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The moments method and damped systems

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Abstract. The moments method was shown to be very useful for determining the linear response of very large harmonic systems. In the presence of anharmonicity or electron–phonon coupling, the phonon self-energy appears in the one-phonon propagator. The phonon frequency is then renormalized and the system is damped. In this paper, we show that it is possible to extend the moments method to compute the response of these damped systems. The method involves introducing a two-dimensional density functional that can be calculated by the moments techniques and which allows the computation of the response function. We illustrate these results via applications to several models: systems with constant damping, systems of coupled relaxation modes and oscillators, and systems with electron–phonon coupling.

1. Introduction

We show in this paper that the moments method provides a new approach to compute dynamical properties of damped systems. The quantum theory of solids describes crystal properties in terms of elementary excitations and their mutual interaction. Dynamical properties are represented by phonons and their interactions mainly with other phonons (anharmonicity), electrons (electron–phonon coupling) and magnons (phonon–magnon coupling).

Model construction is an important part of the theory of lattice vibration. Practically all models developed for very large realistic systems use the harmonic approximation. Only some special studies concerning phase transitions and linear chains (1D systems) use an anharmonic potential (see Currat and Janssen 1988). In the harmonic approximation, the Born–Von Karman theory, forces between atoms are specified by the second derivatives of the crystal potential with respect to the atomic displacements. The squares of the normal-mode frequencies are the eigenvalues of the dynamic matrix. The dynamic matrix being symmetrical, the eigenvalues are real, and in the harmonic approximation, the lifetimes of the phonon states are infinite. Damping arises from the coupling with other elementary excitations. The effect of anharmonic terms or electron–phonon coupling can be summarized in the following way: Each phonon frequency of the harmonic material undergoes a complex shift, the self-energy $\Pi(\omega, T)$, the real part of which gives the change in the value of the frequency and the imaginary part of which is the inverse of the lifetime of the phonon states. Both parts are frequency- and temperature-dependent. The response function can be reduced to an evaluation of the phonon propagator of the system, which depends on the self-energy. In the harmonic approximation, the moments method allows determination of the response functions without any diagonalization of the dynamic matrix. It is thus possible to work with very large harmonic disordered systems (up to $N = 8\,000\,000$ (Royer *et al* 1991, 1992)).

Direct evaluation of the response functions of damped materials requires knowledge of all frequencies and eigenvectors of the undisturbed system. Then one computes the self-energy and then the response functions of the material. In very large disordered material, direct determinations of eigenfrequencies and eigenvectors are impossible. It was therefore interesting to investigate applying the moments method to determinate the response functions of damped systems without any matrix diagonalization. In the first step, we assume here that the self-energy $\Pi(\omega, T)$ is known, since direct evaluation of this function is quite complicated.

In order to outline the formalism, in section 2 we first review the dynamics of harmonic systems, anharmonic systems and systems with electron–phonon coupling in direct space. In section 3 we give some elements of the response theory and we show that the response function is obtained from an integro-differential equation of motion. In section 4, we show how to compute the response function with moments formalism. In the last section, we provide illustrations via examples of usual problems concerning condensed matter.

2. Dynamical theory

2.1. Harmonic systems

Let us consider a d-dimensional system with N atoms. We start from the harmonic Hamiltonian:

$$H = \tfrac{1}{2}\langle P \mid P\rangle + \tfrac{1}{2}\langle X|\mathbf{D}|X\rangle \tag{1}$$

where

$$|X\rangle = \sum_{\alpha n} m_n^{1/2} u_\alpha(n)|\alpha n\rangle = \sum_{\alpha n} \bar{u}_\alpha(n)|\alpha n\rangle \tag{2}$$

$$|P\rangle = \sum_{\alpha n} \frac{p_\alpha(n)}{m_n^{1/2}}|\alpha n\rangle = \sum_{\alpha n} \bar{p}_\alpha(n)|\alpha n\rangle \tag{3}$$

and

$$\langle \alpha n|\mathbf{D}|\beta n'\rangle = \frac{\Phi_{\alpha\beta}(n, n')}{m_n^{1/2} m_{n'}^{1/2}}. \tag{4}$$

Here $u_\alpha(n)$ denotes the Cartesian α component of displacement of the nth atom with mass m_n, $p_\alpha(n)$ is the conjugated momentum of $u_\alpha(n)$, $\mathbf{D}$ is the dynamic matrix of the system, $|\alpha n\rangle$ is the basis in the direct-space representation, and $\Phi_{\alpha\beta}(n, n')$ is the second-order derivative of the potential energy in terms of atomic displacements.

The eigenfrequencies ω_j^2 and the eigenmodes $|j\rangle$ are such that

$$\mathbf{D}|j\rangle = \omega_j^2|j\rangle. \tag{5}$$

In the representation $|j\rangle$ the Hamiltonian is written as

$$H = \tfrac{1}{2}\sum_j (p_j^2 + \omega_j^2 q_j^2) \tag{6}$$

with

$$|X\rangle = \sum_j q_j |j\rangle \qquad \text{and} \qquad |P\rangle = \sum_j p_j |j\rangle. \tag{7}$$

