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Generalized sum rules for the moments of a one-phonon spectral function

E Roger Cowley

Department of Physics, Camden College of Arts and Sciences, Rutgers, the State University of New Jersey, Camden, NJ 08102, USA

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Abstract. The low-order moments of the one-phonon spectral function of a crystal are shown to be related directly to the self-energy of the phonon. These relationships are generalizations of the Placzek sum rule and of a well-known high-temperature extension. The rules can be used to simplify a lattice-dynamical calculation of the moments, or, if the moments have been calculated by some other method, such as a Monte Carlo simulation, the rules can be applied in the other direction to yield information about the self-energy of the mode. This information can, in turn, be used to test the quality of a lattice-dynamical approximation. As an illustration, the rules are applied to transverse and longitudinal zone-boundary phonons in argon at 81 K.

1. Introduction

There have recently been several applications of a moment-expansion method to the calculation of spectral functions in anharmonic crystals [1–5]. The method is potentially useful in providing a route for the calculation of time-dependent properties in a quantum mechanical system, since the moments can be expressed in terms of equal-time averages, which can be calculated by a variety of methods. The limitations of the method are still being explored and many of the calculations to date have been performed for classical systems, so that a comparison could be made with molecular dynamics simulations. In the classical limit, there is a simple sum rule for the second moment of the spectral function [1], closely related to the Placzek sum rule [6]. In our own lattice-dynamics-based work, we found this sum rule to provide a very useful check on the results [5]. One way to derive either of these sum rules is to expand at high frequencies a general relationship between the spectral function and an associated Green function, and to pick out the one term in the expansion that has a simple value. While the other terms in the expansion do not have such well-defined values, they do provide additional relationships between other moments of the spectral function and special values of the self-energy of the phonon, such as the instantaneous contribution to the self-energy. These relationships can be used to provide additional checks on the calculation of the spectral function, or to permit direct calculation of the moments. Conversely, if the moments are known from some other type of calculation, such as a Monte Carlo simulation, their values can be used to infer accurate values of certain features of the self-energy. These can then be compared with the values calculated in some approximation, such as the self-consistent phonon theory.

In section 2, we define the spectral function and its moments as we have used them, and in section 3 we review the relationship between the spectral function and the one-phonon Green function. A number of generalized sum rules are then derived, in section 4, and an application to a model of argon is made in section 5. The results are discussed in section 6.

2. The spectral function

Much of the importance of the one-phonon spectral function stems from the fact that it is closely related to the inelastic scattering cross section for slow neutrons. For a one-dimensional monatomic crystal we can define a spectral function $S(Q, \omega)$ by

$$S(Q, \omega) = \frac{1}{N} \sum_{ij} e^{iQ[R(i)-R(j)]} \int_{-\infty}^{\infty} e^{i\omega t} \langle u_i(t)u_j(0) \rangle dt$$

and this represents the one-phonon contribution to the neutron scattering cross section, except that the Debye–Waller factor has been neglected. The sum is over the atoms i and j , with equilibrium positions $R(i)$ and $R(j)$ and there are N atoms. $\hbar Q$ is the momentum transfer and $\hbar\omega$ is the energy transfer. The atomic displacements are $u_i(t)$ and $u_j(0)$. In three dimensions, the momentum transfer, and the atomic positions and displacements all become vectors. This complicates the notation but does not bring in any insuperable difficulties. We shall therefore usually restrict the equations to the one-dimensional case. There is a possible difficulty for a one-dimensional crystal, that the expectation value in the above expression does not exist for the case $i = j$. For this reason, Cuccoli *et al* [1] initially considered a slightly different spectral function defined in terms of differences of displacements. For Q not equal to a reciprocal-lattice vector, their function reduces to

$$C(Q, \omega) = \frac{1}{N} \sum_{ij} e^{iQ[R(i)-R(j)]} \int_{-\infty}^{\infty} e^{i\omega t} \langle u_i(t)u_j(0) + u_j(0)u_i(t) \rangle dt.$$

It is thus a symmetrized version of the spectral function. In fact

$$C(Q, \omega) = S(Q, \omega) + S(-Q, -\omega)$$

and, for the case in which every atom is on a centre of symmetry, there is inversion symmetry in Q , so

$$C(Q, \omega) = S(Q, \omega) + S(Q, -\omega).$$

Additionally, in the classical limit, S is an even function of ω and then C is just twice S .

