Resonant neutron scattering from certain anharmonic potentials

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Singularities in the classical inelastic neutron-scattering cross section are shown to arise when the scatterer oscillates in a one-dimensional anharmonic potential such that the oscillation frequency contains an extremum as a function of the energy. The effects of friction on the singularity are investigated using an argument due to Soskin. The possible implications of these results for the soft potential model of glasses and undercooled liquids are discussed.

I. INTRODUCTION

Neutron scattering is one of the most powerful tools available for the study of the geometry and dynamics of disordered systems, such as glasses and proteins.[1,2] Under certain circumstances the scatterer is assumed to be confined by a one-dimensional semiphenomenological anharmonic potential, whose relation with the detailed microscopic dynamics of the system we would like to ascertain. A detailed investigation of the relation between the main features of model potentials and the energy dependence of the inelastic cross section would therefore help us optimize the information we extract from the experimental data. The analysis of the origin of structures—such as characteristic peaks and singularities—that are easy to identify in an experiment is of special importance. One type of singularity in the inelastic cross section is well known: If the scatterer moves in a harmonic oscillator potential, δ function singularities in the dynamic structure factor appear at the locations of the characteristic oscillation frequency and its harmonics.[3] These δ function singularities originate in the independence of the oscillation frequency on the oscillator energy: Regardless of its energy, the harmonic oscillator will always contribute to the same scattering lines. In this paper we show that a singularity will also occur for an anharmonic oscillator, provided that the derivative of its oscillation frequency with respect to the energy contains a zero, i.e., that there is an energy at which the frequency variation is infinitely slow.

A few years ago, Soskin showed that the presence of an extremum in the dependence of the oscillator frequency on the energy of an anharmonic oscillator generates a peak in the fluctuation spectrum of the dynamic variables.[4] He analyzed in detail the case of quadratic extrema. Here we apply Soskin's analysis to the dynamic structure factor (which gives the scattering cross section), and generalize his discussion to include nonquadratic extrema.

II. EXISTENCE AND NATURE OF THE SINGULARITY

The dynamic structure factor is defined as

$$S(k,\Omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\Omega t}\langle e^{ikx(t)}e^{-ikx(0)}\rangle, \tag{1}$$

where $x(t)$ is the scatterer coordinate at time t and the angular brackets stand for the equilibrium average.

If the potential $V(x)$ has multiple minima, the intermediate maxima divide the allowed region of the position-energy plane into domains corresponding to different types of periodic solution. We will denote the lower and upper limits of the jth energy domain by E_{jl} and E_{ju}, respectively. The oscillation period in the jth domain is then given by a single-valued function $\tau_j(E)$, which can be calculated in the usual manner[5] as an integral between the turning points $x_{j1}(E)$ and $x_{j2}(E)$. The corresponding frequency is $\omega_j(E)=2\pi[\tau_j(E)]^{-1}$.

Equation (1) can be transformed into the exact expression[6–8]

$$S(k,\Omega)=\frac{1}{Z}\sum_j \sum_{n=-\infty}^{\infty}\int_{E_{jl}}^{E_{ju}} dE\ e^{-\beta E}\tau_j(E)|F_{jn}(E)|^2 \times\delta(\Omega-n\omega_j(E)), \tag{2}$$

where Z is the partition function, β is the usual temperature factor, and F_{jn} is the Fourier coefficient

$$F_{jn}(E)=\frac{1}{\tau_j(E)}\int_0^{\tau_j(E)} dt\ e^{-in\omega_j(E)}e^{ikx_j(E,t)} \tag{3}$$

with $x_j(E,t)$ being the solution of the equation of the motion for the position coordinate at energy E in domain j.

The $n=0$ term gives rise to the elastic component, and will be of no concern to us in this work, while the others generate successive inelastic components. The δ functions in the $n\neq 0$ terms can be rewritten as

$$\delta(\Omega-n\omega_j(E))=\sum_r \frac{\delta(E-E_r^*)}{|n(\partial\omega_j/\partial E)_{E_r^*}|}, \tag{4}$$

where the E_r^*'s solve the equation $n\omega_j(E_r^*)=\Omega$. Equation (4) suggests $S(k,\Omega)$ will be singular if there are energies E^* such that $(\partial\omega/\partial E)_{E^*}=0$. Soskin used this fact to discuss the influence of quadratic extrema on the fluctuation spectrum of real-valued functions of the position and momentum.[4] We will now treat the effects of more general

extrema on $S(k,\Omega)$. For simplicity we will henceforth assume there is a single E^* and omit the indices.