So we have

$$u_\alpha(n) = \sum_j \frac{\langle \alpha n \mid j\rangle}{m_n^{1/2}} q_j \tag{8}$$

and

$$p_\alpha(n) = \sum_j m_n^{1/2} \langle \alpha n \mid j\rangle p_j. \tag{9}$$

In classical mechanics, $p_\alpha(n) = m_n \dot{u}_\alpha(n)$ so that $p_j = \dot{q}_j$ and we obtain the harmonic solution $q_j = q_0 \exp(-\mathrm{i}\omega_j t)$. In quantum mechanics, with the commutation relations $[\tilde{p}_\alpha(n), \tilde{u}_\beta(n')] = \mathrm{i}\hbar\delta_{\alpha\beta}\delta_{nn'}$ for the operators $\tilde{u}_\beta(n')$ and $\tilde{p}_\alpha(n)$, we obtain the Hamiltonian operator $\tilde{H} = \sum_j (\tilde{n}_j + \frac{1}{2})\hbar\omega_j$. The basic properties of the harmonic oscillators are well known and so the main problem, regardless of the formalism used, involves determining the eigenfrequencies ω_j^2 and eigenmodes $|j\rangle$ of the dynamic matrix $\mathbf{D}$.

We focus attention here on determination of the response functions. The temperature or thermodynamics Green function plays a central role (Abrikosov *et al* 1963):

$$G(\bar{u}_\alpha(n,\tau),\ \bar{u}_\beta(n')) = \langle T(\bar{u}_\alpha(n,\tau),\ \bar{u}_\beta(n'))\rangle \tag{10}$$

where $\tau = \mathrm{i}t$ and T is the time ordering operator.

For instance, dielectric properties can be obtained by expanding the dipole moment M of the system in an atomic displacement series

$$M_\alpha = \sum_{\alpha n} \frac{q_{\alpha\beta}(n)}{m_n^{1/2}} \bar{u}_\beta(n) \tag{11}$$

where $q_{\alpha\beta}(n)$ is the atomic charge tensor. The dielectric susceptibility is then given by ($\beta = 1/kT, \varepsilon \to 0_+$) (Cowley 1964a, b)

$$\begin{aligned}\chi_{\alpha\beta}(\omega) &= \beta G(M_\beta M_\alpha, \omega + \mathrm{i}\varepsilon) = \beta \sum_{\gamma\delta nn'} \frac{q_{\alpha\gamma}(n)}{m_n^{1/2}} G(\bar{u}_\delta(n')\bar{u}_\gamma(n), \omega + \mathrm{i}\varepsilon) \frac{q_{\delta\beta}(n')}{m_{n'}^{1/2}} \\ &= \beta \sum_{nn'} \langle \alpha n | \mathbf{QGQ} | \beta n'\rangle\end{aligned} \tag{12}$$

where the elements of the $\mathbf{Q}$ matrix are equal to $[q_{\alpha\beta}(n)/m_n^{1/2}]\delta_{nn'}$ and

$$\langle \alpha n | \mathbf{G} | \beta n'\rangle = G(\bar{u}_\beta(n')\bar{u}_\alpha(n), \omega + \mathrm{i}\varepsilon). \tag{13}$$

$G(\bar{u}_\beta(n')\bar{u}_\alpha(n), \omega + \mathrm{i}\varepsilon)$ is the Fourier transform of $G(\bar{u}_\beta(n')\bar{u}_\alpha(n), \tau)$ obtained by the Matsubara (1956) technique. For instance, the imaginary part of the susceptibility for harmonic systems is given by

$$\chi''_{\alpha\beta}(\omega) = \tfrac{1}{2} \sum_j a_\alpha^*(j) a_\beta(j) \frac{1}{2\omega_j} [\delta(\omega - \omega_j) - \delta(\omega + \omega_j)] \tag{14}$$

with

$$a_\alpha(j) = \sum_{\beta n} \frac{q_{\alpha\beta,n}}{m_n^{1/2}} \langle \alpha n \mid j\rangle. \tag{15}$$

The expressions (14) and (15) have been widely used to determine the linear response using the spectral moments method (Benoit 1987).

2.2. Damped systems

We focus attention here on systems with phonon–phonon or electron–phonon coupling. The phonon propagator is then given by the Dyson equation

$$\mathbf{G}^{-1}(\omega) = (\mathbf{G}^0)^{-1}(\omega) - \beta\Pi(\omega) \tag{16}$$

where $\Pi(\omega)$ is the self-energy of the propagator with $\Pi(\omega) = \Delta(\omega) - \mathrm{i}\Gamma(\omega)$, where $\Delta(\omega)$ and $\Gamma(\omega)$ are even and odd real functions of ω respectively. We consider here two usual forms for self-energy.

2.2.1. Anharmonic systems. To take into account the disorder, we work in direct space or site representation. Then, by the same method used for the perfect crystal (Maradudin and Fein 1962, Cowley 1963), it is possible to show that the contribution of the cubic term of potential energy to self-energy in direct space is given by

$$\langle\alpha n|\Pi(\omega)|\beta n'\rangle = \frac{9\hbar^2}{4}\sum_{j_1 j_2} V(\alpha, n, j_1, j_2)V(\beta, n', j_1, j_2)T(j_1, j_2, \omega) \tag{17}$$

where

$$\begin{aligned} T(j_1, j_2, \omega) = {} & \frac{n_1 + n_2 + 1}{\omega_1 + \omega_2 + (\omega + \mathrm{i}\varepsilon)} + \frac{n_1 + n_2 + 1}{\omega_1 + \omega_2 - (\omega + \mathrm{i}\varepsilon)} + \frac{n_2 - n_1}{\omega_1 - \omega_2 - (\omega + \mathrm{i}\varepsilon)} \\ & + \frac{n_2 - n_1}{\omega_1 - \omega_2 + (\omega + \mathrm{i}\varepsilon)}. \end{aligned} \tag{18}$$

