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Evaluation of the displacement-displacement correlation function of a one-dimensional crystal: A comparison of the results of perturbation theory with the Mori-Dupuis method

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We calculate the spectral shape of the displacement-displacement correlation function of a one-dimensional chain of atoms interacting through a nearest-neighbor potential. We make use of the perturbation treatment developed by Maradudin and Fein. Our calculations are parallel to the corresponding work done using the frequency moments method. As expected the two methods agree best at low temperatures.

I. INTRODUCTION

The calculation of correlation functions for physical systems with nonlinear interactions is an ubiquitous problem in statistical physics and appears in many different contexts. In lattice dynamics the correlation function of the greatest importance is that of the spectral shape, which is the Fourier transform of the correlation function of the product of the displacements. For simplicity we consider a one-dimensional crystal:

$$C(k,\omega)=\frac{1}{N}\sum_{i,j} e^{-ika(i-j)} \times \int_{-\infty}^{\infty} e^{i\omega t}\langle [u_i(t)-u_j(0)]^2\rangle dt \ . \quad (1)$$

Here N denotes the number of atoms in the crystal. The wave vector k is defined within the first Brillouin zone $-(\pi/a)<k\leq\pi/a$, angle brackets denote the quantum average. $u_i(t)$ is the displacement of the ith atom from equilibrium at time t. The peaks of $C(k,\omega)$ describe the phonon structure of the crystal. At sufficiently high temperatures, one can relatively easily calculate the classical thermodynamic quantities by the use of Monte Carlo simulation (MC) or molecular dynamics (MD). However, for the quantum case, the application of MC techniques leads to a very large increase of the computing time. One can try to reduce the calculation of the quantum quantities to that of classical ones through the introduction of an effective potential due to Feynman.[1] The method, originally devised for sufficiently high temperatures and weakly bounded particles, became, in principle, application to the quantum solid due to the refinement introduced independently by Feynman and Kleinert[2] and Giachetti and Tognetti.[3] The use of the above approach for the calculation of the spectral shape is possible using the frequency moments method. The applications of frequency moments method to the calculation of the correlation functions of time-dependent operators have been first worked out by Mori and Dupuis.[4,5] The method since then has been extensively used in condensed matter theory[6-8] for both quantum and classical (high-temperatures) cases. We will briefly summarize the essence of the moments method. Let $A(t)$ be an invariant under time-reversal dynamical variable. Usually $A(t)$ is the correlation function. Then its Fourier image

$$A(\omega)=\int_{-\infty}^{\infty} d\omega\, e^{i\omega t}A(t) \quad (2)$$

can be expanded into the continued fraction representation:

$$A(\omega)=\frac{\mu_0}{\pi}\mathrm{Re}\left[\cfrac{1}{i\omega+\cfrac{\delta_1}{i\omega+\cfrac{\delta_2}{i\omega+\cdots}}}\right] . \quad (3)$$

The δ_n are positive algebraic functions of the even moments,

$$\mu_{2n}=\int_{-\infty}^{\infty} A(\omega)\omega^{2n}d\omega \ , \quad (4)$$

where the first few are given by the formulas

$$\delta_1=\frac{\mu_2}{\mu_0} \ ,$$
$$\delta_2=\frac{\mu_4}{\mu_2}-\frac{\mu_2}{\mu_0} \ , \quad (5)$$
$$\delta_3=\frac{1}{\delta_2}\left[\frac{\mu_6}{\mu_2}-\left[\frac{\mu_4}{\mu_2}\right]^2\right] .$$

Formulas for the first few moments are very easily derived. If truncated after few steps, the infinite continued fraction turns out to be a very convenient expression. This is the main advantage of the frequency moments method. Nevertheless, when applying the method, one faces serious problems. First, the calculation of many

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moments is a formidable computational problem. Another problem is that of the termination of the continued fraction of the moments method, which may strongly influence the final result. In the literature there are many sophisticated termination procedures available. We will refer to the use of molecular dynamics for matching with the classical results of the moments method. However, a convolution procedure must be applied for the removal of the spiky structure generated by MD simulation.[7–9] This affects the resulting line shape, especially for small wave vectors.

Therefore, it is worth presenting a different calculation of the spectral shape of a crystal which leads to independent conclusions concerning the phonon structure of the crystal and simultaneously provides comparison with the results of the moment method. Our article is arranged as follows. In Sec. II we shall outline the general formalism that we utilize to describe the spectral shape of a one-dimensional crystal. In Sec. III we present the explicit calculation of the spectral shape for a one-dimensional chain. The expression for the differential cross section is manipulated into a spectral density. We present a complete analytic evaluation for the classical case and carry out a partially numerical calculation for the quantum case to any accuracy desired. Finally, in Sec. IV, we discuss our results and compare them with those of the moments method.

II. GENERAL FORMALISM

Van Hove[10] derived the expression for the differential cross section per unit solid angle and unit interval of outgoing energy of the scattered neutron in the first Born approximation for coherent scattering

$$\frac{\delta^2\Sigma}{d\Omega\, d\epsilon}=\frac{a_0^2}{\hbar}\frac{|\mathbf{q}_1|}{|\mathbf{q}_0|}S(\kappa,\omega)\ . \tag{6}$$

Here $\mathbf{q}_0$ is the initial wave vector of the neutron and $\mathbf{q}_1=\mathbf{q}_0-\boldsymbol{\kappa}$ is its final wave vector. $\hbar\omega=(\hbar^2/2m)(q_0^2-q_1^2)$ is the energy transferred from the neutron to the crystal, and a_0 is the scattering length of the nuclei. The amplitude $S(\kappa,\omega)$ in the one-dimensional case is defined as follows:

$$S(\kappa,\omega)=Z^{-1}\sum_{i,j}e^{-\beta E_i}\langle E_i|\sum_l \exp[-i\kappa R(l)]|E_j\rangle\langle E_j|\sum_{l'}\exp[i\kappa R(l')]|E_i\rangle\delta\left[\omega+\frac{E_i-E_j}{\hbar}\right]\ . \tag{7}$$

