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Dynamical structure factor for multiple-well configurations

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Abstract. Some general characteristics of the classical dynamic structure factor $S(k, \omega)$ corresponding to a one-dimensional multiple-well potential are analysed. A rich peak structure is shown to emerge in the frequency domain in the case of unbounded potentials that diverge not faster than x^2. This effect is intensified at high temperatures or large values of the momentum transfer.

Double-well potentials are commonly used to model anharmonic motions in ferroelectrics [1, 2] and glasses [3, 4]. In glasses, for example, classical motion in double-well potentials has been invoked to explain dynamical properties both at low and intermediate temperatures. We are interested here in the latter case, where the potential barrier is passed by thermal activation and quantum mechanical effects are negligible. Since inelastic neutron scattering is a powerful tool for the investigation of the dynamical excitations of these systems, exact analytical calculations of the classical dynamic structure factor $S(k, \omega)$ for atomic motion in such potentials are of interest.

It is somewhat surprising that, although the results for the simple harmonic oscillator and for various types of diffusive motion are well known [5–8], there is only one calculation of $S(k, \omega)$ for Hamiltonian motion in a more general potential. This is the work by Iwamatsu and Onodera [9], who treated the case of a quartic potential. They used a generalization of the procedure devised by Matsubara [10] to evaluate the dynamical susceptibility $S(\omega)$ for a classical multiple-well one-dimensional problem. For the quantum case, on the other hand, there are various approximate calculations [11, 12]. In particular, we should mention the vast literature associated with the impulse approximation ([11] and see, for example, [13] and references therein).

In this paper we investigate some interesting, but hitherto unnoticed, properties of the classical $S(k, \omega)$, and show how they are related to the form of the potential $V(x)$. We will illustrate the discussion by presenting explicit results for a double-parabolic potential.

We consider potentials having one or more minima and satisfying the condition $V(|x| \to \infty) \to \infty$. The constant-energy lines defined by the maxima of $V(x)$ divide the classically allowed region of the x, E plane into domains corresponding to different types of periodic motion. The period in the jth domain is given by a single-valued function $T_j(E)$. The corresponding frequency is $W_j(E) = 2\pi[T_j(E)]^{-1}$. As a consequence of the periodicity, the contribution of every energy in each domain to the intermediate scattering function can be expressed as a Fourier series; taking the Fourier transform with respect to the time yields [9, 10]

$$S(k, \omega) = Z^{-1} \sum_j \sum_{n=-\infty}^{\infty} \int_{E_{jl}}^{E_{ju}} \mathrm{d}E \, \mathrm{e}^{-\beta E} \, |F_{jn}(E, k)|^2 T_j(E) \delta(\omega - n W_j(E)). \tag{1}$$

Here E_{jl} and E_{ju} are the lower and upper energy limits of the jth domain, $\beta = (k_B T)^{-1}$,

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Z is the partition function

$$Z=\sum_j \int_{E_{jl}}^{E_{ju}} \mathrm{d}E\, \mathrm{e}^{-\beta E} T_j(E) \tag{2}$$

and

$$F_{jn}(E,k)=[T_j(E)]^{-1} \int_0^{T_j(E)} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}kx(t)}\, \mathrm{e}^{-\mathrm{i}nW_j(E)t} \tag{3}$$

where $x(t)$ is the particle displacement at time t in the given potential. The coefficients $F_{jn}(E)$ are oscillating functions of the energy. The positions of the maxima in $|F_{jn}(E)|^2$ are connected with the commensurability of the inverse of the transferred wavenumber with the amplitude of the particle oscillation at energy E in domain j.

Each delta function in (1) defines a mapping between the internal variable E and the external parameter ω. The oscillations in $|F_{jn}(E)|^2$ are then transferred to the ω domain. Therefore, the properties of $S(k,\omega)$ will depend crucially on the form of the function $W_j(E)$. Some general features of $W_j(E)$ follow easily.

(a) If $V(x)\sim A|x|^q$ when $|x|\to\infty$, then

$$W_J(E\gg\hat{E}_u)\sim E^{1/2-1/q}$$

where the index J indicates the uppermost energy domain, extending up to $E=\infty$ and $\hat{E}_u$ is the maximum height of the intervening barriers (for definiteness we can choose the energy zero at the position of the lowest minimum). This result implies that $W_J(E\to\infty)\to 0$ for $q<2$, and that $W_J(E\to\infty)$ diverges for $q>2$. If $q=2$, $W_J(E)$ goes to the natural oscillation frequency as $E\to\infty$. Similar considerations hold if we consider the energy region in the neighbourhood of the potential minima. In figure 1 we have sketched $W(E)$ for symmetric double-well potentials having the three possible types of asymptotic power-law behaviour (the index j will be omitted whenever there is no possibility of confusion).