Here n_j is the Boltzmann occupation number of one-phonon state $|j\rangle$ and

$$V(\alpha, n, j_1, j_2) = \sum_{\beta n_1 \gamma n_2} \frac{\Phi_{\alpha\beta\gamma}(n, n_1, n_2)}{(\omega_1\omega_2)^{1/2}} \langle\beta n_1 \mid j_1\rangle\langle\gamma n_2 \mid j_2\rangle. \tag{19}$$

$\Phi_{\alpha\beta\gamma}(n_1, n_2, n_3)$ is the cubic term in development of potential energy in terms of the atomic displacement components:

$$\begin{aligned} H_{\mathrm{A}} &= \sum_{\alpha n_1 \beta n_2 \gamma n_3} V_{\alpha\beta\gamma}(n_1, n_2, n_3)u_\alpha(n_1)u_\beta(n_2)u_\gamma(n_3) \\ &= \sum_{\alpha n_1 \beta n_2 \gamma n_3} \Phi_{\alpha\beta\gamma}(n_1, n_2, n_3)\bar{u}_\alpha(n_1)\bar{u}_\beta(n_2)\bar{u}_\gamma(n_3). \end{aligned} \tag{20}$$

It is clearly necessary to compute the eigenfrequencies and eigenvectors of harmonic (undisturbed) systems to evaluate the self-energy. Note that non-diagonal self-energy elements, which are usually neglected in Fourier space, are here taken into account. For large disordered lattices it is not possible to obtain these quantities by direct diagonalization.

2.2.2. Electron–phonon coupling. Let us consider a one-dimensional chain and the Su–Schrieffer–Heeger (SSH) Hamiltonian (Su *et al* 1980):

$$H = -\sum_{n,s} t_{n+1,n}(c^{+}_{n+1,s}c_{n,s} + c^{+}_{n,s}c_{n+1,s}) + \tfrac{1}{2}\sum_{n} K(u_{n+1} - u_n)^2 + \tfrac{1}{2}\sum_{n} M\dot{u}_n^2. \tag{21}$$

Here operator $c^{+}_{n,s}$ ($c_{n,s}$) creates (annihilates) an electron of spin $s(\pm 1/2)$ on the nth atom, M is the atomic mass and K the spring constant for the elastic energy, u_n represents the displacement of the nth atom, and $t_{n+1,n}$ is the hopping integral, which can be expanded as

$$t_{n+1,n} = t_0 - \alpha(u_{n+1} - u_n) \tag{22}$$

where t_0 is the hopping integral for the non-dimerized chain and α the electron–phonon coupling constant. It is possible to show that the phonon self-energy of this chain (Hick and Tinka-Gammel 1988, El Machtani-Idrissi 1993) is given by

$$\begin{aligned}\langle n|\Pi(\omega)|n'\rangle = 2\alpha^2 &\sum_{j_1 j_2 m_1 m_2 n n'} d(m_1, n)B(j_1, j_2, m_1)B(j_2, j_1, m_2)\\ &\times \frac{n_{j_2} - n_{j_1}}{\hbar(\omega + \mathrm{i}\varepsilon) + (E_{j_2} - E_{j_1})} d(m_2, n')\end{aligned} \tag{23}$$

with

$$B(j_1, j_2, n) = \langle n \mid j_1\rangle\langle j_2 \mid n+1\rangle + \langle n+1 \mid j_1\rangle\langle j_2 \mid n\rangle. \tag{24}$$

Here $\langle m \mid j\rangle$ is the mth component of the $|j\rangle$ state with energy $E_j, d(n,n) = -1$, $d(n, n+1) = 1$, zero otherwise, and n_j is the Fermi occupation number of state $|j\rangle$.

2.2.3. Approximate self-energy forms. Evaluation of self-energy is a complicated problem in large disordered systems and different approximations can be discussed. The lowest is constant damping, which is obtained by developing self-energy to first order with respect to frequency. We obtain

$$\langle\alpha n|\Pi(\omega)|\beta n'\rangle = -\mathrm{i}\omega g_{\alpha\beta}(n, n') = -\mathrm{i}\omega\langle\alpha n|\Gamma_0|\beta n'\rangle \tag{25}$$

where Γ_0 is called the dissipation matrix. In the limit of long waves, we obtain the usual dynamic equation with a dissipative force proportional to the velocity.

Now, if we develop self-energy with respect to frequency to the third order, we obtain

$$\langle\alpha n|\Pi(\omega)|\beta n'\rangle = \langle\alpha n|\mathbf{H} + \mathbf{K}\omega^2 - \mathrm{i}(\mathbf{L}\omega + \mathbf{M}\omega^3)|\beta n'\rangle \tag{26}$$

where **H**, **K**, **L** and **M** are constant matrices. We shall show that this situation corresponds to relaxation mode–oscillator coupling.

