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Wave-vector dependence in quasielastic neutron scattering

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The wave-vector (k) dependence of the quasielastic (QE) intensity generated by neutrons scattered by particles moving under the action of one-dimensional potentials and weak stochastic forces is investigated in detail. It is shown that, in the low- k limit, the quasielastic intensity due to scatterers subject to symmetric potentials is proportional to k^4 , while asymmetric potentials will generally give rise to a k^2 term. Formulas to evaluate the coefficient for an arbitrary term in a k expansion of the cross section are derived. It is also shown that the QE line consists of a superposition of Lorentzians generated by energy relaxation modes. A possible application to the soft-potential model of glasses is indicated. [S0163-1829(97)03741-7]

It has often proved useful to model slow excitations in such complex, disordered systems as proteins and glasses by considering localized motions under the action of effective one-dimensional potentials.^{1,2} The effects of fast modes on these excitations can be introduced through a stochastic term in the equations of the motion. This stochasticity gives rise to a quasielastic (QE) line in the neutron-scattering spectrum.^{3,4} Since we usually do not know *a priori*—but would like to ascertain—the nature of the forces that determine the scatterer motion, an analysis of the properties of the scattering cross section corresponding to physically meaningful model systems would be valuable. In particular, a detailed understanding of the relation between the properties of the model potentials and the energy and wave-vector dependence of the cross section would help us optimize the information provided by the experiments.

We have recently examined the behavior of the dynamic structure factor generated by scatterers that move under the influence of potential and weak stochastic forces.^{5–7} In Ref. 5 we showed that a scatterer subject to Hamiltonian motion in one dimension cannot yield a QE line (an exception is provided by potentials containing flat sections). We also argued that, if stochastic forces are added, the total QE intensity can be obtained as the difference between the elastic intensity for the associated Hamiltonian system and the Debye-Waller factor. Using a cumulant expansion, it then follows that the total QE intensity scattered by symmetric

potentials grows as k^4 . The purpose of this paper is to examine in greater detail the correlation between the potential symmetry and the wave-vector dependence of the QE scattered intensity using the more general formalism of Ref. 6. We will also derive explicit formulas for the coefficients in a wave-vector expansion of the cross section. These formulas permit a precise evaluation of the QE line shape when the scatterer is simultaneously subject to potential and stochastic forces.

A Fokker-Planck approach can be used to investigate the QE line generated by scattering from anharmonic single-minimum oscillators subject to weak frictional forces.⁶ Using a method due to Dykman and co-workers,^{8,9} we showed that the QE component of the dynamic structure factor can be obtained from the solution of a generalized diffusion equation in energy space. Our analysis of the k dependence of the scattering cross section will rest on the properties of this energy diffusion equation.

In the following we assume that the scattering potential $U(q)$ is harmonic near its bottom and that $U(|q| \rightarrow \infty) \rightarrow \infty$, where q is the generalized scatterer coordinate. We further assume that the scatterer has unit mass and take the Boltzmann constant to be equal to unity.

The dependence of the neutron-scattering cross section on the momentum transfer $\hbar k$ and the energy transfer $\hbar\Omega$ is given by the dynamic structure factor

$$S(k, \Omega) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty e^{i\Omega t} F(k, t) dt, \quad (1)$$

where t is the time and $F(k, t)$ is the intermediate scattering function (ISF).^{3,4} By means of a change in variables,⁶ the ISF can be expressed in terms of an integral involving the probability density $P(E, \Phi; t)$ of finding the scatterer at a given location in the energy-phase space (E, Φ) at time t

$$F(k, t) = \int_0^\infty dE \int_0^{2\pi} d\Phi e^{ikq(E, \Phi)} P(E, \Phi; t). \quad (2)$$

Since $P(E, \Phi; t)$ is periodic in Φ , it can be expanded in a Fourier series

$$P(E, \Phi, t) = \sum_{m=-\infty}^{\infty} P_m(E, t) e^{im\Phi}. \quad (3)$$

Using this equation, the ISF can be written as the sum $F(k, t) = \sum F_m$, where each F_m involves an energy and phase integral containing a single P_m . The Fourier components P_m undergo little mixing if the friction is weak, i.e., if $\Gamma \ll \omega(E)$ for all $E \leq T$. Under these conditions, only the $m = 0$ component of F gives a substantial contribution to the quasielastic region. This component can then be evaluated as an energy integral

$$F_0(k, t) = 2\pi \int_0^\infty dE P_0(E, t) \langle e^{ikq(E, \Phi)} \rangle. \quad (4)$$