The moments of the spectral function C are defined by

$$\mu_n = \int_{-\infty}^{\infty} \omega^n C(Q, \omega) d\omega. \quad (1)$$

The moments are functions of Q , but that is not shown explicitly here. Since C is an even function of frequency, the odd moments are all zero. In the classical limit, the second moment satisfies the sum rule [1]

$$\mu_2 = \frac{4\pi k_B T}{m} \quad (2)$$

where k_B is Boltzmann's constant, T is the temperature, and m is the atomic mass.

The spectral function is related to the moments through a continued-fraction representation [7]:

$$C(Q, \omega) = \mathcal{R} \left\{ \frac{1}{\pi} \mu_0 / \left\{ z + \delta_1 / \left[z + \delta_2 / \left(z + \dots \right) \right] \right\} \right\}_{z=i\omega}$$

where

$$\delta_1 = \mu_2 / \mu_0$$

$$\delta_2 = \mu_4 / \mu_2 - \mu_2 / \mu_0$$

$$\delta_3 = [\mu_6 / \mu_2 - (\mu_4 / \mu_2)^2] / \delta_2$$

and so on. The termination of the continued fraction has been discussed elsewhere [1–3].

3. Green function formalism

A powerful method for calculating anharmonic contributions to phonon spectral functions is the diagrammatic perturbation expansion for the imaginary-time ordered Green function [8–11]. The Green function is

$$G_\lambda(u) = \langle T A_\lambda(u) A_{-\lambda}(0) \rangle.$$

Here λ is used to label the normal modes. In a one-dimensional crystal, the label can be the wave number q . In a three-dimensional crystal, q becomes a vector, and an additional label, j , is used to label the branches. A_λ and $A_{-\lambda}$ are combinations of creation and destruction operators. T is a time-ordering operator and u is a complex variable whose real component corresponds to an inverse temperature and whose imaginary component is a time divided by \hbar . The A_λ -operators are related to the atomic displacements by

$$u_i(t) = \sqrt{\frac{\hbar}{2Nm}} \sum_\lambda \frac{e^{iq \cdot R(i)}}{\sqrt{\omega_\lambda}} A_\lambda(t)$$

in one dimension, or by

$$u_{i\alpha}(t) = \sqrt{\frac{\hbar}{2Nm}} \sum_\lambda \frac{e_\alpha(\lambda)}{\sqrt{\omega_\lambda}} e^{iq \cdot R(i)} A_\lambda(t)$$

in three dimensions. In this case, α labels the Cartesian axes and $e_\alpha(\lambda)$ is an eigenvector component. $G(u)$ is periodic along the imaginary-time axis for values of u between $-\beta$ and 0, where β is $1/k_B T$. It can therefore be written as a Fourier series, with coefficients defined for an infinite but discrete set of imaginary frequencies. The expression for the coefficients can then be analytically continued to the complex-frequency plane. For a harmonic crystal, the Green function, $g_\lambda(z)$, is

$$g_\lambda(z) = \frac{1}{\beta\hbar} \frac{2\omega_\lambda}{\omega_\lambda^2 - z^2}$$

where ω_λ is the harmonic frequency and z is a (complex) applied frequency. In an anharmonic crystal the Green function can be cast in a similar form, but involving a complex, frequency-dependent, self-energy $D_\lambda(z)$, as

$$G_\lambda(z) = \frac{g_\lambda(z)}{1 - g_\lambda(z)D_\lambda(z)} = \frac{1}{\beta\hbar} \frac{2\omega_\lambda}{\omega_\lambda^2 + 2\omega_\lambda[\Delta_\lambda(z) - i\Gamma_\lambda(z)] - z^2}. \quad (3)$$