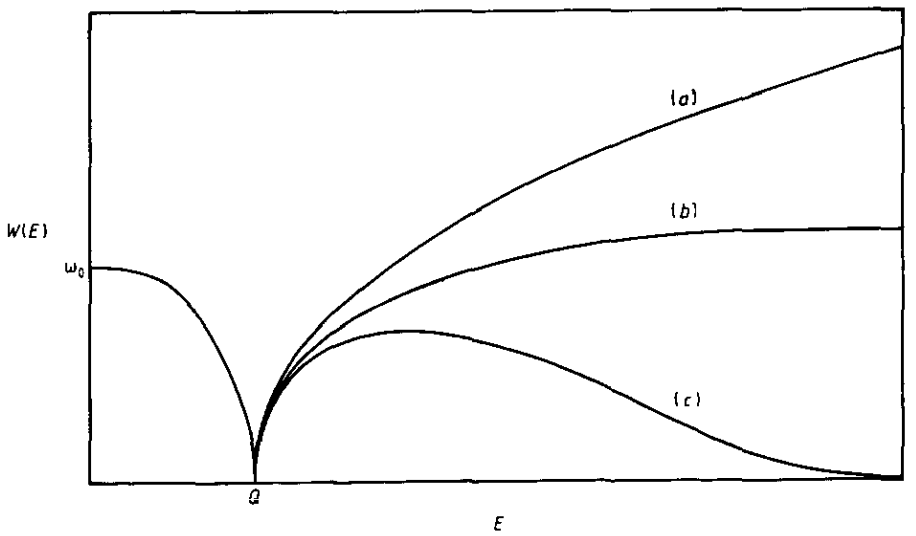

Figure 1. Sketch of the oscillation frequencies for symmetric double-well potentials. The wells are assumed to have a parabolic bottom with a natural frequency ω_0. They are separated by a smooth barrier of height Q. For large $|x|$ the potential is $V(x)\sim|x|^q$, with (*a*) $q>2$, (*b*) $q=2$ and (*c*) $q<2$.

(b) Each intervening barrier having a smooth maximum of height E_u generates a zero in $W(E)$ at $E = E_u$. If the maximum is a cusp, there is a discontinuous decrease in $W(E)$ at the energy of the cusp: when raising the energy beyond the cusp, the period is suddenly increased because a larger region becomes available.

From observation (a) we conclude that, if $q \leqslant 2$, $\delta(\omega - W_j(E))$ maps an infinite E domain onto a finite ω range. If $q < 2$, $\omega = 0$ is an accumulation point for the projected oscillations in $|F_{J1}(E, k)|$. In the case $q = 2$ we may write $V = \frac{1}{2}m\omega_0^2 x^2$ as $|x| \to \infty$, where m is the mass of the particle. The oscillations then accumulate as $\omega \to \omega_0$. At low temperatures the Boltzmann factor in (1) kills the high-energy contributions and the oscillations in the dynamic structure factor are not visible. At higher temperatures, the oscillations become detectable and a plot of $S(k, \omega)$ as a function of ω shows a structure of resonances. The same phenomena are observed in the $n > 1$ bands. The bands will in general overlap, but the location of the densely peaked regions is shifted upwards with increasing n. Consequently, the superposition of the contributions of the different bands does not lead to a smoothening out of the peaks.

In the special case of a purely harmonic motion the whole energy range is mapped onto the points $\omega = n\omega_0$ and the oscillations are undetectable. If $q > 2$, as in the case studied by Iwamatsu and Onodera [9], the infinite E domain is projected onto an infinite ω range. Consequently, there is not a strong compression of the oscillations in the ω range and no structure of resonances arises.

Assuming that $V(x)$ is unbounded as $|x| \to \infty$, two important corollaries follow from the preceding discussion. (i) If $V(x) < A|x|^2$ for all $|x|$ larger than a certain constant M, $\omega = 0$ will be an accumulation point for the oscillations in $S(k, \omega)$. (ii) If $V(x) > A|x|^2$ for all $|x|$ larger than M, there will not be an accumulation point for the oscillations.

From observation (b) it follows that more than one branch, i.e. more than one value of E, may contribute to $S(k, \omega)$ for a given ω. The contributions of the various branches are weighted by the Boltzmann factor. This was already remarked in [9] for the case of the two-well quartic potential.