Here the angular brackets indicate the average over an orbit at fixed E . We are choosing the energy origin at the location of the potential minimum. It can be shown that the function P_0 is a solution of the following generalized energy diffusion equation:⁶

$$\frac{\partial P_0(E, t)}{\partial t} = \Gamma K P_0(E, t), \quad (5)$$

where Γ is the friction coefficient and the operator K is defined as

$$K = \frac{d}{dE} \left[A(E) \frac{d}{dE} + B(E) \right], \quad (6)$$

with

$$A(E) = 2T \langle p^2(E, \Phi) \rangle \quad (7)$$

and

$$B(E) = 2 \langle p^2(E, \Phi) \rangle \left(1 + \frac{T}{\omega(E)} \frac{\partial \omega(E)}{\partial E} \right). \quad (8)$$

Here T is the temperature, $p(E, \Phi)$ is the generalized momentum, and $\omega(E)$ is the oscillation frequency of the associated Hamiltonian system. Note a minor change in notation with respect to Ref. 6: The friction coefficient has been explicitly extracted from the operator K ; in this way we will later obtain Γ -independent eigenvalues. The initial condition for the function $P_0(E, t)$ is⁶

$$P_0(E, 0) = \frac{e^{-E/T}}{2\pi\omega(E)Z} \langle e^{-iq(E, \Phi)} \rangle, \quad (9)$$

with Z being the partition function. On the other hand, the current density j along the energy axis

$$j(E, t) = -\Gamma \left[A(E) \frac{d}{dE} + B(E) \right] P_0(E, t). \quad (10)$$

satisfies the boundary conditions $j(0, t) = j(\infty, t) = 0$.

After applying the usual ansatz $P_0(E, t) = e^{-\lambda\Gamma t} y(E)$ to Eq. (5), we are left with the eigenvalue equation

$$K y(E) + \lambda \Gamma y(E) = 0. \quad (11)$$

Defining

$$G(E) = \exp \left[\int_0^E dx A^{-1}(x) B(x) \right] = \frac{\omega(E)}{\omega(0)} e^{E/T}, \quad (12)$$

we can use the boundary conditions on $j(E, t)$ to verify that

$$\int_0^\infty dE y_1(E) G(E) K y_2(E) = \int_0^\infty dE y_2(E) G(E) K y_1(E), \quad (13)$$

i.e., the operator $G(E)K$ is self-adjoint. We can then work with a set $\{y_\lambda\}$ of real and orthogonal eigenfunctions of the operator K . Moreover, the corresponding eigenvalues are real, nondegenerate, and non-negative. The lowest eigenvalue $\lambda = 0$ corresponds to the equilibrium solution $y_0(E) = [\omega(E)Z]^{-1} \exp(-E/T)$. The evolution from the initial distribution $P_0(E, 0)$ to the equilibrium distribution $y_0(E)$ proceeds according to the energy relaxation process described by Eq. (5).

If $\lambda \neq 0$ we can easily prove the following results:

$$\int_0^\infty dE y_\lambda(E) = 0 \quad (14)$$

and

$$\int_0^\infty dE' y_\lambda(E') \int_0^\infty dE y_\lambda(E) (\langle q^n \rangle \langle q'^m \rangle - \langle q^m \rangle \langle q'^n \rangle) = 0, \quad (15)$$

where we have abbreviated $\langle q \rangle \equiv \langle q(E) \rangle$ and $\langle q' \rangle \equiv \langle q(E') \rangle$.

Implementing the initial condition, Eq. (9), we write an eigenfunction expansion for $P_0(E, t)$,

$$P_0(E, t) = \sum_\lambda C_\lambda e^{-\lambda\Gamma t} y_\lambda(E), \quad (16)$$

with

$$C_\lambda = \frac{1}{\omega(0)Z} \int_0^\infty dE y_\lambda(E) \langle e^{-ikq(E, \Phi)} \rangle. \quad (17)$$

The ISF can now be expressed as

$$F_0(k, t) = \frac{2\pi}{\omega(0)Z} \sum_{\lambda} e^{-\lambda\Gamma t} \int_0^{\infty} dE' y_{\lambda}(E') \int_0^{\infty} dE y_{\lambda}(E) \times \langle e^{-ikq(E', \Phi')} \rangle \langle e^{ikq(E, \Phi)} \rangle. \quad (18)$$

Next we expand the exponentials in powers of kq . It is easy to see that the averages in Eq. (18) can be written as

$$\langle e^{-ikq'} \rangle \langle e^{ikq} \rangle = \sum_{n=0}^{\infty} (A_{2n} k^{2n} + i A_{2n+1} k^{2n+1}). \quad (19)$$

By substituting Eq. (19) into Eq. (18), relabeling some sums, and using Eq. (15) we can show that all the odd powers of k cancel if $\lambda \neq 0$.