In the second form, the self-energy has been written in terms of a z -dependent shift and width:

$$D_\lambda(z) = \beta\hbar[-\Delta_\lambda(z) + i\Gamma_\lambda(z)].$$

The form given above for the Green function is a result of summing all diagrams containing the proper self-energy repeated any number of times:

$$G_\lambda(z) = g_\lambda(z) + g_\lambda(z)D_\lambda(z)g_\lambda(z) + g_\lambda(z)D_\lambda(z)g_\lambda(z)D_\lambda(z)g_\lambda(z) + \dots \quad (4)$$

While this is a more primitive equation, it will be useful for the development of the sum rules. In the general three-dimensional case, the equation for the Green function is complicated by the coupling of contributions from different polarizations. In the one-dimensional case, and in high-symmetry situations in three dimensions, this does not occur and we shall ignore it.

Associated with the Green function, we can define a simple correlation function

$$F_\lambda(t) = \langle A_\lambda(t) A_{-\lambda}(0) \rangle$$

and its Fourier transform

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

The Fourier transform of the Green function can then be shown to be [10]

$$G_\lambda(z) = \frac{1}{\beta\hbar} \int_{-\infty}^{\infty} \rho_\lambda(\omega) \frac{1 - e^{-\beta\hbar\omega}}{\omega - z} d\omega. \quad (5)$$

The generalized sum rules all follow from this equation.

4. Sum rules

The sum rules are obtained by expanding each side of equation (5) in inverse powers of z , and equating the coefficients on the two sides. The harmonic Green function has an expansion

$$g_\lambda(z) = -\frac{2\omega_\lambda}{\beta\hbar} \left\{ \frac{1}{z^2} + \frac{\omega_\lambda^2}{z^4} + \frac{\omega_\lambda^4}{z^6} + \dots \right\} \quad (6)$$

and the proper self-energy has an expansion

$$D_\lambda(z) = D^{(0)} + D^{(-2)}/z^2 + \dots = -\beta\hbar\{\Delta^{(0)} + \Delta^{(-2)}/z^2 + \dots\}. \quad (7)$$

The first term on the right-hand side arises because there is, in general, an instantaneous contribution to the self-energy. The second form above involves only the real part, $\Delta_\lambda(z)$, because the imaginary part has no instantaneous contribution and, at least in all of the approximations that we shall consider, is cut off at some finite frequency and therefore has no dependence as $1/z^2$. For simplicity, the λ -dependence of the terms on the right has not been shown. The distinction between the instantaneous shift, $\Delta^{(0)}$, and the shift at zero applied frequency, $\Delta(0)$, is important. When the expansions equations (6) and (7) are substituted in equation (4), the first three, non-vanishing, terms give

$$\begin{aligned} \int_{-\infty}^{\infty} \omega \rho_\lambda(\omega) (1 - e^{-\beta\hbar\omega}) d\omega &= 2\omega_\lambda & (8) \\ \int_{-\infty}^{\infty} \omega^3 \rho_\lambda(\omega) (1 - e^{-\beta\hbar\omega}) d\omega &= 2\omega_\lambda [\omega_\lambda^2 + 2\omega_\lambda \Delta^{(0)}] \\ \int_{-\infty}^{\infty} \omega^5 \rho_\lambda(\omega) (1 - e^{-\beta\hbar\omega}) d\omega &= 2\omega_\lambda [\{\omega_\lambda^2 + 2\omega_\lambda \Delta^{(0)}\}^2 + 2\omega_\lambda \Delta^{(-2)}]. \end{aligned}$$

Also, by setting $z = 0$, we obtain an additional useful relationship:

$$\int_{-\infty}^{\infty} \frac{1}{\omega} \rho_\lambda(\omega) (1 - e^{-\beta\hbar\omega}) d\omega = \frac{2\omega_\lambda}{\omega_\lambda^2 + 2\omega_\lambda \Delta(0)} \quad (9)$$

where $\Delta(0)$ is the value of Δ at zero applied frequency.