3. Linear response

For harmonic systems, the phonon propagator is given by

$$\mathbf{G}^0(\omega) = (1/\beta)(\mathbf{D} - \mathbf{I}\omega^2)^{-1}. \tag{27}$$

To evaluate the linear response, it is very useful to note that the susceptibility (12) is formally identical (see appendix) to the response obtained from the following equation of motion:

$$|\ddot{X}\rangle = -\mathbf{D}|X\rangle - \int \Pi(t-t')|X(t')\rangle\,\mathrm{d}t' + \mathbf{Q}|E(t)\rangle \tag{28}$$

where $|E(t)\rangle$ represents an external electric field

$$|E(t)\rangle = \sum_{\alpha n} E_\alpha(t)|\alpha n\rangle. \tag{29}$$

The Green function is given by (from equations (16) and (27) and from Martin and Schwinger (1959), Wehner (1966) and Doniach and Sondheimer (1974))

$$\ddot{\mathbf{G}} + \mathbf{D}\mathbf{G} - \int \Pi(t-t'')\mathbf{G}(t''-t')\,\mathrm{d}t'' = \frac{1}{\beta}\mathbf{I}\delta(t-t'). \tag{30}$$

We now show that it is possible to determine the response function of the system from equations (12), (28) and (30) without determining the eigenfrequencies and eigenvectors. We first develop the method for a simple damped system. It is very useful to transform the equation in order to manipulate matrices that are not dependent on the frequency. The method for the general situation will be presented in a subsequent section.

With constant damping the equation of motion (28), without the electric field, can be written with the help of (25):

$$|\ddot{X}\rangle + \Gamma_0|\dot{X}(t)\rangle + \mathbf{D}|X(t)\rangle = 0 \tag{31}$$

which can be expressed by introducing velocity

$$\mathrm{d}|X\rangle/\mathrm{d}t = |V\rangle \tag{32}$$

and

$$\mathrm{d}|V\rangle/\mathrm{d}t = -\mathbf{D}|X\rangle - \Gamma_0|V\rangle. \tag{33}$$

Equations (32) and (33) can be written in matrix form with

$$|R\rangle = \begin{pmatrix} |X\rangle \\ |V\rangle \end{pmatrix} \tag{34}$$

The motion equation is now written

$$\mathrm{d}|R\rangle/\mathrm{d}t = -\bar{\mathbf{D}}|R\rangle \tag{35}$$

with

$$\bar{\mathbf{D}} = \begin{pmatrix} 0 & -\mathbf{I} \\ \mathbf{D} & \Gamma_0 \end{pmatrix}. \tag{36}$$

The matrix $\bar{\mathbf{D}}$ is non-symmetric and the eigenvectors are complex. If $\Gamma_0 = 0$, the imaginary part of the eigenvalues of $\bar{\mathbf{D}}$ are the square roots of the eigenvalues of $\mathbf{D}$, and this form of $\bar{\mathbf{D}}$ can be used to determine directly the density of the phonon states $g(\omega)$ of the system (Rahmani 1993, Rahmani *et al* 1993b). Let $|j\rangle_\mathrm{R}$ and $|j\rangle_\mathrm{L}$ be the right and left eigenvectors of the matrix $\mathbf{D}$. These eigenvectors satisfy

$$\bar{\mathbf{D}}|j\rangle_\mathrm{R} = \lambda_j|j\rangle_\mathrm{R} \tag{37}$$

and

$$_\mathrm{L}\langle j|\bar{\mathbf{D}} =_\mathrm{L} \langle j|\mu_j. \tag{38}$$

Equation (38) is equivalent to

$$\bar{\mathbf{D}}^+|j\rangle_\mathrm{L} = \mu_j^*|j\rangle_\mathrm{L} \tag{39}$$

where $\bar{\mathbf{D}}^+$ is the adjoint matrix of $\bar{\mathbf{D}}$. Left and right eigenvectors are distinct and biorthogonal (Gantmacher 1966, Isaacson and Keller 1966):

$$_\mathrm{L}\langle j \mid j'\rangle_\mathrm{R} = \delta_{jj'}. \tag{40}$$

The set of 'left' and 'right' eigenvalues are identical. If the matrix $\bar{\mathbf{D}}$ is simple, the eigenvectors are linearly independent and a vector $|v\rangle$ can be written

$$|v\rangle = \sum_j a_j|j\rangle_\mathrm{R}. \tag{41}$$

We multiply (41) on both sides by $_\mathrm{L}\langle j|$. With the help of (40), we obtain

$$_\mathrm{L}\langle j|v\rangle = a_j \tag{42}$$

and with the help of (41) and (42), we obtain

$$|v\rangle = \sum_j (|j\rangle_\mathrm{R}\,{}_\mathrm{L}\langle j|)|v\rangle. \tag{43}$$

We thus obtain the following relation, which is equivalent to the closure relation with Hermitian matrix:

$$\sum_j (|j\rangle_\mathrm{R}\,{}_\mathrm{L}\langle j|) = \mathbf{I} \tag{44}$$

with both sets of eigenvalues arranged in the same order.

Eigenvalues and eigenvectors of $\bar{\mathbf{D}}$ and $\bar{\mathbf{D}}^+$ are determined using the DSPEV program of the IMSL library. From (37) and (40) we obtain

$$_\mathrm{L}\langle j|\bar{\mathbf{D}}|j'\rangle_\mathrm{R} = \lambda_j\delta_{jj'} \tag{45}$$

and similarly from (44)

$$\sum_j |j\rangle_\mathrm{R}\lambda_j\,{}_\mathrm{L}\langle j| = \sum_j \bar{\mathbf{D}}|j\rangle_\mathrm{R}\,{}_\mathrm{L}\langle j| = \bar{\mathbf{D}}. \tag{46}$$

These relations are used in the following calculations of the linear response of the systems. We now consider the evaluation of the response function with the expression (35) for the motion equation.