Since the system is bound, $F_0(k, \infty)$ has a nonvanishing value, which is responsible—through the $\lambda = 0$ term—for the existence of the elastic component

$$S_{el}(k, \Omega) = f(k) \delta(\Omega), \quad (20)$$

with $f(k) = 2\pi\omega(0)Z|C_0|^2$ being the Debye-Waller factor.

If we restrict ourselves to the QE line, the right-hand side of Eq. (19) can be rearranged to read

$$\sum_{j=0}^{\infty} \sum_{m=0}^{\infty} (-1)^{j+m} (k)^{2(j+m)} \left[\frac{\langle q'^{2j} \rangle \langle q^{2m} \rangle}{(2j)!(2m)!} + \frac{\langle q'^{2j+1} \rangle \langle q^{2m+1} \rangle}{(2j+1)!(2m+1)!} k^2 \right].$$

For *symmetric* potentials, $\langle q'^{2j+1} \rangle = 0$. Moreover, by using Eq. (14) we can eliminate those terms containing $j=0$ or $m=0$. The quasielastic line can then be expressed as a superposition of Lorentzians whose width is determined by the friction constant

$$S_Q(k, \Omega) = \frac{2}{\omega(0)Z} \sum_{j=1}^{\infty} \sum_{m=1}^{\infty} (-1)^{j+m} k^{2(j+m)} \times \sum_{\lambda>0} \frac{\lambda\Gamma}{(\lambda\Gamma)^2 + \Omega^2} J_{2n}(\lambda) J_{2m}(\lambda), \quad (21)$$

with

$$J_n(\lambda) = \frac{1}{n!} \int_0^{\infty} dE y_{\lambda}(E) \langle q^n \rangle. \quad (22)$$

It is now clear that the leading contribution of a symmetric potential to the QE line is proportional to k^4 ,

$$S_Q(k, \Omega) \approx \frac{2k^4}{\omega(0)Z} \sum_{\lambda>0} \frac{\lambda\Gamma}{(\lambda\Gamma)^2 + \Omega^2} J_2^2(\lambda). \quad (23)$$

This confirms what was argued in Ref. 5, but here we also have a simple prescription for the evaluation of the QE line shape. The simple harmonic oscillator result⁶ can be obtained easily after substituting the suitable expressions for λ and y_{λ} .

In the case of *asymmetric* potentials, the QE line can be evaluated as

$$S_Q(k, \Omega) = \frac{2}{\omega(0)Z} \sum_{m=0}^{\infty} \sum_{j=1}^{\infty} (-k^2)^{j+m} \sum_{\lambda>0} \times \frac{\lambda\Gamma}{(\lambda\Gamma)^2 + \Omega^2} D_{j,m}(\lambda), \quad (24)$$

where

$$D_{j,m}(\lambda) = (1 - \delta_{m,0}) J_{2j}(\lambda) J_{2m}(\lambda) - J_{2j-1}(\lambda) J_{2m+1}(\lambda).$$

The leading term is now of order k^2 ,

$$S_Q(k, \Omega) \approx \frac{2k^2}{\omega(0)Z} \sum_{\lambda>0} \frac{\lambda\Gamma}{(\lambda\Gamma)^2 + \Omega^2} J_1^2(\lambda). \quad (25)$$

A few further considerations are in order.

(1) For symmetric potentials there are cancellations that conspire to eliminate the k^2 term; the loss of correlation that generates the QE line is weaker than for unsymmetrical potentials. We note that the cancellations are even more drastic in the case of the spectral distribution $S(\Omega)$ of the position-position correlation function. In that case, Dykman *et al.* showed that the QE peak vanishes completely for single-minimum symmetric potentials.⁸

(2) In the zero-friction limit ($\Gamma \rightarrow 0$) we can use the completeness relation for $\{y_{\lambda}\}$ to prove that the QE component collapses to an elastic line, whose intensity we call $S_H(k)$. The absence of friction implies that the correlations persist for all times and that the system does not equilibrate.⁵

(3) The introduction of stochasticity ($\Gamma \neq 0$) makes the problem ergodic and induces the transfer of intensity from the elastic to the QE region. The difference between the elastic intensity $S_H(k)$ for the Hamiltonian system and the surviving intensity $f(k)$ for the ergodic system gives the total intensity of the QE line in the equilibrating system, as it was argued in Ref. 5. If we wait long enough, all memory of the periodicity is lost even for the smallest nonzero Γ . Therefore, the total transferred intensity, $S_H(k) - f(k)$ is independent of Γ , a fact that can be easily verified.