The spectral functions $S(Q, \omega)$ and $C(Q, \omega)$ are proportional to the spectral density $\rho_\lambda(\Omega)$, provided that the wave vector of the normal mode differs from Q only by a reciprocal-lattice vector. The relationships can be found by substituting the expression for the atomic displacements into the definition of the appropriate spectral function, as

$$\rho_\lambda(\omega) = \frac{m\omega_\lambda}{\pi\hbar} S(Q, \omega) = \frac{m\omega_\lambda}{\pi\hbar} \frac{C(Q, \omega)}{1 + e^{-\beta\hbar\omega}}.$$

Clearly, the sum rules given above can also be written in terms of $S(Q, \omega)$ or $C(Q, \omega)$. For example, equation (8) gives

$$\int_{-\infty}^{\infty} \omega S(Q, \omega) (1 - e^{-\beta\hbar\omega}) d\omega = \frac{2\pi\hbar}{m}$$

$$\int_{-\infty}^{\infty} \omega C(Q, \omega) \tanh\left(\frac{\beta\hbar\omega}{2}\right) d\omega = \frac{2\pi\hbar}{m}.$$

The other relationships can be transformed in a similar way.

There are several ways to develop simpler, and more useful, relationships. The spectral functions $S(Q, \omega)$ and $\rho_\lambda(\omega)$ satisfy the detailed-balance condition, e.g.

$$S(Q, -\omega) = e^{-\beta\hbar\omega} S(Q, \omega).$$

From this it is simple to show that, for odd values of n ,

$$\int_{-\infty}^{\infty} \omega^n e^{-\beta\hbar\omega} S(Q, \omega) d\omega = - \int_{-\infty}^{\infty} \omega^n S(Q, \omega) d\omega$$

and hence that

$$\int_{-\infty}^{\infty} \omega^n S(Q, \omega) (1 - e^{-\beta\hbar\omega}) d\omega = 2 \int_{-\infty}^{\infty} \omega^n S(Q, \omega) d\omega.$$

When these results are used, the sum rules for $S(Q, \omega)$ become

$$\int_{-\infty}^{\infty} \omega S(Q, \omega) d\omega = \frac{\pi\hbar}{m} \tag{10}$$

$$\int_{-\infty}^{\infty} \omega^3 S(Q, \omega) d\omega = \frac{\pi\hbar}{m} [\omega_\lambda^2 + 2\omega_\lambda \Delta^{(0)}]$$

$$\int_{-\infty}^{\infty} \omega^5 S(Q, \omega) d\omega = \frac{\pi\hbar}{m} [(\omega_\lambda^2 + 2\omega_\lambda \Delta^{(0)})^2 + 2\omega_\lambda \Delta^{(-2)}]$$

$$\int_{-\infty}^{\infty} \frac{1}{\omega} S(Q, \omega) d\omega = \frac{\pi\hbar}{m} \frac{1}{\omega_\lambda^2 + 2\omega_\lambda \Delta(0)}.$$

The last of these comes from the equation for zero frequency, equation (9). Equation (10) is called the Placzek sum rule [6]. The original paper does not emphasize this result. Useful discussions have been given by Rahman, Singwi, and Sjolander [12] and by Ambegaokar, Conway, and Baym [13].

This line of development is not useful for the function $C(Q, \omega)$, which is an even function, so its odd moments are zero. However, we can get a useful simplification for this case by taking the high-temperature limit. This leads directly to expressions for the moments μ_n defined in equation (3), in the form

$$\mu_0 = \frac{4\pi}{\beta m} \frac{1}{\omega_\lambda^2 + 2\omega_\lambda \Delta(0)}$$

$$\mu_2 = \frac{4\pi}{\beta m}$$

$$\mu_4 = \frac{4\pi}{\beta m} [\omega_\lambda^2 + 2\omega_\lambda \Delta^{(0)}]$$

$$\mu_6 = \frac{4\pi}{\beta m} [(\omega_\lambda^2 + 2\omega_\lambda \Delta^{(0)})^2 + 2\omega_\lambda \Delta^{(-2)}].$$