E_i are energy eigenstates of the crystal and Z is the partition function. The position vector can be written as $R(l)=x(l)+u(l)$. $u(l)$ is the displacement of the lth atom away from equilibrium, a is primitive translation vector of the crystal, and l is an integer,

$$x(l)=la\ .$$

If one takes into account the lowest nonvanishing order in the anharmonic force constants, (7) can be transformed into the form:

$$S(\kappa,\omega)=\frac{e^{-2M}}{2\pi}\sum_{l,l'}\exp[-i\kappa a(l-l')]\int_{-\infty}^{\infty}dt\, e^{i\omega t}\exp[\langle\kappa^2 u(l,t)u(l',0)\rangle]\ . \tag{8}$$

Here e^{-2M} is the Debye-Waller factor corrected for anharmonic effects. The problem of calculating $S(\kappa,\omega)$ becomes that of calculating the correlation function. In the approximation of the lowest nonvanishing order in the anharmonic force constants it turns out to be related to the spectral shape function. If we expand the last exponent in Eq. (8) in powers of its argument and retain first two terms, we obtain

$$S(\kappa,\omega)=S_0(\kappa,\omega)+S_1(\kappa,\omega)\ .$$

$S_0(\kappa,\omega)$ corresponds to the coherent elastic scattering of neutrons and differs from zero only when k equals a vector of the reciprocal lattice. The term $S_1(\kappa,\omega)$ corresponds to the inelastic coherent scattering of neutrons by one phonon processes. It has been evaluated by applying perturbation theory methods, when the cubic and quartic anharmonic terms (in atomic displacements) are retained in the crystal Hamiltonian with nearest-neighbor interactions.[11] The calculation goes as follows. $S_1(\kappa,\omega)$ is given by

$$S_1(\kappa,\omega)=\frac{e^{-2M}}{2\pi}\sum_{l,l'}e^{-i\kappa a(l-l')}\kappa^2 B(l,l';\omega)\ . \tag{9}$$

$B(l,l';\omega)$ is defined in the following way:

$$B(l,l';\omega)=\int_{-\infty}^{\infty}dt\, e^{i\omega t}\langle u(l,t)u(l',0)\rangle\ ,$$

and is evaluated as follows:

$$B(l,l';\omega)=\frac{2\pi\beta\hbar}{1-e^{-\beta\hbar\omega}}\lim_{\varepsilon\to+0}\frac{a(\omega+i\varepsilon)-a(\omega-i\varepsilon)}{2\pi i}\ .$$

The expression for $a(\nu)$ has the form

$$a(\nu)=\frac{\hbar}{2Nm}\sum_k\frac{1}{\omega(k)}e^{2\pi i k a(l-l')}A_\nu(k)\ . \tag{10}$$

$A_\nu(k)$ is the Fourier coefficient of the correlation function, $k=\kappa/2\pi$.

$$F(k,u)\equiv\langle Te^{uH}(a^{+}_{-k}+a_k)e^{-uH}(a_{-k}+a_k^{+})\rangle \tag{11}$$

and is given by

$$A_\nu(k)=2\frac{\omega(k)}{\beta\hbar}\frac{1}{-\nu^2+\omega^2(k)-2\dfrac{\omega(k)}{\beta\hbar}G(k,\nu)}\ . \tag{12}$$

At this point Maradudin and Fein use an approximation concerning the magnitude of the self-energy $G(k,\nu)$. They assume it to be very small, so that they can substitute instead of this expression the following one:

$$A_\nu(k)=\frac{1}{\beta\hbar}\left[\frac{1}{\nu+\omega(k)-\dfrac{1}{\beta\hbar}G(k,\nu)}+\frac{1}{-\nu+\omega(k)-\dfrac{1}{\beta\hbar}G(k,\nu)}\right]\ . \tag{13}$$

We decided not to use this approximation. In hindsight in turns out that it influences only the low-frequency part of S. For low temperatures the influence is indeed negligible. For higher temperatures we obtain much better agreement with the results obtained by MD. Our final result is as follows:

$$S_1(k,\omega)=\frac{8\pi\hbar N}{m}e^{-2M}\frac{1}{1-e^{-\beta\hbar\omega}}\frac{k^2\omega(k)\Gamma(k,\omega)}{[-\omega^2+\omega^2(k)+2\omega(k)\Delta(k,\omega)]^2+[2\omega(k)\Gamma(k,\omega)]^2}\ . \tag{14}$$

$\Gamma(k,\omega)$ and $\Delta(k,\omega)$ are defined in the relation

$$-\lim_{\varepsilon\to+0}\frac{1}{\beta\hbar}G(k,\omega\pm i\varepsilon)=\Delta(k,\omega)\mp i\Gamma(k,\omega)\ .$$

Physically they represent the broadening and the shift of the dispersion curve due to anharmonicity. m is the atomic mass; $\omega(k)=\omega_m|\sin(ka/2)|$, is the frequency of the normal mode, described by the wave vector k.

III. EVALUATION OF THE DISPLACEMENT-DISPLACEMENT CORRELATION FUNCTION

A. Derivation of the formula for the spectral shape

Equation (1) can be transformed as follows:

$$\begin{aligned}C(k,\omega)=&\frac{1}{N}\sum_{i,j}e^{-ika(i-j)}\int_{-\infty}^{\infty}dt\,e^{i\omega t}[\langle u_i^2(t)\rangle+\langle u_j^2(0)\rangle]\\&-\frac{1}{N}\sum_{i,j}e^{-ika(i-j)}\int_{-\infty}^{\infty}dt\,e^{i\omega t}[\langle u_i(t)u_j(0)\rangle+\langle u_j(0)u_i(t)\rangle]\ .\end{aligned} \tag{15}$$

The first term differs from zero only for $k=0$ and, therefore, is omitted. In the second, we will omit the minus sign, following Ref. 7. So

$$C(k,\omega)=\frac{1}{N}\sum_{i,j}e^{-ika(i-j)}\int_{-\infty}^{\infty}dt\,e^{i\omega t}[\langle u_i(t)u_j(0)\rangle+\langle u_j(0)u_i(t)\rangle]\equiv C_1(k,\omega)+C_2(k,\omega)\ .$$

Making use of the equality

$$\langle u_i(t)u_j(0)\rangle=\langle u_i(0)u_j(-t)\rangle\ ,$$

we see that

$$C_1(k,\omega)=\frac{1}{N}\frac{1}{2\pi k^2}e^{2M}S_1(k,\omega)\ ,$$

$$C_2(k,\omega)=\frac{1}{N}\frac{1}{2\pi k^2}e^{2M}S_1(-k,-\omega)\ ,$$

so that

$$C(k,\omega)=\frac{1}{N}\frac{1}{2\pi k^2}e^{2M}[S_1(k,\omega)+S_1(-k,-\omega)]\ . \tag{16}$$