(4) Energy relaxation and system equilibration become faster with increasing stochasticity. Consequently, the width of the Gaussians is an increasing function of Γ .

(5) The cross section depends on the temperature through Z , λ , and C_{λ} . In addition, the friction coefficient itself may depend on the temperature.

(6) The sum of the elastic and QE contributions can be expressed as

$$S_{el}(k, \Omega) + S_Q(k, \Omega) = f(k) \left[\delta(\Omega) + \frac{1}{\pi} \sum_{\lambda} \left(\frac{C_{\lambda}}{C_0} \right)^2 \times \frac{\lambda\Gamma}{(\lambda\Gamma)^2 + \Omega^2} \right], \quad (26)$$

i.e., the Debye-Waller factor affects the elastic and QE components. The QE line consists of a superposition of Lorentzians generated by energy relaxation modes. The widths of these Lorentzians increase with increasing stochasticity, due to faster energy relaxation.

As an example we next analyze the asymmetric harmonic oscillator $V(q) = \frac{1}{2}(\omega_2 q)^2$ ($q < 0$) and $V(q) = \frac{1}{2}(\omega_1 q)^2$ ($q > 0$). The oscillation frequency

$$\omega = \frac{2\omega_1\omega_2}{\omega_1 + \omega_2}, \quad (27)$$

does not depend on the energy $\langle p^2 \rangle = E$ and the coordinate q can be expressed as

$$q(E, \Phi) = (2E/\omega_1^2)^{1/2} \cos(\Phi), \quad \text{if } -\pi/2 < \Phi < \pi/2$$

and

$$q(E, \Phi) = (2E/\omega_2^2)^{1/2} \cos(\Phi), \quad \text{if } \pi/2 < \Phi < 3\pi/2.$$

The eigenvalues and eigenfunctions are, respectively, $\lambda_m = 2m$ and $y_m(E/T) = T^{-1/2} \exp(-E/T) L_m(E/T)$, where m is a natural number and L_m is a Laguerre polynomial.¹⁰ The integrals in Eq. (25) are easily evaluated and we obtain

$$S_Q(k, \Omega) \approx \frac{Tk^2}{2\pi^2} \left(\frac{1}{\omega_2} - \frac{1}{\omega_1} \right)^2 \sum_{m=1}^{\infty} \left[\frac{(2m-3)!!}{(2m)!!} \right]^2 \times \frac{2m\Gamma}{(2m\Gamma)^2 + \Omega^2}. \quad (28)$$

Obviously, this contribution vanishes for the symmetric oscillator and increases when we increase the asymmetry. Note also that the intensity of the successive Gaussians decreases very fast with m ; generally we will not need to keep many terms in the eigenvalue expansion.

It is not difficult to compute contributions to higher orders in k explicitly. A term proportional to k^{2n} will be accompanied by a factor of the order of $\langle q^{2n} \rangle \sim (T/M_e \omega^2)^n$, where M_e is the effective scatterer mass. Hence, the leading term for a symmetric harmonic oscillator would be proportional to T^2 , while for an asymmetric oscillator it should grow linearly with T .

For low and moderate values of k we expect a much stronger scattering from an asymmetric oscillator. The range

of k for which a simple power law could be observed will depend on such parameters as potential curvature and scatterer mass. In the soft potential model of glasses, this range may be quite large, since between 20 and 100 atoms are thought to participate in the soft mode.¹ (In the case of vitreous silica, it seems appropriate to take M_e to be the mass of the oxygen tetrahedron.²) Estimates such as that presented in Ref. 6 for the harmonic oscillator indicate that the lowest-order term could describe the scattering for values of k as large as several $(\text{\AA})^{-1}$. In their study of vitreous boron trioxide,¹¹ Bermejo and co-workers observed a linear decrease of the *elastic* intensity as a function of temperature for data spanning a broad temperature range and for various values of k . This suggests that the scattering is due to asymmetric harmonic or approximately harmonic oscillators, for which we expect the intensity transferred to the QE line to increase linearly with temperature.

In this work we have clarified the relation between potential symmetry and the wave-vector dependence of the neutron-scattering cross section, showing that asymmetric potentials give rise to a stronger scattering signal. A k^2 dependence of the QE line would be the signature of an asymmetry in the effective potential recorded by the scatterer. We have also provided adequate expressions for the evaluation of the dynamic structure factor in terms of the eigenfunctions of a generalized energy diffusion equation. Our results should make it a little easier to extract information about effective potentials from the QE scattering data.

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