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QUASIELASTIC NEUTRON SCATTERING IN METAL HYDRIDES: EFFECTS OF THE QUANTUM MECHANICAL MOTION OF INTERSTITIAL HYDROGEN ATOMS*

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The traditional theme of metal hydride transport analysis has employed an equation for the probability $P_\ell(t)$ that a hydrogen atom occupies an interstitial site ℓ in the host metal at a time t

$$\frac{d}{dt} P_\ell(t) = \sum_{\ell'} [\Gamma_{\ell\ell'} P_{\ell'}(t) - \Gamma_{\ell'\ell} P_\ell(t)] \quad (1)$$

where $\Gamma_{\ell\ell'}$ is the hopping rate from site ℓ' to site ℓ . The inadequacy of such treatments has led more recent investigations to consider correlations between jumps and correlations in continuous time.² We will discuss here a transport instrument particularly well suited to the analysis of such memory effects, and we will illustrate the nature of these effects on the quasielastic scattering function.

The hopping picture of hydrogen motion can be understood as arising through a process of coarse-graining from a microscopic, "flowing" picture, wherein motion is described by the Schrödinger equation. Under certain initial conditions (including the completely (de)localized ones) the Schrödinger equation has been shown to lead, without approximation, to the generalized master equation³

$$\frac{d}{dt} P_\ell(t) = \int_0^t dt' \sum_{\ell'} \{W_{\ell\ell'}(t-t') P_{\ell'}(t') - W_{\ell'\ell}(t-t') P_\ell(t')\}. \quad (2)$$

As a direct consequence of quantum mechanics, (2) includes effects not accessible to (1), which is recovered under the Markoffian approximation, in which the "memory functions" $W_{\ell\ell'}(t)$ are replaced by time delta functions $\delta(t)\Gamma_{\ell\ell'}$. In the case of translationally invariant systems one of us⁴ has calculated the memory functions of

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(2), which may be simply written in the Fourier-Laplace domain as

$$\tilde{W}^q(\epsilon) = - \left\{ \frac{1}{N} \sum_k [\epsilon + i(V^{k+q} - V^k)] \right\}^{-1} \quad (3)$$

where N is the number of sites, $V_{\ell\ell'}$ the intersite Hamiltonian matrix element (The discrete Fourier space (q) is conjugate to the lattice.). Dimensionality does not restrict (3), so (2) and (3) together give a purely quantal description of motion in perfect crystalline matter.⁴

A familiar description of motion with site-to-site interaction V and a randomizing parameter α is provided by stochastic Liouville equations for the density matrix ρ ⁵

$$\frac{\partial}{\partial t} \rho_{\ell m} = \frac{1}{i\hbar} [V, \rho]_{\ell m} - \alpha(1 - \delta_{\ell m}) \rho_{\ell m} + \delta_{\ell m} \sum_{\ell'} (\Gamma_{\ell\ell'} \rho_{\ell' \ell} - \Gamma_{\ell' \ell} \rho_{\ell \ell'}) \quad (4)$$

shown here without a term in $\rho_{m\ell}$, often neglected for simplicity. It has further been shown⁶ that (4) is equivalent to (2) with

$$W_{\ell\ell'}(t) = \Gamma_{\ell\ell'} \delta(t) + W_{\ell\ell'}^C(t) e^{-\alpha t} \quad (5)$$

where $W_{\ell\ell'}^C(t)$ is the memory function whose Fourier-Laplace transform is (3). The two-channel form of (5) is directly due to the natural separation of transport events into a class assisted by a change in the bath state, and a class in which no such change occurs. Furthermore, the last term in (5), even by itself, provides a simple, continuous bridge between the "hopping" and "flowing" extremes of transport. The two primary aspects of microscopic motion being thus accessible to the generalized master equation (2) with (5), we take it as the instrument for our calculation.