Now we make use of the symmetry properties:

$$\begin{aligned}&\Gamma(k,\omega)=-\Gamma(k,-\omega),\quad \Gamma(k,\omega)=\Gamma(-k,\omega),\quad \Delta(k,\omega)=\Delta(k,-\omega)\ ,\\&\Delta(k,\omega)=\Delta(-k,\omega),\quad \omega(k)=\omega(-k)\ ,\end{aligned} \tag{17}$$

and obtain

$$C(k,\omega)=\frac{4\hbar}{m}\coth\frac{\beta\hbar\omega}{2}\frac{\omega(k)\Gamma(k,\omega)}{[-\omega^2+\omega^2(k)+2\omega(k)\Delta(k,\omega)]^2+[2\omega(k)\Gamma(k,\omega)]^2}\ . \tag{18}$$

B. Evaluation of auxiliary functions

The broadening of the spectral line $\Gamma(k,\omega)$ can be evaluated exactly. We will assume everywhere that k is positive and ω is non-negative. Further one should recall the reflection formulas in the end of Sec. III A. The general expression for $\Gamma(k,\omega)$ has been worked out in Ref. 11 [formula (5.5b)] and here we reproduce it for a one-dimensional crystal:

$$
\begin{aligned}
\Gamma(k,\omega)=\frac{\pi\hbar}{16N\omega(k)}\sum_{k_1,k_2=-N/2+1}^{N/2}&\frac{|\Phi(-k,k_1,k_2)|^2}{\omega(k_1)\omega(k_2)}\Delta(-k+k_1+k_2)\\
&\times\{-[n(\omega(k_1))+n(\omega(k_2))+1]\delta(\omega+\omega(k_1)+\omega(k_2))\\
&\quad+[n(\omega(k_1))+n(\omega(k_2))+1]\delta(\omega-\omega(k_1)-\omega(k_2))\\
&\quad-[n(\omega(k_1))-n(\omega(k_2))]\delta(\omega-\omega(k_1)+\omega(k_2))\\
&\quad+[n(\omega(k_1))-n(\omega(k_2))]\delta(\omega+\omega(k_1)-\omega(k_2))\}\ , \qquad (19)\\
n(\omega)=\left[\exp\left[\frac{\hbar\omega}{kT}\right]-1\right]^{-1}\ ;&\quad \omega(k)=\omega_m\left|\sin\frac{\pi k}{N}\right|\ ,\\
|\Phi(-k,k_1,k_2)|^2=\frac{\delta^2}{\gamma^3}&\omega^2(k)\omega^2(k_1)\omega^2(k_2)\ .
\end{aligned}
$$

$\Phi(-k,k_1,k_2)$ is the Fourier transform of the cubic anharmonic force term. γ and δ are the nearest-neighbor force constants of the second and third order, respectively (Ref. 12). k_1,k_2 are confined to the first Brillouin zone. N is a large even number of atoms in the crystal. We assume cyclic boundary conditions. Finally, $\Delta(k)$ is the periodic Kronecker symbol in the space of the reciprocal lattice. We transform δ functions and replace summation over k by an integration as in Ref. 13. In addition, we make use of the following equalities:

$$
\begin{aligned}
&\frac{1}{e^{\hbar\omega/kT}-1}+\frac{1}{2}=\frac{1}{2}\coth\frac{\hbar\omega}{2kT}\ ,\\
&\Delta(k)=\frac{1}{N}\sum_{n=-N/2+1}^{N/2}e^{2\pi ink/N}\ ,
\end{aligned}\qquad (20)
$$

Then, making use of

$$J_{2m+1}(x)=\frac{2}{\pi}\int_0^{\pi/2}\sin(x\sin y)\sin(2m+1)y\,dy \qquad (21)$$

we arrive at [In (19), k is an integer $-N/2+1\le k\le N/2$. Here it is the wave vector]

$$
\begin{aligned}
\Gamma(k,\omega)=\frac{\hbar}{8\pi}\frac{\delta^2}{\gamma^3}\omega_m^2\omega(k)\int_{-\infty}^{\infty}\sin\omega t\,dt\int_0^{\pi/2}&\cos(\omega_m t\sin x)\sin x\coth\left[\frac{\hbar\omega_m}{2kT}\sin x\right]dx\\
&\times\sum_{p=-\infty}^{\infty}\cos 2px\,e^{-ipka}[J_{2p+1}(\omega_m t)-J_{2p-1}(\omega_m t)]\ .
\end{aligned}\qquad (22)
$$

In order to perform the summation we use a definition from the theory of Bessel functions:

$$e^{-iz\sin\beta}=\sum_{p=-\infty}^{\infty}J_p(z)e^{-ip\beta}\ ,$$

and the following formula:

$$\cos(z\sin\beta)=J_0(z)+2\sum_{p=1}^{\infty}J_{2p}(z)\cos 2p\beta\ ,$$

(Ref. 14, p. 974) and obtain

$$
\begin{aligned}
\Gamma(k,\omega)=\frac{\hbar}{8\pi}\frac{\delta^2}{\gamma^3}\omega_m^2\omega(k)\int_{-\infty}^{\infty}dt\int_0^{\pi/2}dx\,&\sin\omega t\sin x\cos(\omega_m t\sin x)\coth\left[\frac{\hbar\omega_m}{2kT}\sin x\right]\\
&\times\left\{\sin\left[x-\frac{ka}{2}\right]\sin\left[\omega_m t\sin\left[x-\frac{ka}{2}\right]\right]\right.\\
&\quad\left.+\sin\left[x+\frac{ka}{2}\right]\sin\left[\omega_m t\sin\left[x+\frac{ka}{2}\right]\right]\right\}\ .
\end{aligned}\qquad (23)
$$