Next we consider the dependence of $S(k, \omega)$ on k. Suppose that $A_j(E)$ is the amplitude of the motion with energy E in region j and that there is a maximum in $|F_{jn}(E)|^2$ when E and k are related by $kA_j(E) = \alpha$, α being a numerical constant. Since $A_j(E)$ is a non-decreasing function of E, an increase in k will generally mean that the relation $kA_j(E) = \alpha$ is fulfilled at a lower energy. Thus increasing k will likely pull the oscillations of $|F_{jn}(E)|^2$ towards lower energies and will make the resonances visible at lower temperatures. The evolution of the position of the maxima in $|F_n(E)|^2$ as a function of k is easily visualized in the case of the simple harmonic oscillator, for which $F_n(E) \sim J_n[kA(E)]$, with J_n being a Bessel function.

The $0 < q < 2$ case is most simply exemplified by choosing $V(x) = \alpha|x|$. The integral in (3) is easy to evaluate and $S(k, \omega)$ can be expressed in terms of Fresnel functions. We can then readily see the emergence of a rich peak structure at high T or k in the low-$|\omega|$ region. We will present explicit results in a future publication [14].

Let us now discuss a specific example of the $q = 2$ case. Consider the double-parabolic potential

$$V(x) = \tfrac{1}{2}m\omega_0^2(|x| - l)^2. \tag{4}$$

There is a single barrier of height $Q = \frac{1}{2}m\omega_0^2 l^2$ and the frequency is given by

$$W(E) = \begin{cases} \omega_0 & E < Q \\ \omega_0[1 + (2/\pi)\arcsin(Q/E)^{1/2}]^{-1} & E > Q. \end{cases} \tag{5}$$

The frequency $W(E)$ jumps from ω_0 to $\frac{1}{2}\omega_0$ at $E = Q$ and then grows monotonically, approaching $\omega = \omega_0$ as $E \to \infty$.

The contribution $S^<(k, \omega)$ of the $E < Q$ regions to the dynamic structure factor is given by a superposition of delta function peaks:

$$S^<(k, \omega) = (4\pi/\omega_0 Z) \sum_{n=-\infty}^{\infty} \int_0^Q dE\, e^{-\beta E} |J_n[kA(E)]|^2 \delta(\omega - n\omega_0). \tag{6}$$

The intensity of the elastic peak decreases monotonically as a function of the temperature, whereas each of the $|n| > 0$ peaks has a single maximum at a finite temperature. If $Q \to \infty$ the harmonic oscillator results are recovered (cf [5]).

More interesting is the contribution $S^>(k, \omega)$ of the $E > Q$ region. Aside from an elastic peak, we obtain the factorized expression

$$S^>(k, \omega) = \sum_n f_n(\omega, T) |g_n(\omega, k)|^2 \tag{7}$$

where the nth term contributes only in the frequency range $\frac{1}{2}n\omega_0 \leqslant \omega \leqslant n\omega_0$. The function $f_n(\omega, T)$ is dominated by the factor $\exp[-\beta Q d^{-2}(\omega)]$, with $d(\omega) = \cos(\pi n\omega_0/2\omega)$, which makes $S^>$ vanish as ω approaches the top of a band. The factor

$$g_n(\omega, k) = \int_0^\pi dy \cos\left\{ kl\left[1 + d^{-1}(\omega) \cos\left(\frac{n\omega_0}{\omega}(y - \pi/2)\right)\right] - ny \right\} \tag{8}$$

contains all the k dependence and has the form of a 'generalized' Bessel function. In agreement with our previous discussion, an increase in k pulls the peak structure towards lower values of ω in each band. The first few bands are shown in figure 2 for $kl = 10$ and $\beta Q = 1$. The resonance structure is more impressively exhibited in figure 3, where high values of both the temperature and the transferred wavenumber were chosen.