In the usual vein we write the scattering function $S(q, \omega)$ as a product of a Debye-Waller factor involving only the mean square displacement $\langle u^2 \rangle$ and the scattering function $S^D(q, \omega)$ arising from the hydrogen transport alone¹

$$S(q, \omega) = e^{-q^2 \langle u^2 \rangle} S^D(q, \omega) \quad (6)$$

The quantity of interest is $S^D(q, \omega)$, which is related to the van Hove self-correlation function $G_s(\ell, t)$ through $G(q, \epsilon)$ as

$$S^D(q, \omega) = \text{Re} \tilde{G}_s(q, i\omega) \quad (7)$$

Defining $\Lambda_{\ell\ell'}(t) \equiv -W_{\ell\ell'}(t)$, $\Lambda_{\ell\ell'}(t) \equiv \sum_{\ell''} W_{\ell\ell''}(t)$, and invoking the translational invariance of the system, we see that the propagator $\psi_\ell(t)$ of (2) has the Fourier-Laplace transform

$$\tilde{\psi}^q(\epsilon) = \{\epsilon + \Lambda^q(\epsilon)\}^{-1} = \{\epsilon + \tilde{W}^0(\epsilon) - \tilde{W}^q(\epsilon)\}^{-1} \quad (8)$$

and is identical to $G_s(\ell, t)$ at high enough temperatures. Therefore,

within the approximations discussed, we have the result.

$$S^D(q, \omega) = \text{Re} \{ \tilde{W}_c^q (\alpha + i\omega) - \alpha + (\Gamma^0 - \Gamma^q) \}^{-1} \quad (9)$$

The restriction to high temperatures (narrow bands) is made only because this is the normal regime of hydrogen transport; the extension of (9) to arbitrary temperature has been developed,⁷ but is not presented here.

For simplicity we shall consider a one-dimensional crystal with nearest-neighbor interactions V and nearest-neighbor hopping rates Γ , whereupon (9) results in

$$S^D(q, \omega) = \text{Re} \{ \sqrt{(\alpha + i\omega)^2 + 16V^2 \sin^2(q/2)} - \alpha + 4\Gamma \sin^2(q/2) \}^{-1} \quad (10)$$

The "flowing" limit is obtained from (10) by allowing α and Γ to vanish: defining $V_q \equiv 4V \sin(q/2)$ and $\Gamma_q \equiv 4\Gamma \sin^2(q/2)$, we have

$$S^D(q, \omega) = \{ \sqrt{V_q^2 - \omega^2} - \Gamma_q \}^{-1} \quad (11)$$

The "hopping" limit is extracted by keeping $2V^2/\alpha$ finite as both α and V are allowed to diverge, resulting in the Lorentzian

$$S^D(q, \omega) = \frac{4(\Gamma + 2V^2/\alpha) \sin^2(q/2)}{\omega^2 + [4(\Gamma + 2V^2/\alpha) \sin^2(q/2)]^2} \quad (12)$$

The intermediate regime forsakes such simplicity, requiring the more complicated form

$$\begin{aligned} S^D(q, \omega) = & \{ [V_q^2 - \omega^2 - \Gamma_q (\alpha - \Gamma_q)] \left[\frac{1}{2} \left((V_q^2 + \alpha^2 - \omega^2)^2 + 4\alpha^2 \omega^2 \right)^{\frac{1}{2}} + \frac{1}{2} (V_q^2 + \alpha^2 - \omega^2) \right]^{\frac{1}{2}} \\ & + \alpha \omega \left[\frac{1}{2} \left((V_q^2 + \alpha^2 - \omega^2)^2 + 4\alpha^2 \omega^2 \right)^{\frac{1}{2}} - \frac{1}{2} (V_q^2 + \alpha^2 - \omega^2) \right]^{\frac{1}{2}} \\ & + (\alpha - \Gamma_q) [V_q^2 - \omega^2 - \Gamma_q] \} / \{ [V_q^2 - \Gamma_q (\alpha - \Gamma_q) - \omega^2]^2 + 4\alpha^2 \omega^2 \} \end{aligned} \quad (13)$$