We can evaluate the integral over t in a straightforward manner and then apply the standard rule of the calculation of integrals containing δ functions. After some lengthy calculations we arrive at:

$$
\begin{aligned}
\Gamma(k,\omega)={}&\frac{\hbar}{16}\frac{\delta^2}{\gamma^3}\omega_m\omega(k)\\
&\times\Bigg\{\vartheta\left[-\omega+2\omega_m\cos^2\frac{ka}{4}\right]\left[-\sin^2\frac{ka}{4}+\frac{\omega^2}{4\omega_m^2\cos^2(ka/4)}\right]\frac{1}{\sqrt{4\cos^2(ka/4)-\omega^2/\omega_m^2}}\\
&\quad\times\coth\left[\frac{\hbar\omega}{4kT}+\frac{\hbar\omega_m}{2kT}\sin\frac{ka}{4}\left[1-\frac{\omega^2}{4\omega_m^2\cos^2(ka/4)}\right]^{1/2}\right]\\
&\quad-\vartheta\left[\omega_m\sin\frac{ka}{2}-\omega\right]\left[-\sin^2\frac{ka}{4}+\frac{\omega^2}{4\omega_m^2\cos^2(ka/4)}\right]\frac{1}{\sqrt{4\cos^2(ka/4)-\omega^2/\omega_m^2}}\\
&\quad\times\coth\left[-\frac{\hbar\omega}{4kT}+\frac{\hbar\omega_m}{2kT}\sin\frac{ka}{4}\left[1-\frac{\omega^2}{4\omega_m^2\cos^2(ka/4)}\right]^{1/2}\right]\\
&\quad-\vartheta\left[2\omega_m\sin\frac{ka}{4}-\omega\right]\vartheta\left[\omega-\omega_m\sin\frac{ka}{2}\right]\left[\cos^2\frac{ka}{4}-\frac{\omega^2}{4\omega_m^2\sin^2(ka/4)}\right]\frac{1}{\sqrt{4\sin^2(ka/4)-\omega^2/\omega_m^2}}\\
&\quad\times\coth\left[\frac{\hbar\omega}{4kT}-\frac{\hbar\omega_m}{2kT}\cos\frac{ka}{4}\left[1-\frac{\omega^2}{4\omega_m^2\sin^2(ka/4)}\right]^{1/2}\right]-\vartheta\left[2\omega_m\sin\frac{ka}{4}-\omega\right]\\
&\quad\times\vartheta\left[\omega-2\omega_m\sin^2\frac{ka}{4}\right]\left[\cos^2\frac{ka}{4}-\frac{\omega^2}{4\omega_m^2\sin^2(ka/4)}\right]\\
&\quad\times\frac{1}{\sqrt{4\sin^2(ka/4)-\omega^2/\omega_m^2}}\coth\left[\frac{\hbar\omega}{4kT}+\frac{\hbar\omega_m}{2kT}\cos\frac{ka}{4}\left[1-\frac{\omega^2}{4\omega_m^2\sin^2(ka/4)}\right]^{1/2}\right]\\
&\quad+\vartheta\left[\omega_m\sin\frac{ka}{2}-\omega\right]\left[\cos^2\frac{ka}{4}-\frac{\omega^2}{4\omega_m^2\sin^2(ka/4)}\right]\frac{1}{\sqrt{4\sin^2(ka/4)-\omega^2/\omega_m^2}}\\
&\quad\times\coth\left[-\frac{\hbar\omega}{4kT}+\frac{\hbar\omega_m}{2kT}\cos\frac{ka}{4}\left[1-\frac{\omega^2}{4\omega_m^2\sin^2(ka/4)}\right]^{1/2}\right]\\
&\quad+\vartheta\left[\omega-\omega_m\sin\frac{ka}{2}\right]\vartheta\left[2\omega_m\cos\frac{ka}{4}-\omega\right]\left[-\sin^2\frac{ka}{4}+\frac{\omega^2}{4\omega_m^2\cos^2(ka/4)}\right]\\
&\quad\times\frac{1}{\sqrt{4\cos^2(ka/4)-\omega^2/\omega_m^2}}\coth\left[\frac{\hbar\omega}{4kT}-\frac{\hbar\omega_m}{2kT}\sin\frac{ka}{4}\left[1-\frac{\omega^2}{4\omega_m^2\cos^2(ka/4)}\right]^{1/2}\right]\\
&\quad+\vartheta\left[\omega-2\omega_m\cos^2\frac{ka}{4}\right]\vartheta\left[2\omega_m\cos\frac{ka}{4}-\omega\right]\left[-\sin^2\frac{ka}{4}+\frac{\omega^2}{4\omega_m^2\cos^2(ka/4)}\right]\\
&\quad\times\frac{1}{\sqrt{4\cos^2(ka/4)-\omega^2/\omega_m^2}}\coth\left[\frac{\hbar\omega}{4kT}+\frac{\hbar\omega_m}{2kT}\sin\frac{ka}{4}\left[1-\frac{\omega^2}{4\omega_m^2\cos^2(ka/4)}\right]^{1/2}\right]\\
&\quad-\vartheta\left[2\omega_m\sin^2\frac{ka}{4}-\omega\right]\left[\cos^2\frac{ka}{4}-\frac{\omega^2}{4\omega_m^2\sin^2(ka/4)}\right]\frac{1}{\sqrt{4\sin^2(ka/4)-\omega^2/\omega_m^2}}\\
&\quad\times\coth\left[\frac{\hbar\omega}{4kT}+\frac{\hbar\omega_m}{2kT}\cos\frac{ka}{4}\left[1-\frac{\omega^2}{4\omega_m^2\sin^2(ka/4)}\right]^{1/2}\right]\Bigg\}\,. \qquad (24)
\end{aligned}
$$

Here $\vartheta(x)$ is the Heaviside step function. It is with the evaluation of $\Gamma(k,\omega)$ for $\omega=\omega(k)$ that we will be concerned in the next section.

One must handle with care the calculation of $\Gamma[k,\omega(k)]$. Some terms are not defined for $\omega=\omega(k)$ and we must apply L'Hopital's rule. It turns out that

$$\Gamma[k,\omega(k)]=\frac{kT}{4}\frac{\delta^2}{\gamma^3}\omega_m \ .$$

This agrees with the result obtained by Maradudin.[13] Nevertheless in his calculation Maradudin assumed the high-temperatures limit:

$$\frac{1}{e^{\hbar\omega/kT}-1}\rightarrow\frac{kT}{\hbar\omega} \ . \tag{25}$$

We ask the question. Why did this *approximation* by Maradudin lead to an exact result valid for *all* temperatures? The result is due to peculiar properties of one-dimensional crystals and is explained in Appendix C.