3.1. Dielectric properties

The motion equation (35) now becomes with (28)

$$\mathrm{d}|R\rangle/\mathrm{d}t = -\bar{\mathbf{D}}|R\rangle + \mathbf{Q}^{\mathrm{A}}|E\rangle \tag{47}$$

with the charge matrix $\mathbf{Q}^{\mathrm{A}}$ given by

$$\mathbf{Q}^{\mathrm{A}} = \begin{pmatrix} 0 & 0 \\ 0 & \mathbf{Q} \end{pmatrix} \tag{48}$$

where matrix $\mathbf{Q}$ is the $(\mathrm{d}N \times \mathrm{d}N)$ charge matrix.

We introduce the Green matrix $\mathbf{g}$ such that $(\beta = 1)$

$$\mathrm{d}\mathbf{g}/\mathrm{d}t + \bar{\mathbf{D}}\mathbf{g} = \mathbf{I}\delta(t - t'). \tag{49}$$

The solution of (47) can be written

$$|R(t)\rangle = \int_{-\infty}^{t} \mathbf{g}(t - t')\mathbf{Q}^{\mathrm{A}}|E(t')\rangle\,\mathrm{d}t'. \tag{50}$$

Equation (11) is now written as

$$|M\rangle = \mathbf{Q}^{\mathrm{R}}|R\rangle \tag{51}$$

where the charge matrix $\mathbf{Q}^{\mathrm{R}}$ is given by

$$\mathbf{Q}^{\mathrm{R}} = \begin{pmatrix} \mathbf{Q} & 0 \\ 0 & 0 \end{pmatrix}. \tag{52}$$

From (49), the Fourier transform of the Green function $\mathbf{g}$ is given by

$$\mathbf{g}(\omega) = (\bar{\mathbf{D}} - \mathrm{i}\mathbf{I}\omega)^{-1}. \tag{53}$$

Combining equations (50) and (51), and following the same method as described in the appendix, for dielectric susceptibility, we obtain

$$\chi_{\alpha\beta}(\omega) = \sum_{nn'} \langle \alpha n|\mathbf{Q}^{\mathrm{R}}\mathbf{g}(\omega)\mathbf{Q}^{\mathrm{A}}|\beta n'\rangle. \tag{54}$$

Now, taking into account relations (45) and (46) and the closure equation (44), we obtain

$$\chi_{\alpha\beta}(\omega) = \sum_{j=1}^{2N} \frac{R_\alpha(j)S_\beta^*(j)}{\lambda_j - \mathrm{i}\omega} \tag{55}$$

with

$$R_\alpha(j) = \sum_{\beta,n=1}^{N} \frac{q_{\alpha\beta}(n)}{m_n^{1/2}} \langle \beta n|j\rangle_{\mathrm{R}} \tag{56}$$

and

$$S_\beta(j) = \sum_{\alpha,n=N+1}^{2N} \frac{q_{\alpha\beta}(n-N)}{m_{n-N}^{1/2}} \langle \alpha n|j\rangle_{\mathrm{L}}. \tag{57}$$

Before developing the moments method to evaluate (55), we show how to evaluate scattering properties of damped materials.

3.2. Scattering properties

In the previous section, the response of a material to an external macroscopic field was studied. Another way to study a material is to scatter particles from them. Two examples of this type of experiment are the Raman scattering of light and the scattering of thermal neutrons. These different types of scattering can be treated with the same formalism.

Let $\hbar \boldsymbol{Q}_{\mathrm{d}}$ and $\hbar\omega$ be momentum and energy transferred by the neutron to the scattering system and $\boldsymbol{k}_0$ and $\boldsymbol{k}$ the initial and final wavevectors of the neutron. Then, the differential cross section $\sigma(\boldsymbol{Q}_{\mathrm{d}}, \omega)$ for slow neutron scattering can be written

$$\sigma(\boldsymbol{Q}_{\mathrm{d}}, \omega) = \mathrm{d}^2\sigma/\mathrm{d}\Omega\,\mathrm{d}E = (k/k_0)S(\boldsymbol{Q}_{\mathrm{d}}, \omega). \tag{58}$$

The scattering law $S(\boldsymbol{Q}_{\mathrm{d}}, \omega)$ is the Fourier transform of the thermodynamic correlation function $g(\boldsymbol{Q}_{\mathrm{d}}, t)$ (Van Hove 1954, Glauber 1955, Lovesey 1986)

$$S(\boldsymbol{Q}_{\mathrm{d}}, \omega) = \frac{1}{2\pi\hbar}\int \exp(\mathrm{i}\omega t)\; g(\boldsymbol{Q}_{\mathrm{d}}, t)\,\mathrm{d}t \tag{59}$$

with

$$g(\boldsymbol{Q}_{\mathrm{d}}, t) = \langle A(-\boldsymbol{Q}_{\mathrm{d}}, t)A(\boldsymbol{Q}_{\mathrm{d}}, t)\rangle \tag{60}$$

where $A(\boldsymbol{Q}_{\mathrm{d}}, t)$ is analogous to the $\boldsymbol{Q}_{\mathrm{d}}$ component of the density of the system:

$$A(\boldsymbol{Q}_{\mathrm{d}}, t) = \sum_n b_n \exp(\mathrm{i}\boldsymbol{Q}_{\mathrm{d}} \cdot \boldsymbol{r}_n(t)). \tag{61}$$