Suppose that in the neighborhood of E^* the oscillation frequency has the form

$$\omega(E)=\omega^*+A(E-E^*)^q \quad (q>1). \tag{5}$$

Application of Eq. (4) immediately shows that the nth component of $S(k,\Omega)$ is singular at $\Omega=n\omega^*$,

$$S_n(k,\Omega)\sim(\Omega-n\omega^*)^{-(q-1)/q}. \tag{6}$$

Some features should be noted:

(a) The singularity arises because a large energy domain near E^* contributes to a small frequency range near ω^*. Consequently, a flatter $\omega(E)$ will originate a sharper singularity.

(b) If $\omega(E)$ has a constant segment, the singularity is a δ function. This is the case for the simple harmonic oscillator[3] and for the double parabola.[8]

(c) The singularity is always integrable.

(d) The wave number k appears only through the Fourier components F_{jn} [see Eq. (3)]. Therefore, the singularity position and shape do not depend on k.

(e) Due to the presence of the Boltzmann factor in Eq. (2), the intensity will decrease as we move to higher bands, but all bands will exhibit the same kind of singularity.

III. EXAMPLES

Next we indicate some simple potentials that may generate the frequency behavior described by Eq. (5). First, we consider single-minimum symmetric potentials $V(x)$ and set the coordinate origin at the location of the minimum. The energy minimum will also be taken to be zero. Under these conditions, $V(x)$ can be obtained using a standard formula[5]

$$x(V)=\frac{1}{2\pi(2m)^{1/2}}\int_0^V\frac{\tau(E)dE}{(V-E)^{1/2}}, \tag{7}$$

where m is the oscillator mass. Let us now examine the special case when q is an integer and $E^*=0$. Near its minimum, the potential is readily found to have the form

$$V(x)=\frac{m}{2}\omega^{*2}x^2+\frac{AC_q}{\omega^*}\left(\frac{m}{2}\omega^{*2}x^2\right)^{q+1}, \tag{8}$$

with

$$C_q=\frac{(2q+2)!!}{(q+1)(2q+1)!!}. \tag{9}$$

The addition of a small anharmonic perturbation suffices to give rise to the singularity. However, since we must have $q>1$, a potential containing only quadratic and quartic terms would generate no singularities. If $E^*\neq 0$, $V(x)$ can be found by numerical inversion of Eq. (7).

These results can be easily understood: While a nonzero frequency range (as for the above-mentioned simple-harmonic and double-parabola potentials) generates a δ-function singularity, a region where $\omega(E)$ varies very slowly gives rise to a weaker (power-law) form of singularity. This is the case for the potentials of Eq. (8), which depart very slightly from harmonicity near their minima.

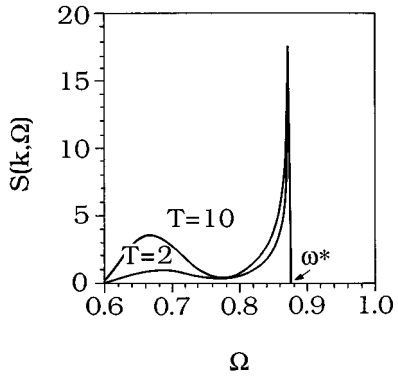

FIG. 1. First inelastic band ($n=1$) corresponding to the potential of Eqs. (12) and (13) for two temperatures. See the text for the parameter values. The singularity at $\Omega=\omega(\hat{Q})$ is evident.

A different class of potentials leading to singularities in $S(k,\Omega)$ can be analyzed if we note that the energy dependence of the oscillation frequency corresponding to potentials having the form

$$V(x)=D|x|^q \tag{10}$$

is given by

$$\omega(E)\sim E^{1/2-1/q}. \tag{11}$$

It is therefore obvious that

(a) The frequency corresponding to a potential that behaves as a power law with an exponent smaller than 2 near its minimum and as a power law with an exponent larger than 2 in the $|x|\to\infty$ region must have a minimum at a nonzero energy.

(b) The frequency corresponding to a potential that behaves as a power law with an exponent larger than 2 near its minimum and as a power law with an exponent smaller than 2 in the $|x|\to\infty$ region must have a maximum at a nonzero energy.

These potentials will thus generate singularities in $S(k,\Omega)$. Possible generalizations of cases (a) and (b) are immediate.