The second of these is equation (2). Of course, a similar simplification is obtained in the high-temperature limit for the moments of the other spectral functions. The corresponding expressions for the related quantities δ_n are

$$\begin{aligned}\delta_1 &= \omega_\lambda^2 + 2\omega_\lambda \Delta(0) \\ \delta_2 &= 2\omega_\lambda \{\Delta^{(0)} - \Delta(0)\} \\ \delta_3 &= \frac{\Delta^{(-2)}}{\Delta^{(0)} - \Delta(0)}\end{aligned}$$

and, in addition,

$$\mu_4/\mu_2 = \omega_\lambda^2 + 2\omega_\lambda \Delta^{(0)} \quad (11)$$

$$\mu_6/\mu_2 - (\mu_4/\mu_2)^2 = 2\omega_\lambda \Delta^{(-2)}. \quad (12)$$

These results can be useful applied in either direction. We originally developed them to simplify the calculation of the moments from a given approximation for the self-energy. It is much more convenient, and more accurate, to use these results than to find the moments of the spectral function numerically. However, their usefulness may be greater as a test of approximate theories. For example, equation (11) involves only the instantaneous contribution to the self-energy. This should be easier to calculate than the complete expression. The value of μ_4 can be calculated in a simulation, and μ_2 is given exactly, so a very accurate estimate can be obtained of the complete instantaneous self-energy, for comparison with approximate theories.

Our results are all presented in terms of the real part of the self-energy, which is interpreted as a shift. However, the shift and width functions are related by

$$\Delta(z) = \Delta^{(0)} - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Gamma(\omega)}{\omega - z} d\omega.$$

From this we obtain the relationships

$$\Delta(0) - \Delta^{(0)} = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Gamma(\omega)}{\omega} d\omega$$

and

$$\Delta^{(-2)} = \frac{1}{\pi} \int_{-\infty}^{\infty} \omega \Gamma(\omega) d\omega.$$

It is thus possible to express the moments in terms of either the shift or the width.

Two other results are easily obtained from the formalism developed here. The mean square displacement components of an atom are

$$\langle u_\alpha(i) u_\beta(i) \rangle = \frac{\hbar}{2Nm} \sum_\lambda \frac{e_\alpha(\lambda) e_\beta(\lambda)}{\omega_\lambda} \langle A_\lambda(0) A_{-\lambda}(0) \rangle = \frac{\hbar}{2Nm} \sum_\lambda \frac{e_\alpha e_\beta}{\omega_\lambda} \int_{-\infty}^{\infty} \rho_\lambda(\omega) d\omega.$$

We have again neglected polarization mixing. In the high-temperature limit, equation (9) becomes

$$\int_{-\infty}^{\infty} \rho_\lambda(\omega) d\omega = \frac{1}{\beta\hbar} \frac{2\omega_\lambda}{\omega_\lambda^2 + 2\omega_\lambda \Delta(0)}.$$

In this limit, therefore, the mean square displacement elements are

$$\langle u_\alpha(i) u_\beta(i) \rangle = \frac{1}{\beta Nm} \sum_\lambda \frac{e_\alpha(\lambda) e_\beta(\lambda)}{\omega_\lambda^2 + 2\omega_\lambda \Delta(0)}.$$

This is of exactly the harmonic form, except that the frequency is shifted by the shift calculated for zero applied frequency. This result has been shown explicitly by Shukla and

Hübschle [14] for a number of terms in the perturbation expansion. It holds as long as the Green function can be written in the form of equation (3).