Here b_n and $\boldsymbol{r}_n(t)$ are the Fermi scattering length and the position of the nth atom respectively. The correlation function can be written

$$g(\boldsymbol{Q}_{\mathrm{d}}, t) = \sum_{nn'} b_n b_{n'} \exp[\mathrm{i}\boldsymbol{Q}_{\mathrm{d}} \cdot (\boldsymbol{r}^0_{n'} - \boldsymbol{r}^0_n)] \exp(-W_n - W_{n'}) \exp\left(\sum_{\alpha\beta} Q_{\mathrm{d}\alpha} Q_{\mathrm{d}\beta} C_{\alpha\beta}(n, n', t)\right) \tag{62}$$

with $\boldsymbol{r}_n(t) = \boldsymbol{r}^0_n + \boldsymbol{u}_n(t)$ where $\boldsymbol{r}^0_n$ is the equilibrium position of the nth atom. W_n is the Debye–Waller factor of the nth atom and

$$C_{\alpha\beta}(n, n', t) = \langle u_{n\alpha}(t)u_{n'\beta}(0)\rangle. \tag{63}$$

Expanding the correlation function $g(\boldsymbol{Q}_{\mathrm{d}}, t)$ we can write the scattering law

$$\begin{aligned} S(\boldsymbol{Q}_{\mathrm{d}}, \omega) = \frac{1}{\hbar}\sum_{nn'} & b_n b_{n'} \exp[\mathrm{i}\boldsymbol{Q}_{\mathrm{d}} \cdot (\boldsymbol{r}^0_{n'} - \boldsymbol{r}^0_n)] \\ & \times \exp(-W_n - W_{n'})\left(\delta(\omega) + \sum_{\alpha\beta} Q_{\mathrm{d}\alpha} Q_{\mathrm{d}\beta} c_{\alpha\beta}(n, n', \omega) + \ldots\right) \end{aligned} \tag{64}$$

where $c_{\alpha\beta}(n, n', \omega)$ is the Fourier transform of $C_{\alpha\beta}(n, n', t)$.

Similarly the dielectric susceptibility is directly related to the Fourier transform of the displacement correlation function. It is well known that

$$\chi''_{\alpha\beta}(\omega) = \frac{1}{2\pi}\frac{1}{2\hbar}\int_{-\infty}^{+\infty} \langle [M_\alpha(t), M_\beta]\rangle \mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t. \tag{65}$$

Now if we define the auxiliary functions

$$\bar{S}_{\alpha\beta}(\omega) = \int \langle u_\alpha(n,t)u_\beta(n')\rangle e^{i\omega t}\,dt \tag{66}$$

and

$$\bar{\chi}_{\alpha\beta}(\omega) = \int \langle [u_\alpha(n,t), u_\beta(n')]\rangle e^{i\omega t}\,dt \tag{67}$$

it is easy to show that

$$\bar{\chi}_{\alpha\beta}(\omega) = (1 - e^{-\beta\hbar\omega})\bar{S}_{\alpha\beta}(\omega). \tag{68}$$

This is the fluctuation–dissipation theorem, which is found in many various forms in the literature. Now with the help of (11) and (65), we obtain

$$\chi''_{\gamma\delta}(\omega) = \frac{1}{2\pi}\frac{1}{2\hbar}\sum_{nn'\alpha\beta} q_{\gamma\alpha}(n)q_{\delta\beta}(n')\bar{\chi}_{\alpha\beta}(\omega) \tag{69}$$

and from (63), (64) and (66)

$$\sigma(\boldsymbol{Q}_{\mathrm{d}'}\omega) = \frac{1}{2\pi}\frac{k}{k_0\hbar}\sum_{nn'\alpha\beta} b_n b_{n'} \exp(-W_n - W_{n'}) \exp[i\boldsymbol{Q}_{\mathrm{d}}\cdot(\boldsymbol{r}_{n'} - \boldsymbol{r}_n)]Q_{\mathrm{d}\alpha}Q_{\mathrm{d}\beta}\bar{S}_{\alpha\beta}(\omega). \tag{70}$$

Equation (70), with (68), is exactly the same form as (69). The only difference is that the charge tensor $q_{\alpha\beta}(n)/m_n^{1/2}$ has been replaced by $(b_n/m_n^{1/2})Q_{\mathrm{d}\alpha}\exp(-W_n)\exp(-i\boldsymbol{Q}_{\mathrm{d}}\cdot\boldsymbol{r}_n)$ and the result multiplied by the factor

$$2(k/k_0)(1 - e^{-\beta\hbar\omega})^{-1} = 2(k/k_0)[n(\omega) + 1] \tag{71}$$

where $n(\omega)$ is the Boltzmann occupation number. Thus, relations (68), (69) and (70) show that inelastic neutron scattering of damped systems can be obtained by relation (55) but with a different potential seen by the plane wave. However, direct determination of (55) requires determination of the eigenvalues and left and right eigenvectors of matrix $\bar{\mathbf{D}}$. It is well known that there are some problems in direct diagonalization and determination of eigenvectors of non-symmetrical matrices in the presence of zero eigenvalues and degeneracy. We shall not have such difficulties with the moments method. In several publications (Benoit *et al* 1992a, b and references therein), we have shown that for harmonic systems the moments method is a powerful tool to study dynamic properties of solids and that the response functions can be obtained without any diagonalization of the dynamic matrix. We now show how these moment techniques can be applied to compute physical properties of damped systems.

