pi} \sum_{i=1}^{p} c_i \mathrm{Re}\left\{\frac{1}{i\omega + \tilde{\phi}[i\omega]\mu_i(\mathbf{k})}\right\}. \tag{2.5}$$

In the exponential memory approximation, we have the result

$$S(\mathbf{k}, \omega) = \frac{1}{\pi} \sum_{i=1}^{p} c_i \left\{\frac{\mu_i(\mathbf{k})\alpha^2}{(\mu_i(\mathbf{k})\alpha - \omega^2)^2 + \omega^2\alpha^2}\right\}. \tag{2.6}$$

This scattering function is a superposition of component lines having the same form, differing only in the detail of their parametric dependence on momentum transfer. Each has the same form as that which obtains for a two-site system. It is simple to understand why this should be so. The coherent memory for a pair of sites is simply $2V^2$ if V is the tunneling matrix element; that is, $\mathcal{W}^c(t)$ is constant in time. *Any* introduction of decay into the evolution of a two-site system therefore results in a memory which is trivially separable: $\mathcal{W}(t) = \mathcal{W}^c(0)\phi(t)$. Since a separable memory results in a separable jump matrix, the spatial structure which distinguishes the extended lattice from the two-state system is transformed into the **k**-dependence of the eigenvalues of the Markoffian jump matrix. The composite lineshape is indistinguishable from that of a **k**-dependent superposition of p-dimers.

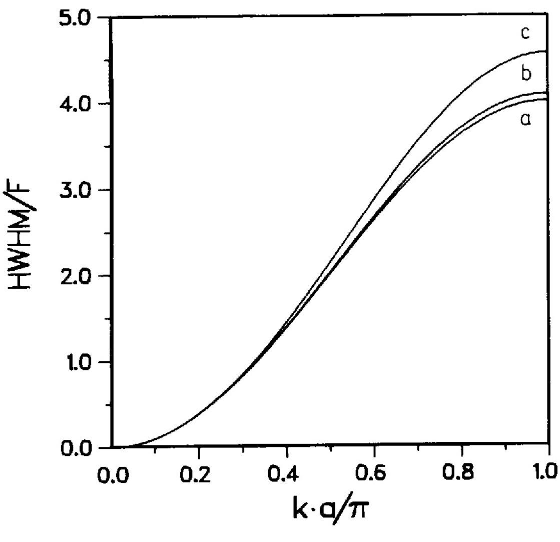

Fig. 1. Half-width at half-maximum for a linear chain with nearest neighbor tunneling interactions. Curve (a) results in the incoherent limit, and is equivalent to the corresponding master equation result. Curve (c) results when $2V/\alpha = 0.5$ and is the case of marginal validity, since $V(\mathbf{k})/\alpha = 1$ at the zone boundary while our approach assumes this parameter to be small. All greater degrees of incoherence result in half-width curves which fall between (a) and (c). Representative of these is curve (b), for which $2V/\alpha = 0.1$.

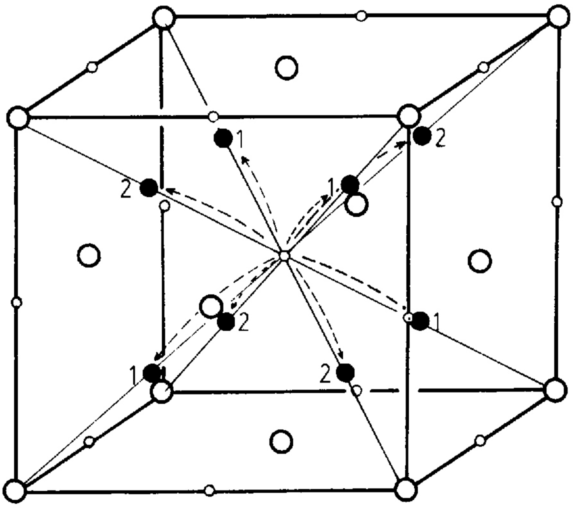

Fig. 2. Face-centered cubic unit cell showing lattice sites (O), octahedral interstices (O), tetrahedral interstices (●), and jump vectors (→) between nearest neighbors in the octahedral–tetrahedral lattice. Tetrahedral interstices having the same label are of the same symmetry.