Figure 1 displays the general features of our result for the case of negligible Γ_q and fixed V_q . The parameter V_q/α represents the degree of persistence of quantum mechanical phase. The decrease in linewidth (after an initial increase) with increasing randomization of phase testifies to the occurrence of motional narrowing. The diffusion constant varies among the curves of Fig. 1; therefore, if known (e.g., from measurements of the mean square displacement at long times) the ratio $2V^2/\alpha$ may be used to present our results in another meaningful way. Fig. 2 displays $S^D(q, \omega)$ for fixed $2V^2/\alpha$ and negligible Γ_q , which requires both α and V_q to vary. At fixed q , the content of Fig. 2 is essentially the same as Fig. 1; however, in the experimentally reasonable case that α and V are fixed (and probably

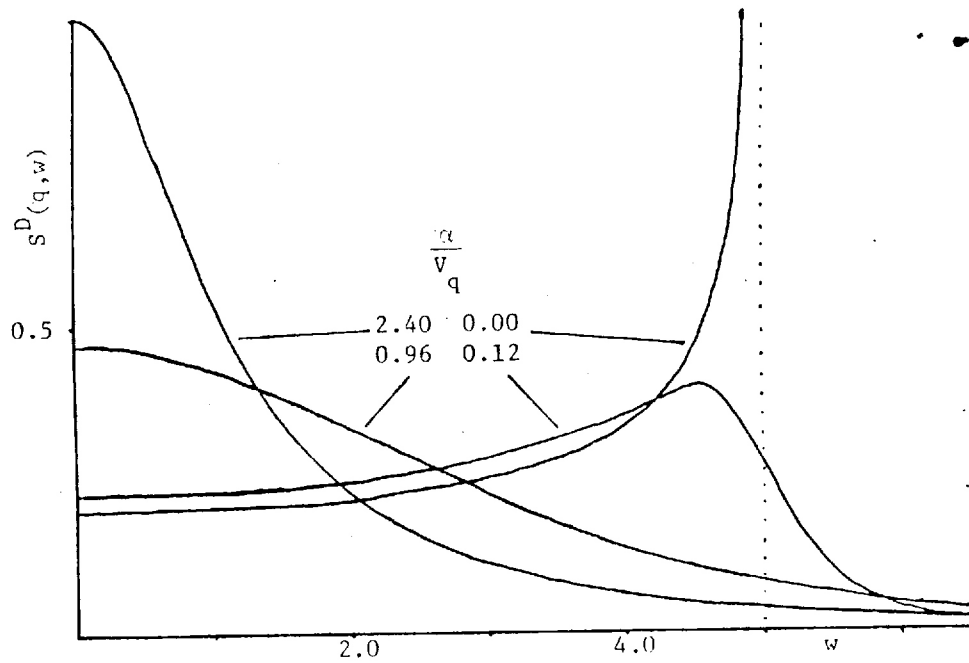


Fig. 1. Scattering function $S^D(q, w)$ plotted against frequency w for several values of α/v_q for $\Gamma_q=0$. v_q has been set arbitrarily 5.