4. Moments method

For harmonic solids, the moments method was first used by Montroll (1942) to calculate the density of one-phonon states. The method was improved by Blumstein and Wheeler (1973) and Wheeler *et al* (1974). In the dynamics of condensed matter, the possibility of directly determining moments of the response function from the dynamic matrix was pointed out for the first time by Galtier and Benoit (1981) and the exact evaluation of the response was developed later by Benoit (1987, 1989) and applied to different systems (Benoit *et al* 1990, 1992a, b, Poussigue *et al* 1991, Royer *et al* 1991, 1992, Royer 1992, Rahmani 1993, Rahmani *et al* 1993, 1994).

Brownian motion and Markovian processes (Dupuis 1967, Scheunders and Naudts 1990) and excitation transfer in disordered systems (McGraw and Merry 1985) have also been studied by the moments technique. In solid-state physics concerning studies of electronic properties, the moments method has been developed by Cyrot-Lackmann (1967), Gaspard and Cyrot-Lackmann (1973), Lambin and Gaspard (1982), Turchi *et al* (1982) and Jurczek (1985). These moments methods, which have been called, successively, modified (Blumstein and Wheeler 1973), generalized (Lambin and Gaspard 1982), orthogonalized (Jurczek 1985), spectral (Benoit 1989) and inverse (Scheunders and Naudts 1990), are mathematically equivalent to the Lanczos (1950) or the recursion procedure (Haydock *et al* 1972, Haydock 1980) in many aspects (Jurczek 1985, Benoit *et al* 1992b). In fact the method of moments is much more general than the Lanczos procedure and was solved by Stieltjes (1884). Furthermore, for many physical problems, moments of density of states play a central role: they represent or are directly connected to the physical properties of the systems, heat capacity (Maradudin *et al* 1963), sum rules (Benoit 1987, Luck 1992), and they are linear with the density of states (Gaspard and Lambin 1984). Thus we prefer to work with moments and we simply call the method by which the moments are actually computed the 'moments method'.

With this method, in harmonic solids, to evaluate the response function (14), we introduce an auxiliary density function, which is a sum of delta peaks (Benoit 1987). This function is developed in a continued fraction and the method involves determining the coefficients of this continued fraction directly from the dynamic matrix. With damped systems, we cannot represent the response function (55) as a sum of Dirac peaks. Furthermore, the matrix $\bar{\mathbf{D}}$ is non-symmetric and sometimes complex. Very few studies have dealt with the computation of the eigenvalues of large non-symmetric matrices. The biorthogonalization Lanczos algorithm can be used to obtain a few eigenvalues (Kim and Chronopoulos 1992) but this method is sometimes unstable (Saad 1980). Dominant eigenvalues and corresponding eigenvectors can also be obtained with the Arnoldi method (Saad 1980). However, evaluation of the response function (55) requires determination of *all* eigenvectors and eigenvalues of the $\bar{\mathbf{D}}$ matrix, which cannot be obtained by the biorthogonalization Lanczos algorithm or by the Arnoldi method. It is thus necessary to develop a new technique where the eigenvectors and eigenvalues are not explicitly computed.

Let us define the following auxiliary density function

$$g_{\alpha\beta}(x, y) = \sum_j \lambda_j R_\alpha(j) S_\beta^\star(j) \delta(x - \alpha_j) \delta(y - \beta_j) \tag{72}$$

with $\lambda_j = \alpha_j + \mathrm{i}\beta_j$. Recall that λ_j and $\lambda_j^\star$ are eigenvalues of $\bar{\mathbf{D}}$. Now let us define the following transform of $g_{\alpha\beta}(x, y)$

$$\Phi_{\alpha\beta}(u) = \int \frac{g_{\alpha\beta}(x, y)}{z - u} \, \mathrm{d}x \, \mathrm{d}y \tag{73}$$

with $z = x + \mathrm{i}y$ and $u = \mathrm{i}\omega$.

Combining relations (72) and (73), we obtain

$$\Phi_{\alpha\beta}(u) = -\sum_j \sum_{m=0}^{\infty} R_\alpha(j) S_\beta^\star(j) \lambda_j^{m+1} / u^{m+1} \tag{74}$$

and with the help of (56) and (57) and closure relation (44), we obtain

$$\Phi_{\alpha\beta}(u) = -\sum_{m=0}^{\infty} \mu_m^{\alpha\beta}/u^{m+1} \tag{75}$$

where

$$\mu_m^{\alpha\beta} = \int g_{\alpha\beta}(x, y) z^m \,\mathrm{d}x\,\mathrm{d}y = \sum_{nn'} \langle \alpha n | \mathbf{Q}^{\mathrm{R}} \bar{\mathbf{D}}^{m+1} \mathbf{Q}^{\mathrm{A}} | \beta n' \rangle. \tag{76}$$

The quantities $\mu_m^{\alpha\beta}$ are real (from (76)) but are not the two-dimensional moments of the function $g_{\alpha\beta}(x, y)$ in the classical sense (Shohat and Tamarkin 1963). However, these quantities are directly connected to the two-dimensional moments of the function $g_{\alpha\beta}(x, y)$. In the following we continue to call the $\mu_m^{\alpha\beta}$ moments of $g_{\alpha\beta}(x, y)$ according to the definition (76). We note that these quantities can be determined directly from dynamic and charge matrices without any computation of eigenvalues or eigenvectors. It is now necessary to connect them to the dielectric susceptibility.