The expression for the shift is given by

$$\begin{aligned}\Delta(k,\omega)=&\frac{\hbar}{8N\omega(k)}\sum_{k_1}\frac{\Phi(-k,k,k_1,-k_1)}{\omega(k_1)}[2n(\omega(k_1))+1]+\frac{\hbar}{16N\omega(k)}\sum_{k_1,k_2}\frac{|\Phi(-k,k_1,k_2)|^2}{\omega(k_1)\omega(k_2)}\Delta(-k+k_1+k_2)\\&\times\left[-\frac{[n(\omega(k_1))+n(\omega(k_2))+1]}{(\omega+\omega(k_1)+\omega(k_2))P}+\frac{[n(\omega(k_1))+n(\omega(k_2))+1]}{(\omega-\omega(k_1)-\omega(k_2))_P}\right.\\&\left.-\frac{[n(\omega(k_1))-n(\omega(k_2))]}{(\omega-\omega(k_1)+\omega(k_2))_P}+\frac{[n(\omega(k_1))-n(\omega(k_2))]}{(\omega+\omega(k_1)-\omega(k_2))_P}\right] \ .\end{aligned} \tag{26}$$

The principal part $1/\omega_P$ is defined in Ref. 11.

$\Phi(-k,k,k_1,-k_1)$ is the Fourier transform of the quartic anharmonic term and is given by (the formula has been derived in Ref. 12)

$$\Phi(-k,k,k_1,-k_1)=16\frac{\kappa}{m^2\omega_m^4}\omega^2(k)\omega^2(k_1) \ . \tag{27}$$

κ is the nearest-neighbor anharmonic force constant of the quartic order. The expression for the shift has the following form:

$$\Delta(k,\omega)=\frac{4\hbar\kappa\omega(k)}{\pi m^2\omega_m^3}\int_0^{\pi/2}dy\ \sin y\ \coth\left[\frac{\hbar\omega_m}{2kT}\sin y\right]-\frac{1}{\pi}\lim_{\varepsilon\to 0}\int_{-\infty}^{\infty}\frac{\Gamma(k,\Omega)d\Omega}{(\Omega-\omega)^2+\varepsilon^2}(\Omega-\omega) \ . \tag{28}$$

To arrive at this formula, we must remember the fact that the second term in the expression for $\Delta(k,\omega)$ is connected with $\Gamma(k,\omega)$ through the Kramers-Kronig relation.

The expression (28) can be evaluated numerically to any accuracy desired. The high-temperature limit of (28) can be evaluated exactly (see Appendix A). Then the expression for the shift reduces to

$$\begin{aligned}\Delta(k,\omega)=4\frac{\kappa\omega(k)}{m^2\omega_m^4}kT-\frac{kT}{8}\frac{\delta^2}{\gamma^3}\omega(k)&\left[2-\frac{1}{\sqrt{1-4(\omega_m^2/\omega^2)\sin^2(ka/4)}}\vartheta\left[\omega-2\omega_m\sin\frac{ka}{4}\right]\right.\\&\left.-\frac{1}{\sqrt{1-4(\omega_m^2/\omega^2)\cos^2(ka/4)}}\vartheta\left[\omega-2\omega_m\cos\frac{ka}{4}\right]\right] \ .\end{aligned} \tag{29}$$

The exact evaluation of classical limit of $\Delta(k,\omega)$ provides us with a good opportunity to check the reliability of the Kramers-Kronig relation

$$\Delta_2(k,\omega)=-\frac{1}{\pi}\lim_{\varepsilon\to 0}\int_{-\infty}^{\infty}\frac{\Gamma(k,\Omega)d\Omega}{(\Omega-\omega)^2+\varepsilon^2}(\Omega-\omega) \ .$$

$\Delta_2(k,\omega)$ is the second term in Eq. (28). Due to the antisymmetry of $\Gamma(k,\omega)$ over ω the interval of integration over Ω is reduced to $[0,2\omega_m\cos(ka/4)]$. [Of course, one must use the high-T limit of $\Gamma(k,\omega)$.] If one applies the trapezoidal integration rule, a million intervals and $\varepsilon=0.01\omega_m$ are sufficient to get a percentage error of only a few percents. These considerations are very useful of the quantum case, where we were unable to get analytic expression for $\Delta(k,\omega)$. Now we are in a position to calculate the spectral shape.

IV. CONCLUSIONS

The preliminary results have been published earlier.[15] We adopt the nearest-neighbor Lennard-Jones potential:

$$V(r)=4\varepsilon\left[\left[\frac{\sigma}{r}\right]^{12}-\left[\frac{\sigma}{r}\right]^{6}\right] \tag{30}$$

in order to be able to compare our results with those obtained by Mori's method.[7,8] Before summarizing the results we must address the possible problems with perturbation theory. The peculiar features of a one-dimensional crystal are well known (Ref. 16). There is a well-known proof due to Peierls,[17] of the instability of one-dimensional chain with respect to thermal fluctuations. The root mean square of the thermal deviation of an atom in such crystal diverges thus making the chain unstable. Nevertheless, the one-dimensional crystal has been widely used as a model system. The stability may be reached by putting additional pressure on the edges of the chain or, as in our case, by imposing periodic boundary conditions. That stabilizes the crystal. The second question is whether the lowest order anharmonic perturbation theory (LOAPT) is useful at nonzero temperatures. Our results have been obtained in the framework of perturbation theory. $\Gamma(k,\omega)$ and $\Delta(k,\omega)$ are, correspondingly, the imaginary and real part of the proper self-energy and, provided they are small in comparison with ω, the perturbation theory is, in principle, valid. So at points $2\omega_m\cos(ka/4)$, $2\omega_m\sin(ka/4)$ the perturbation theory breaks down. Therefore, we concentrate on the case $ka/\pi=1$. Then the singularities of $\Gamma(k,\omega)$ and $\Delta(k,\omega)$ at the points $2\omega_m\sin(ka/4)$ and $2\omega_m\cos(ka/4)$ coalesce. We hope that this assumption makes the perturbation theory applicable for almost all frequencies interesting from a physical point of view in the range of temperatures we consider.