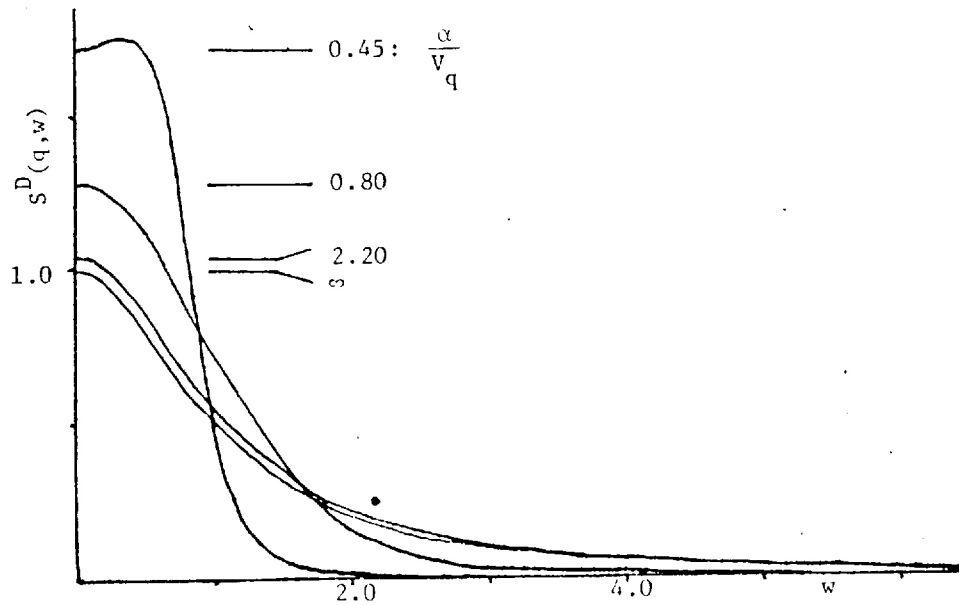


Fig. 2. Scattering function $S^D(q, w)$ in which $\Gamma_q=0$ and $2v^2/\alpha=4$. When $\alpha/v \gg 1$, $2v^2/\alpha$ represents the diffusion constant.

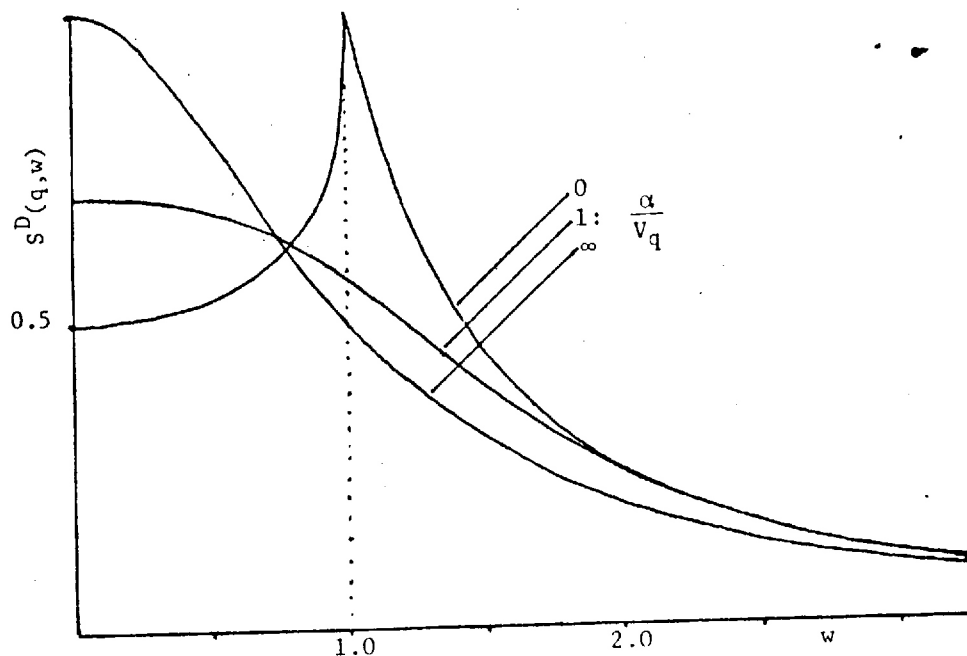


Fig. 3. Scattering function $S^D(q,w)$ in the presence of bath-assisted transport. Γ_q and V_q have been set arbitrarily to 1.