A related sum arises in the determining equation for μ_0 . This moment is given by [1]

$$\mu_0 = \frac{4\pi}{N} \sum_{ij} \cos(\mathbf{Q} \cdot [\mathbf{R}(i) - \mathbf{R}(j)]) \langle u_i u_j \rangle$$

where the value of \mathbf{Q} and, in three dimensions, the polarization vectors, control the value of λ . Since μ_2 has an exact value, the ratio δ_1 can be found once μ_0 has been calculated, in a simulation, for example. We now know that δ_1 is the renormalized squared frequency at zero applied frequency. Zhong *et al* recently made such calculations for a model of a ferroelectric crystal displaying a soft mode [15]. They presented their results as an approximate calculation of the soft-mode frequency, but we see that it has a quite precise meaning.

Table 1. Monte Carlo results for the moments for the longitudinal (L) and transverse (T) modes at the [100] zone boundary, in argon at 81 K, based on reference [3]. The unit for μ_n is $\text{m}^2 \text{s}^{-n}$.

Moment	L	T
μ_0	$(0.215 \pm 0.002) \times 10^{-20}$	$(0.478 \pm 0.009) \times 10^{-20}$
μ_2	0.235296×10^6	0.235296×10^6
μ_4	$(0.359 \pm 0.004) \times 10^{32}$	$(0.172 \pm 0.002) \times 10^{32}$
μ_6	$(0.7406 \pm 0.0009) \times 10^{58}$	$(0.2357 \pm 0.0004) \times 10^{58}$

5. Numerical implementation and results

We present here an application of the sum rules to a realistic three-dimensional model of argon. We have previously studied this model using a variety of techniques [3, 16, 17], so many numerical results are available. The model assumes a pair potential derived by Aziz and Chen [18]. The forces are taken to act between an atom and three shells of neighbours. In this work, as in reference [17], we neglect three-body forces. Calculations are made for a temperature of 81 K and at the experimentally observed lattice spacing of 5.465 Å. The calculation of the low-order moments of the spectral functions for both longitudinal and transverse modes was reported in reference [3]. Values of the moments up to μ_6 are given in table 1. μ_8 was also calculated in reference [3], but we do not use that value here.

For comparison purposes, we have calculated several approximations to the moments using anharmonic perturbation theory and self-consistent phonon theory. To show clearly the magnitude of the effects, we note that, for a harmonic crystal, μ_4/μ_2 and δ_1 are each equal to ω_λ^2 , and δ_2 is zero. In the lowest-order perturbation theory, there are two contributions to the phonon self-energy [9, 11]. There is an instantaneous term, which we shall write as Δ_4 , arising in first order from the quartic anharmonicity, and there is a frequency-dependent term, $\Delta_{33}(\omega)$, arising from the cubic anharmonicity in second order. Expressions for the two shifts have been given many times. Both terms contribute to the shift at zero frequency, but only the cubic term contributes to $\Delta^{(-2)}$. A long-standing difficulty in analysing experimental results is that there can be substantial cancellation between the different contributions to the shifts. The moment analysis offers the possibility of disentangling the various contributions. We make the identifications

$$\mu_4/\mu_2 \simeq \omega_\lambda^2 + 2\omega_\lambda \Delta_4$$

$$\begin{aligned}\delta_2 &= 2\omega_\lambda \{\Delta^{(0)} - \Delta(0)\} \simeq -2\omega_\lambda \Delta_{33}(0) \\ \delta_1 &= \omega_\lambda^2 + 2\omega_\lambda \Delta(0) \simeq \omega_\lambda^2 + 2\omega_\lambda (\Delta_4 + \Delta_{33}(0)) \\ \mu_6/\mu_2 - (\mu_4/\mu_2)^2 &= 2\omega_\lambda \Delta^{(-2)} \simeq 2\omega_\lambda \Delta_{33}^{(-2)}.\end{aligned}$$

The quantity on the left-hand side of the last of these is proportional to δ_3 , but is more accurately found as written. We can thus test separately the quartic shift, and the cubic shift at zero frequency and in the limit of very large frequency.

Table 2. Various approximations to the phases, using anharmonic perturbation theory (PT), or self-consistent phonon theory (SC1). All values are in units of 10^{26} s^{-2} except for the bottom line in each group, which is in units of 10^{52} s^{-4} .