It is well known that perturbation theory for three-dimensional crystal is valid for thermodynamic functions up to about one-third of Debye temperature.[18] We hope that this criterion also holds for one-dimensional argon. The reduced temperature $t=0.3$ corresponds to 36 K and meets this requirement. We are encouraged by the fact that the ratios $\Gamma(k,\omega)/\omega$ and $\Delta(k,\omega)/\omega$ are small up to about $\omega/\bar{\omega}=15$, which is the range of frequencies we use. The application of LOAPT to a model of one-dimensional chain goes back to the 1950's (Ref. 19) and since then has been extensively used. An early application to LOAPT to the description of phonon structure of this model is due to Maradudin [13]. For the classical case our results should be checked against the relation[7]

$$\mu_2=\int_{-\infty}^{\infty} C(k,\omega)\omega^2 d\omega=\frac{4\pi}{m}kT\ . \tag{31}$$

For $t=0.05$ the ratio of our result to the exact one is 0.9 and for $t=0.1$ it is 0.8. If one takes into account that our theory cuts off the tail of $C(k,\omega)$ which, due to the factor ω^2, gives a large contribution to the integral, the agreement should be considered very good. The procedure due to Gursey[20] provides an exact evaluation of μ_0. For $t=0.1$ the ratio of our result to the exact one equals 1.0.[21] These results provide some support for the validity of LOAPT in our case.

The results of our calculation are presented on Figs. 1–4. We present frequencies in units of $\bar{\omega}=\sqrt{\varepsilon/m\sigma^2}$ and $C(k,\omega)$ in units of $\sigma^2/\bar{\omega}$, which are natural for a

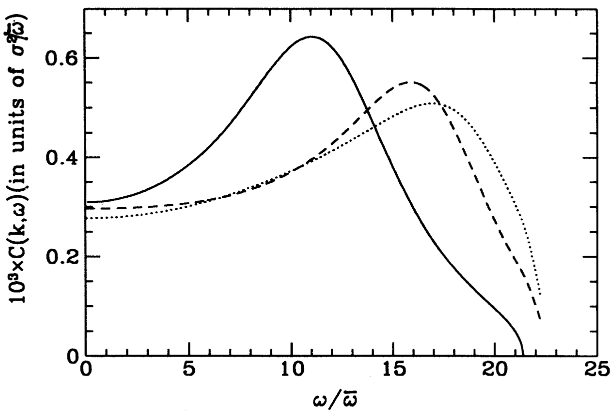

FIG. 2. The same as in Fig. 1, at $kT/\epsilon=0.3$.

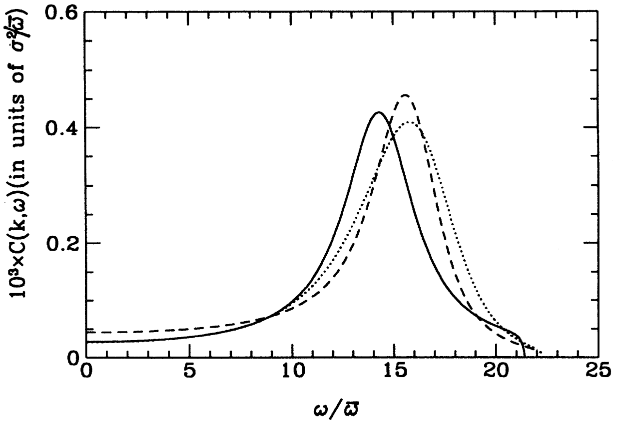

FIG. 1. Spectral shape of the Lennard-Jones crystal (classical case) at $ka/\pi=1.0$ and $kT/\epsilon=0.1$. The solid line is our result. The dashed line corresponds to the Gaussian termination at second order. The dotted line is that at third order. In the latter, the width of the Gaussian δ_4 was used as a free parameter to fit MD data (Refs. 7 and 8).

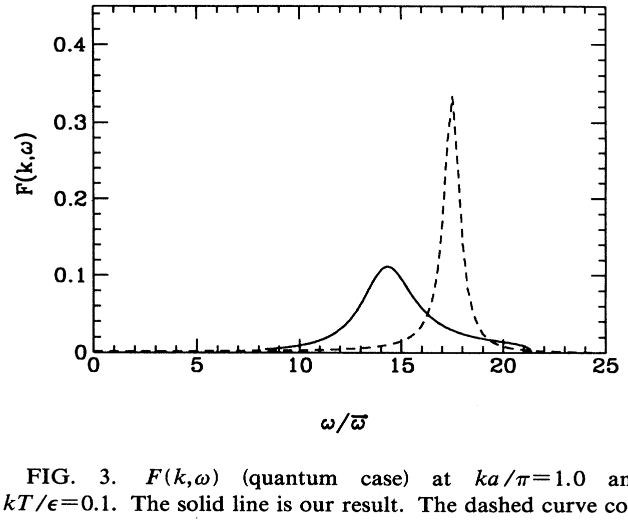

FIG. 3. $F(k,\omega)$ (quantum case) at $ka/\pi=1.0$ and $kT/\epsilon=0.1$. The solid line is our result. The dashed curve corresponds to the moments theory as given in Ref. 7.

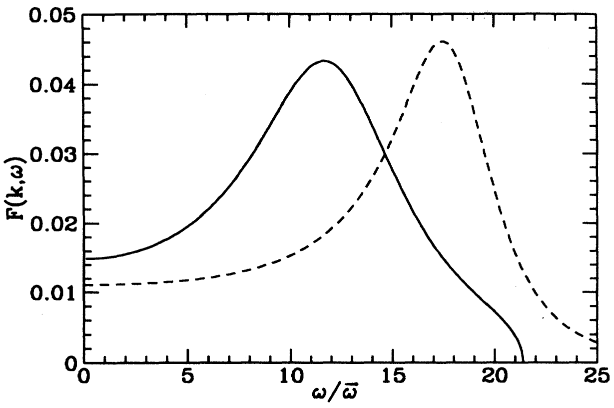

FIG. 4. The same as in Fig. 3, at $kT/\epsilon=0.3$.