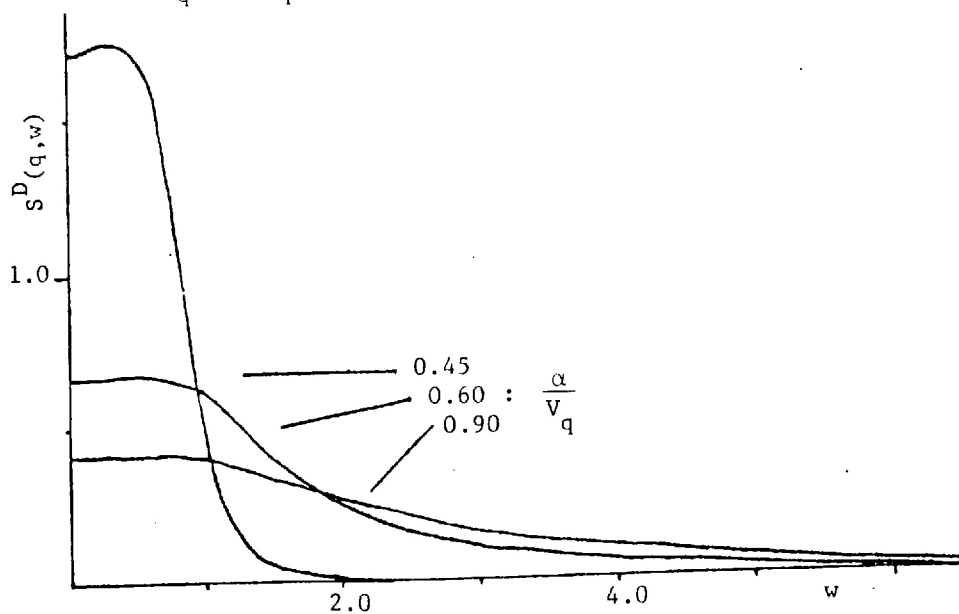


Fig. 4. Scattering function in the presence of bath-assisted transport. For comparison with Fig. 3, $(2V^2/(\alpha+\Gamma))=4$ and $V=.9$. When $\alpha/V \gg 1$, $(2V^2/(\alpha+\Gamma))$ represents the diffusion constant.

unknown), Fig. 2 displays the dependence of the lineshape on momentum transfer [$\alpha/q = \alpha/4V \sin(q/2)$]. It must be noted that whatever values of α and V may be available in a system, observable effects become completely washed out at low momentum transfers (large α/V).

Figs. 3 and 4 relax the restriction that Γ_q vanish in Figs. 1 and 2 respectively. In Fig. 3, V_q and Γ_q are fixed at nontrivial values, showing now the effect of phase randomization in the presence of bath-assisted transport. Characteristic features are that $S^D(q,0)$ is pinned between the values Γ_q^{-1} and $(V_q + \Gamma_q)^{-1}$, and that the maximum value attained by $S^D(q,w)$ in both limits of Γ is Γ_q^{-1} . Motional narrowing is again evident; however, the lines now narrow to the Lorentzian (12) whereas there was no Lorentzian in Fig. 1. The hopping rate $1/\tau$ appearing in the usual Master equation treatments¹ of hydrogen motion corresponds, in the presence of bath-assisted transport, to $2V^2/\alpha + \Gamma$. Specifying this quantity fixes the diffusion constant, and conversely, the existence of a diffusion constant fixes lower and upper bounds for α and Γ respectively (fixed V). Thus the curve in Fig. 2 appropriate to a system with a known diffusion constant reflects the most extreme effect of phase persistence which can be observed in that system. The sense of this statement is shown in Fig. 4, where we have chosen one of the Fig. 2 curves and allowed Γ to increase from zero.

We have illustrated the manifestations in the scattering observable of two distinct features of the microscopic motion of the hydrogen atom: (i) quantum mechanical phase persistence and (ii) competition of bath-assisted and bath-hindered transport. Such manifestations include generally non-Lorentzian lines, motional narrowing, and a characteristic distension in the half-widths of near-Lorentzian lines. Limitations on the possible appearance of these have been noted, importantly the experimental demand of significant momentum transfer. Our transport instrument in this analysis has been the well-known stochastic Liouville equation in a high-temperature approximation, or equivalently, the corresponding generalized master equation. The detailed analysis of these effects for realistic lattices and arbitrary temperatures will be reported elsewhere.

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