	Longitudinal			
	Monte Carlo	Harmonic	PT	SC1
μ_4/μ_2	1.53 ± 0.02	0.851	1.658	1.430
δ_2	0.43 ± 0.02	0.0	0.450	0.362
δ_1	1.09 ± 0.01	0.851	1.208	1.068
$\mu_6/\mu_2 - (\mu_4/\mu_2)^2$	0.82 ± 0.05	0.0	0.364	0.467
	Transverse			
	Monte Carlo	Harmonic	PT	SC1
μ_4/μ_2	0.73 ± 0.01	0.442	0.825	0.693
δ_2	0.24 ± 0.01	0.0	0.256	0.212
δ_1	0.49 ± 0.01	0.442	0.569	0.481
$\mu_6/\mu_2 - (\mu_4/\mu_2)^2$	0.47 ± 0.01	0.0	0.199	0.262

A second, more sophisticated, theory is self-consistent phonon theory (SC1) [19]. In this theory, an infinite class of contributions to the instantaneous self-energy is summed to give a renormalized frequency. At this level of approximation, there are no frequency-dependent contributions. However, we can use the renormalized frequencies and the smeared derivatives of the potential to evaluate the cubic contribution to the self-energy, using, apart from this, the same expression as for the perturbation theory. This is not a consistent procedure, but certainly gives the largest missing contribution. In this case, we make the identifications

$$\begin{aligned}\mu_4/\mu_2 &\cong \omega_{\lambda,SC1}^2 \\ \delta_2 &\cong -2\omega_{\lambda,SC1} \langle \Delta_{33}(0) \rangle \\ \delta_1 &\cong \omega_{\lambda,SC1}^2 + 2\omega_{\lambda,SC1} \langle \Delta_{33}(0) \rangle \\ \mu_6/\mu_2 - (\mu_4/\mu_2)^2 &\cong 2\omega_{\lambda,SC1} \langle \Delta_{33}^{(-2)} \rangle.\end{aligned}$$

The angular brackets indicate that smeared force constants and SC1 frequencies are used in the evaluation of the cubic shift. The results of the three calculations are shown in table 2. It can be seen that the harmonic values are completely inadequate. Argon is close to melting at 81 K and the anharmonic terms are large. The perturbation theory results are an improvement but are still not satisfactory. Each of the contributions Δ_4 and $\Delta_{33}(0)$ is overestimated. The results of the self-consistent calculation are closer to the simulation values in almost all cases. The instantaneous contribution is now underestimated. The SC1 estimate of δ_1 is very accurate. The worst agreement is in the values of $\Delta^{(-2)}$, shown in the last line of each group. All of the lattice-dynamical estimates of this term are too small. We believe that this reveals a genuine shortcoming of the theories.

6. Summary and conclusions

We have identified a number of relationships between the low-order moments of the spectral function of a phonon and specific features of its self-energy. The simplest use to be made of these is in a lattice-dynamics-based calculation of the moments. It is simpler and more accurate to use these formulae than to generate the whole spectral function and then to integrate numerically to find the moments.

A much more valuable application is to use the formulae in the reverse direction, to isolate specific parts of the self-energy from values of the moments found in a simulation. It has been recognized for many years that the different contributions to the self-energy tend to cancel and that this makes a comparison with experiment a difficult and over-sensitive test [11, 20, 21]. The formulae given here allow the separation of the instantaneous and frequency-dependent parts of the self-energy, at least at zero frequency and in the high-frequency limit. It will be interesting to make comparisons for a variety of materials, such as alkali halides, to see how the different contributions are reproduced by approximate theories.

The comparison with analytical theories presented here already shows one shortcoming that we had not anticipated. The values of the shift in the high-frequency limit, $\Delta^{(-2)}$, given by perturbation theory and self-consistent phonon theory are both too small. Both calculations include only processes where one phonon decays into two intermediate phonons. Processes involving three or more intermediate phonons would also contribute to $\Delta^{(-2)}$, and we believe that it is the neglect of these terms that is causing the discrepancy.

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