A smoothening of the $x = 0$ maximum (to make it more 'realistic') would make the fundamental frequency decrease to zero as $E \to Q$ (see figure 1). At higher energies it would raise again monotonically towards $W(\infty) = \omega_0$. Two values of E would then

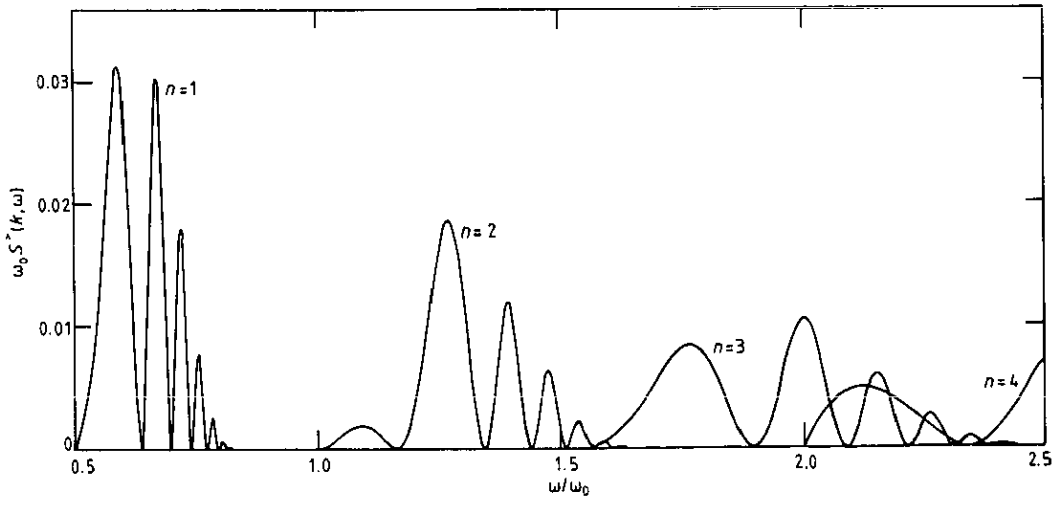

Figure 2. Double parabolic potential: $E > Q$ contribution to $S(k, \omega)$ plotted as a function of ω for $kl = 10$ and $\beta Q = 1$. The different terms in (7) have been plotted separately.

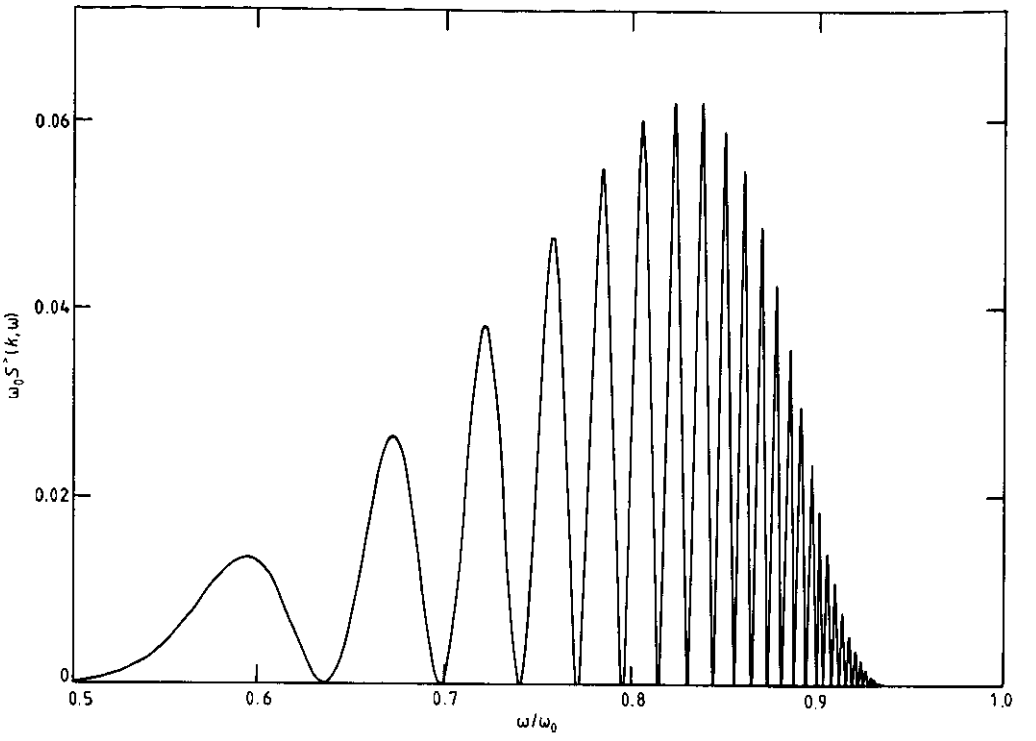

Figure 3. Double parabolic potential: $E > Q$ contribution to the fundamental band of $S(k, \omega)$ for $kl = 10$ and $\beta Q = 0.1$.

contribute to $S(k, \omega)$ for each value of ω. Although the $|\omega| < \frac{1}{2}\omega_0$ gap would disappear, there would not be any fundamental modification in the peak structure, which originates from large-E contributions.

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