We next analyze the case of the two-minima potential:

$$V(x)=Q-\frac{1}{2}\gamma x^2 \quad |x|<b, \tag{12}$$

$$V(x)=\alpha(|x|-b) \quad |x|>b, \tag{13}$$

for which $\omega(E)$ can be computed exactly. It has a quadratic maximum at the energy

$$\hat{Q}=Q+\alpha\left(\frac{Q}{2\gamma}\right)^{1/2}. \tag{14}$$

From the preceding discussion we can predict that $S(k,\Omega)$ will be singular at $\Omega=n\omega^*$, with $\omega^*=\omega(\hat{Q})$. The $n=1$ component of $S(k,\Omega)$ was evaluated for $k=1$ using Eqs. (2) and (3) and the result is shown in Fig. 1. We chose $\alpha=b=Q=1$. Hence, $\gamma=2$ and $\hat{Q}=1.5$. If we further choose

$2m=1$, then $\omega^*=0.874$. The resonance is clearly visible in the figure as $\Omega\to\omega^*$ from below. The intensity on the upper side of the resonance is much lower and cannot be seen on the selected scale. Due to the larger transfer from the elastic line, the inelastic intensity increases with the temperature.

IV. EFFECTS OF DISSIPATION

What happens if dissipative effects are present? Dissipative effects will smear out the singularity, transforming it into a finite peak. We will now introduce a small frictional constant Γ and estimate how the width and height of this peak depend on Γ and the exponent q in Eq. (5). We follow the argument in Ref. 4.

A correlation time t_c can be defined as the time over which the friction destroys the phase correlation. Soskin defines t_c as the time over which a phase shift $\Delta\Psi=\pi$ emerges between an oscillator subject to friction and its Hamiltonian counterpart. This is the criterion we adopt.

We assume that the oscillator starts with an energy E_o close to E^*. At short times the oscillator energy changes mainly because of energy diffusion. The energy displacement is thus approximately,

$$\Delta E(t)\approx[D(E)t]^{1/2}, \tag{15}$$

where $D(E)=\Gamma T\overline{p^2}$ is the diffusion coefficient for diffusion along the energy coordinate and $\overline{p^2}$ represents the average of the square of the linear momentum over a period.[9] Since the contribution to the singularity will essentially come from energies in the immediate neighborhood of E^*, we may choose E_o so close to E^* that $|E_o-E^*|\ll\Delta E(t_c)$. In this case, we can use Eq. (5) to find that the magnitude of the frequency shift due to this energy displacement is approximately given by

$$\Delta\omega\approx A(\Delta E)^q\approx A(\Gamma T\overline{p^2}t)^{q/2}. \tag{16}$$

We can obtain t_c from the condition that $\Delta\Psi(t_c)=\pi$, i.e., $\Delta\omega t_c=\pi$. After solving for t_c, we estimate the peak width to be

$$\Delta\Omega\sim\frac{1}{t_c}\sim\Gamma^{q/(q+2)}. \tag{17}$$

Following Ref. 4, we can now check the consistency of the approximation by estimating the contribution of energy trajectories starting at $|E_o-E^*|>\Delta E(t_c)$. These can be shown to contribute very little to the central part of the peak.

We can next argue that the peak height $\hat{S}$ will be proportional to the width of the band of contributing energies and inversely proportional to the peak width

$$\hat{S}\sim\frac{\Delta E(t_c)}{\Delta\Omega}\sim\Gamma^{-(q-1)/(q+2)}. \tag{18}$$

These results reduce to Soskin's if $q=2$. As we could have expected, a sharp resonance (high q) will result in a high, narrow peak. No singular behavior obtains if $q\to1$: The frequency is varying too fast as a function of the energy to allow for a peak in the cross section. If $q\to\infty$, on the other hand, the results are similar to those resulting from a harmonic oscillator with friction, for which the δ function singularity is replaced by a Lorentzian.[11]

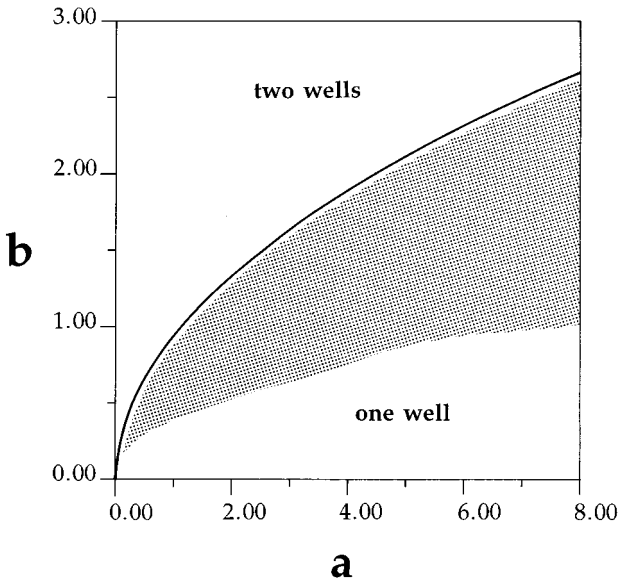

FIG. 2. Parameter space for the San Petersburg version of the soft potential model of glasses. The shaded area indicates the singularity-yielding region.