In the present case the lineshape for a given **k** is rather simple, particularly since we must confine ourselves to the nearly incoherent regime where we expect the lineshape to be very nearly a sum of Lorentzians. The dependence of the lineshape on momentum transfer is considerably more complex, as a result of the multiplicity of eigenvalues and their distinct spatial structure, and is usually studied in the behavior of the half-width at half-maximum (HWHM).

In the incoherent limit of transport on a Bravais lattice, the lineshape is Lorentzian with a HWHM which vanishes at $\mathbf{k} = 0$ and increases toward the edge of the Brillouin zone. Small degrees of coherence cause the HWHM to exceed that found in the incoherent limit. The excess width which may be ascribed to coherence varies with respect to **k**. The neutron scattering technique probes transport properties on the extrinsic length scale $|\mathbf{k}|^{-1}$ while the transport properties themselves depend on intrinsic length scales, e.g. through the relative values of the mean free path and the dimensions of a unit cell. The extrinsic coherence parameter ($\sim V(\mathbf{k})/\alpha$) is generally an increasing function of $\mathbf{k}\cdot\mathbf{a}$, reflecting the greater sensitivity of the probe to coherent processes at high momentum transfers. This is exemplified in Fig. 1, where we show the HWHM which results for transport on a linear chain with nearest neighbor tunneling interactions. This result may be obtained straightforwardly from eqn (2.6) (which consists of a single compound in this case) or from the exact calculation in Ref. [2]. The curve (a) represents the HWHM for purely incoherent transport, viz. transport which is incoherent on all length scales. Curves (b) and (c) result when the degree of transport coherence is nonvanishing. The convergence of all curves in the neighborhood of $\mathbf{k} = 0$ reflects the fact that in each case, transport is incoherent over macroscopic length scales. On the other hand, the distinct nature of the several widths at large momentum transfers reflects the coherence of transport over length scales accessible to the experimental probe.

The corresponding result for a non-Bravais lattice is complicated by the fact that the HWHM contains a mixture of behaviors due to the multiplicity of eigenvalues, which generally possess distinct **k** dependences. As an example of results which follow from the present approach, we consider nearly incoherent transport among the tetrahedral (t) and octahedral (o) interstices of and f.c.c. lattice. We have calculated width functions for the same case as presented in reference [14], viz. we have considered only the shortest jump path (o-t-o-t-o-) to contribute. For simplicity, we neglect any preferred occupancy of any class of sites ($c_i = \frac{1}{3}$). The jump vectors are shown in Fig. 2, and in Fig. 3 we show the HWHM which follows from eqn (2.6) for the principal crystallographic directions. The consequences of small degrees of coherence are seen to be qualitatively identical to those which result in the case of Bravais lattices.

In these calculations care was taken to remain near the incoherent limit in each case. The multicomponent lineshape (2.6) is an asymptotic result, and may display suggestive but unsupportable structure when the degree of coherence becomes too large. Specifically, the lineshape develops side peaks as the degree of coherence is increased arbitrarily. Such side peaks would normally be indicative of tunneling states; however, in obtaining the asymptotic lineshape the structure of the original density of states has been lost. The development of side peaks of any kind is spurious, since our approach is sensitive only to the *existence* of coherence, and not the structure of the evolution which it characterizes. In the results presented in Fig. 3, the degrees of coherence considered were sufficiently small that the broadest component of each multicomponent line remained singly peaked.