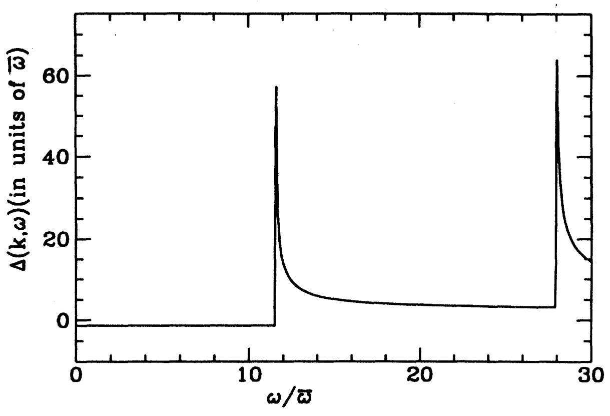

FIG. 6. $\Delta(k,\omega)$ at $ka/\pi=0.5$ and $kT/\epsilon=0.5$ for the classical case.

Lennard-Jones crystal. For the quantum case, following Refs. 7 and 8 we plotted the dependence of the normalized dimensionless $C(k,\omega)$, namely

$$F(k,\omega)=\varpi\frac{C(k,\omega)}{\mu_0}\ . \tag{32}$$

μ_0 is the zeroth moment. t is the reduced temperature kT/ε. In the remainder of this section, we quote the moments method result of Cuccoli *et al.*[7,8] Figures 1 and 2 include a classical case. Figures 3 and 4 correspond to the quantum case. (The De Boer quantum coupling parameter $\lambda=\sqrt{72/2^{1/3}}\hbar/\sigma\sqrt{m\epsilon}$ has been given the value 0.23, corresponding to argon. See Ref. 7 for more details.) At first, let us turn to the classical case ($\lambda=0$). [Despite the complicated analytical dependence of $\Gamma(k,\omega)$ its behavior is rather simple. See Fig. 5 as a typical example. The quantum and classical $\Gamma(k,\omega)$ are very close]. We also present the classical (Fig. 6) and quantum (Fig. 7) $\Delta(k,\omega)$. We can draw the following conclusions. Increasing the temperature leads to the broadening of the peak of $C(k,\omega)$, i.e., an increase of $\Gamma(k,\omega)$ with tempera-

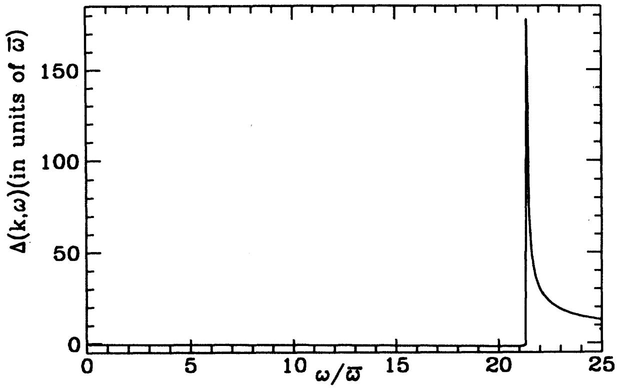

FIG. 7. $\Delta(k,\omega)$ at $ka/\pi=1.0$ and $kT/\epsilon=0.3$ for the quantum case.

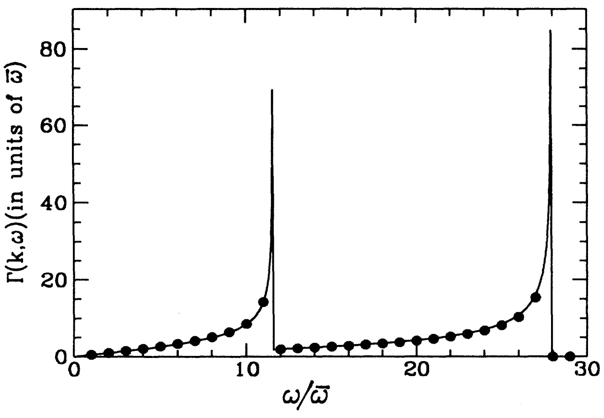

FIG. 5. $\Gamma(k,\omega)$ at $ka/\pi=0.5$ and $kT/\epsilon=0.5$ for classical (filled circles) and quantum (solid line) cases.

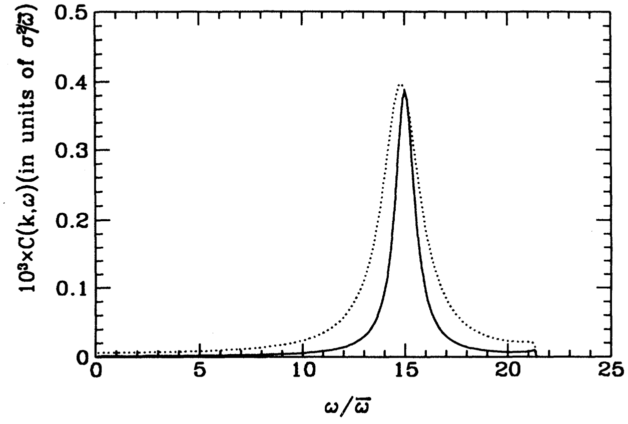

FIG. 8. The classical spectral shape at $ka/\pi=1.0$ and $kT/\epsilon=0.025$ (solid line) and $kT/\epsilon=0.05$ (dotted line).

ture. It follows from the following qualitative considerations: broadening must be inversely proportional to the phonon lifetime. For high temperatures the probability of the disintegration of the phonon due to anharmonicity is, evidently, much higher. The peak itself shifts to the left as the temperature increases. This is due to the fact that the shift $\Delta(k,\omega)$, which defines the location of the peak monotonically decreases with increase of temperature. We observe the same dependence for the quantum case. The peak, nevertheless, is a little bit wider. Our results provide us with a good opportunity to compare the results of the frequency moments method with ours. We show the results of the moments theory for the second- and third-order termination of the continued fraction. From Fig. 1 we see that for low temperatures the results of these two approaches agree well. The locations of the peaks differ by about 10%; the widths and the heights agree pretty well. Moreover, the curves corresponding to the different orders of truncation of the continued fraction are pretty close one to another. For the classical limit and $t=0.3$, the results of two methods differ significantly (see Fig. 2). Namely (a) the maximum of $C(k,\omega)$ is shifted by 50% and heights differ strongly too and (b)the maximum (in comparison with $t=0.1$) is shifted to the right in the moments method while our results shift to the left. Further the difference between the results obtained by different orders of truncation of the continued fraction is substantial.