V. AN APPLICATION: THE SOFT POTENTIAL MODEL

In this section we wish to address the possible relevance of our calculation to the soft potential model of undercooled liquids and glasses. In this model the scatterer is assumed to be subject to the anharmonic potential,[12,13]

$$V_1(x)=W\left(Ax+\frac{B}{2}x^2+\frac{1}{4}x^4\right). \tag{19}$$

The energy dependence of the oscillator frequency $\omega(E)$ for this potential was studied by Dykman *et al.* for the special case $B=1$.[10] These authors showed that $\omega(E)$ has a minimum if $|A|>8/7^{1.5}\simeq0.43$. The minimum becomes wider and shallower with increasing $|A|$. A larger range of energies will then contribute to frequencies in the immediate neighborhood of ω^*, originating a sharper peak.

By shifting x by a constant, we obtain the form of the soft potential model favored by the San Petersburg Group,[14,15]

$$V_2(x)=W\left(ax^2+bx^3+\frac{1}{4}x^4\right). \tag{20}$$

We have obtained numerically the singularity-yielding domain in the parameter space (a,b), which is represented by the shaded region in Fig. 2. The line $b=\sqrt{8a/9}$ separates the one- and two-minima domains. The two-minima domain extends over the whole of the $a<0$ half-plane. The figure is symmetric about the b axis. No singularity appears in the two-well domain because the minimum in $\omega(E)$, which corresponds to the hilltop in $V(x)$, is too sharp. According to the discussion following Eq. (9) there can be no singularity along the $b=0$ line, either. Indeed, if b is small enough, $\omega(E)$ is monotonical and the $E=0$ minimum is of the

$q<1$ type. In the ''soft'' one-well region there is, however, a wide band of parameters that should generate resonant behavior.

Since in a real glass we will have a distribution of parameters (a,b),[16] the divergences will be somewhat smeared out. We expect, however, that a relatively well-defined inelastic peak will survive if the distribution is centered somewhere in the shaded region of Fig. 2. A feature that may help with the identification of the origin of a given structure is that the location of the peaks arising from extrema of $\omega(E)$ should be independent of the magnitude of the momentum transfer k. The presence (absence) of peaks at the predicted locations should help to validate (invalidate) the model and to optimize the parameter choice.

VI. FURTHER APPLICATIONS

The peaks in the neutron-scattering cross section described in this paper could be useful to identify sample impurities and other defects. In the last part of this paper we describe two situations that may give rise to resonant behavior.

(a) The potential $V_1(x)$ of Eq. (19) can be also used to describe anharmonic vibrations in a doped crystal subject to a uniform electrical field.[10,17] The size of the linear term may be controlled by varying the field. According to the analysis of Ref. 10 and the discussion following our Eq. (19), we predict no resonant behavior if there is no field or if the field is weak. Resonances should appear if the field is increased beyond the threshold value $A_T=8/7^{1.5}$. Their sharpness should grow with the field intensity.

(b) Some molecules in crystals have an orientational degree of freedom. Their rotational motion can be described using a periodic potential which we can expand in Fourier components.[1] The precise form of this potential will depend on the symmetry of the structure surrounding the rotator. If the rotation is hindered by two types of barriers, we may keep only the two lowest Fourier components

$$V(\varphi)=-B[\cos(\varphi)-\eta\cos(2\varphi)], \tag{21}$$

where φ is the rotation angle. If $\eta>0.25$, this potential has two rounded maxima of different heights in each period. The height of the smaller maximum is given by $V(0)=B(\eta-1)$, while that of the larger maximum is $V(\pi)=B(\eta+1)$. The intervening minima, located at $\varphi_m=\arccos(1/4\eta)$, have all the same depth, $V(\varphi_m)=-B(\eta+1/8\eta)$. Since the frequency must go to zero at the energies of the maxima, $E_m=V(0)$ and $E_M=V(\pi)$, there must exist an intermediate energy E^* $(E_m<E^*<E_M)$ such that $\omega(E)$ has a maximum at E^*. Consequently, the dynamic structure factor will exhibit a resonance at $\omega^*=\omega(E^*)$. Similar predictions can be made for other variations of the potential $V(\varphi)$.

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