While we have used a $\phi(t)$ which was exponential, the method may be applied equally well to nonexponential $\phi(t)$ which decay sufficiently rapidly. While our intent in this paper has been to consider the influence of tunneling interactions on lineshapes, the well-known equivalence between generalized master equations and continuous time random walk equations may be used to extend applications of the method to transport problems involving a variety of random processes [5, 16]. The existence of this avenue of extension underscores the caution of the preceding paragraph that the method is sensitive primarily to the finite duration of memory. It is entirely possible for the same asymptotic lineshape to be consistent both with transport through quantum mechanisms and purely stochastic processes. Coherence in either case is a quantifiable attribute of transport. The nearly Lorentzian nature of lineshapes which result for most metal hydrides suggests that the mildly generalized lineshapes such as (2.5) or (2.6) should provide adequate means of obtaining a measure of coherence from neutron scattering experiments.

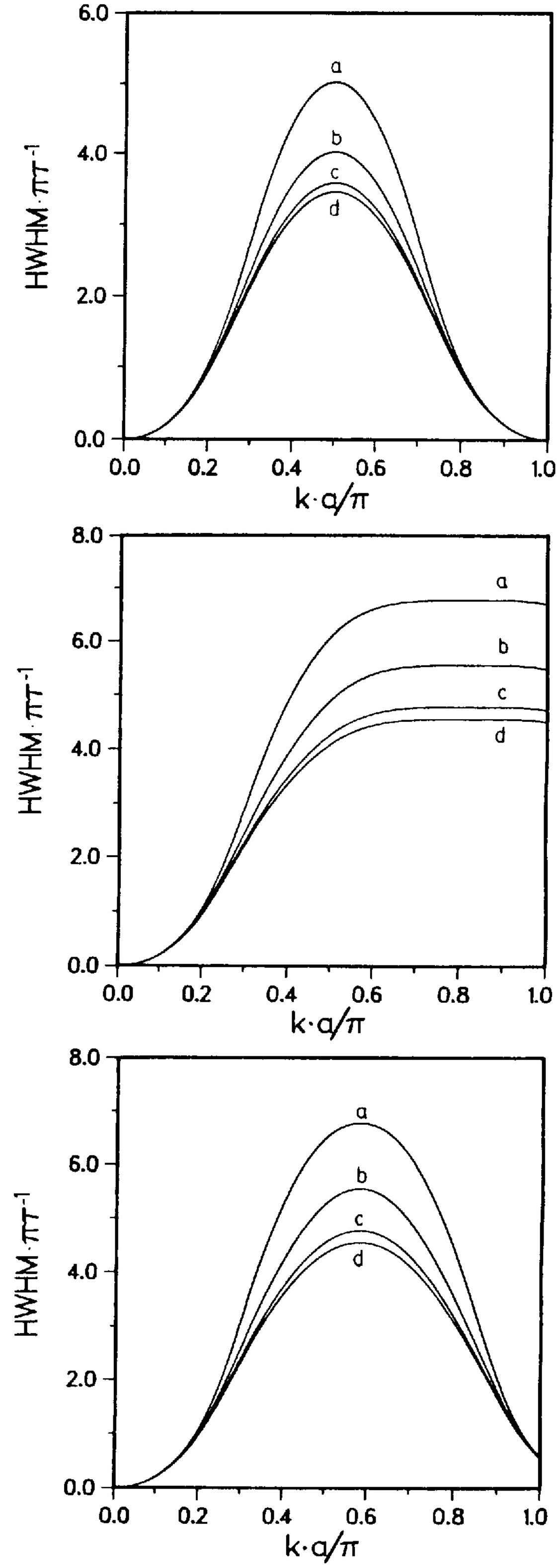

Fig. 3. Half-widths at half-maximum evaluated from eqn (2.6) for the principal crystallographic directions in an f.c.c. lattice (3.1: [111], 3.2: [110], 3.3: [100]). Jumps occur between octahedral and tetrahedral interstices only, and all jump times have been taken to be identical ($\tau_{ot} = \tau_{to} = \tau$). Curves display the effect of small degrees of coherence on linewidths. Parameter values: (a) $\alpha\tau = 10.0$, (b) $\alpha\tau = 25.0$, (c) $\alpha\tau = 100.0$, (d) $\alpha\tau = \infty$.

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