We conclude that the two approaches only agree at low temperatures; which is more reliable at elevated temperatures must be left to further studies. As the temperature decreases, the peak becomes narrower (Fig. 8) and this result is hard to obtain in the framework of the moments method. Problems with the moments method have been noted earlier.[22]

APPENDIX A

The calculation of high-T limit of the first term in (28) $[\Delta_1(k,\omega)]$ is straightforward. The second term $[\Delta_2(k,\omega)]$ is evaluated as follows. We transform it exactly as the expression for $\Gamma(k,\omega)$ with the only difference that instead of

$$\delta(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}dt$$

we substitute

$$\frac{\omega}{\omega^2+\epsilon^2}=\int_{-\infty}^{\infty} C(t)e^{i\omega t}dt \ ,$$

$$C(t)=-\frac{i}{2}e^{-|\epsilon|t}\mathrm{sgn}(t) \ .$$

The result is as follows:

$$\Delta_2(k,\omega)=-\frac{\hbar\omega(k)\omega_m^2}{4\pi}\frac{\delta^2}{\gamma^3}\lim_{\varepsilon\to 0}\int_0^{\infty}\int_0^{\pi/2}dt\,dx e^{-|\epsilon|t}\sum_{l=-\infty}^{\infty}e^{-ilka}\cos\omega t\,\sin x\,\coth\left[\frac{\hbar\omega_m}{2kT}\sin x\right]$$
$$\times\cos 2lx\,\cos(\omega_m t\,\sin x)[J_{2l+1}(\omega_m t)-J_{2l-1}(\omega_m t)] \ . \qquad (A1)$$

For high temperatures:

$$\sin x\,\coth\left[\frac{\hbar\omega_m}{2kT}\sin x\right]\to\frac{2kT}{\hbar\omega_m} \ .$$

We make use of (Ref. 14, p. 401),

$$\int_0^{\pi/2}\cos(\omega_m t\,\sin x)\cos 2lx\,dx=\frac{\pi}{2}J_{2l}(\omega_m t) \ .$$

If we apply the result of Appendix B and make use of the easily proved formula [it holds for $\mathrm{Re}(a+ib)>0$]

$$\int_0^{\infty}dx\,e^{-ax}J_1(bx)=-\frac{i}{\pi}\int_0^{\pi}\frac{\cos\alpha}{a-ib\cos\alpha} \ ,$$

the integrals are reduced to those evaluated by the standard methods and the calculation of $\Delta(k,\omega)$ is completed.

APPENDIX B

The aim of this appendix is the calculation of the sum

$$\Sigma\equiv\sum_{l=-\infty}^{\infty}e^{-2il\alpha}J_{2l}(z)[J_{2l+1}(z)-J_{2l-1}(z)] \ .$$

We will derive the formula

$$J_{2l}(z)J_{2l\pm 1}(z)=\frac{1}{2\pi}\int_{-\pi}^{\pi}J_{4l\pm 1}(2z\cos\alpha)e^{-i\alpha}d\alpha \ . \qquad (B1)$$

Let us write down the fundamental equality of the theory of Bessel functions and its evident consequence:

$$e^{-iz\sin\beta}=\sum_{p=-\infty}^{\infty}J_p(z)e^{-ip\beta} \ ,$$

$$e^{-i\alpha-iz\sin\alpha}=\sum_{n=-\infty}^{\infty}J_{n-1}(z)e^{-in\alpha} \ .$$

By multiplying these equalities and introducing the new variables

$$x=\frac{\alpha+\beta}{2};y=\frac{\alpha-\beta}{2} \ ,$$

we readily arrive to the formula

$$\sum_{k=-\infty}^{\infty} J_k(2z\cos y)e^{-iy-i(k+1)x} = \sum_{n,p=-\infty}^{\infty} J_p(z)J_{n-1}(z)e^{-i(n+p)x-i(n-p)y} .$$

From here it follows that

$$J_k(2z\cos y)e^{-iy} = \sum_{\substack{n,p=-\infty \\ n+p=k+1}}^{\infty} J_p(z)J_{n-1}(z)e^{-i(n-p)y} .$$

By integrating both sides of the equality above from $-\pi$ to π and setting $k=4l\pm 1$ we obtain

$$J_{2l}(z)J_{2l\pm 1}(z) = \frac{1}{2\pi}\int_{-\pi}^{\pi} e^{-iy}J_{4l\pm 1}(2z\cos y)dy .$$

Now we can rewrite the sum in question as

$$\Sigma = \sum_{l=-\infty}^{\infty} \frac{1}{(2\pi)^2}\int_{-\pi}^{\pi} dy \int_{-\pi}^{\pi} d\beta\, e^{-iy}e^{-2iz\cos y\sin\beta}[e^{i(4l+1)\beta-2il\alpha} - e^{i(4l-1)\beta-2il\alpha}]$$

and turn to its evaluation. The integrand is transformed using

$$\sum_{l=-\infty}^{\infty} e^{il\alpha} = 2\pi \sum_{n=-\infty}^{\infty} \delta(\alpha - 2\pi n)$$

and, after some calculations, we obtain the main result of Appendix B,

$$\sum_{l=-\infty}^{\infty} e^{-2il\alpha}J_{2l}(z)[J_{2l+1}(z) - J_{2l-1}(z)] = \cos\frac{\alpha}{2}J_1\left[2z\cos\frac{\alpha}{2}\right] + \sin\frac{\alpha}{2}J_1\left[2z\sin\frac{\alpha}{2}\right] . \tag{B2}$$

APPENDIX C

The explanation is as follows: in order to give nonzero contributions to the sum in (19) k_1, k_2 must be such that $\Delta(-k+k_1+k_2)=1$ and one of the arguments of the δ functions equals zero. This happens if and only if $\omega(k_1)$ or $\omega(k_2)$ equal zero. For $\omega(k)\to 0$

$$\frac{1}{e^{\hbar\omega(k)/kT}-1} \to \frac{kT}{\hbar\omega(k)} ,$$

which is equivalent to the high-temperatures limit. If, say $\omega(k_1)=0$, the brackets $(n_1 \pm n_2) \to kT/\hbar\omega(k_1)$. This is the answer to the question and an alternative way of the derivation of the main result of Ref. 13. Conway[23] used these considerations for derivation $\Gamma[k,\omega(k)]$.

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