Let us introduce the following function:

$$\Theta_{\alpha\beta}(u) = \sum_j \int \frac{R_\alpha(j) S_\beta^\star(j)}{z - u} \delta(x - \alpha_j)\delta(y - \beta_j)\,\mathrm{d}x\,\mathrm{d}y. \tag{77}$$

It is easily shown that on one side

$$\Theta_{\alpha\beta}(u) = -\frac{1}{u} \sum_m \frac{\mu_m^{\alpha\beta}}{u^{m+1}} = \frac{1}{u} \phi_{\alpha\beta}(u) \tag{78}$$

and on the other side from (55) and (77)

$$\chi_{\alpha\beta}(\omega) = \Theta_{\alpha\beta}(u). \tag{79}$$

From (75), (76), (78) and (79) we can evaluate the dielectric susceptibility. Let us now introduce the continued fraction. Following Stieltjes (1884) and Royer (1992), we define a polynomial $Q_n(z)$ of degree n such that

$$Q_n(z) = \sum_{m=0}^{n} f_{nm} z^m \tag{80}$$

with the conditions (index α and β are omitted for polynomials)

$$\int g^{\alpha\beta}(x, y) Q_n(z) z^k \,\mathrm{d}x\,\mathrm{d}y = 0 \qquad (k = 0, 1, 2, \ldots, n - 1). \tag{81}$$

With the help of relation (76) we obtain with (80) in (81)

$$\sum_{m=0}^{n} f_{nm} \mu_{k+m+1}^{\alpha\beta} = 0. \tag{82}$$

In classical moment problems (Stieltjes 1884, Walls 1948, Akhieser 1965, Jones and Thron 1980, Shohat and Tamarkin 1963) a necessary and sufficient condition for the existence of a solution is the positiveness of the Hankel determinants constructed with the moments (Stieltjes 1884, Hamberger 1920) ($\Delta_n \geqslant 0$ for spectra with distinct points). However, recall that the moments problem consists of finding a bounded non-decreasing function in a given interval such that its moments have a prescribed set of values. Here we know the moments of this function and that this function exists. The problem is to find a good development to compute it. In our problem, with the distribution function (72), the Hankel determinants are real but not always positive and there are no mathematical studies on the existence of solutions, our problem not being equivalent to the moments problem of two-dimensional distribution function. We conjecture that solutions to equation (82) exist and we shall verify this with several physical examples.

Now we follow the method developed for the classical moment problem (Royer 1992). The polynomials $Q_n(z)$ obey the following recurrence law:

$$Q_{n+1}(z) = (z - \bar{a}_{n+1})Q_n(z) - \bar{b}_n Q_{n-1}(z) \tag{83}$$

with $Q_{-1}(z) = 0$, $Q_0(z) = 1$ where

$$\bar{a}_{n+1} = \bar{\nu}_{nn}/\nu_{nn} \tag{84}$$

and

$$\bar{b}_n = \nu_{nn}/\nu_{n-1,n-1} \tag{85}$$

with

$$\nu_{nn} = \int g^{\alpha\beta}(x,y)Q_n(z)Q_n(z)\,\mathrm{d}x\,\mathrm{d}y \tag{86}$$

and

$$\bar{\nu}_{nn} = \int z g^{\alpha\beta}(x,y)Q_n(z)Q_n(z)\,\mathrm{d}x\,\mathrm{d}y. \tag{87}$$

Quantities ν_{nn} and $\bar{\nu}_{nn}$ are equivalent to the generalized moments introduced for the usual moments problem (Cyrot-Lackmann 1967). It is possible to show that the function $\Phi_{\alpha\beta}(u)$ defined in (75) can be developed in a continued fraction, with demonstration identical to those developed in the classical moments problem (Royer 1992). Then we obtain

$$\phi_{\alpha\beta}(u) = \cfrac{b_0}{u - a_1 - \cfrac{b_1}{u - a_2 - \cfrac{b_2}{u - a_3 - \Phi_\infty}}}. \tag{88}$$

The continued fraction is a limit of a fraction of polynomials and we obtain

$$\Phi_{\alpha\beta}(u) = \frac{P_{n-1}(u) - P_{n-2}(u)\Phi_\infty}{Q_n(u) - Q_{n-1}(u)\Phi_\infty} \tag{89}$$

where

$$P_{n+1}(u) = (u - a_{n+2})P_n(u) - b_{n+1}P_{n-1}(u) \tag{90}$$

with $P_0(u) = -b_0$, $P_{-1}(u) = 0$ and

$$Q_{n+1}(u) = (u - a_{n+1})Q_n(u) - b_n Q_{n-1}(u) \tag{91}$$

with $Q_0(u) = 1$, $Q_{-1}(u) = 0$.

As $n \to \infty$, relations (88) or (89) are formally identical to relation (75) and then

$$\bar{a}_n = a_n \qquad \bar{b}_n = b_n. \tag{92}$$

Relations (84)–(92) allow determination of the dielectric susceptibility or the inelastic scattering cross section for damped systems. In practice, the same procedure as described in Benoit *et al* (1992b) is followed exactly. However, the $\bar{\mathbf{D}}$ matrix being non-symmetric, it is necessary to introduce left and right Krylov subspace. We now illustrate this method with some examples.

5. Tests and illustrations

5.1. One-dimensional linear chain

Let us consider a chain of N masses, each coupled to its nearest neighbours. We study the longitudinal vibrations of this chain and impose cyclic boundary conditions (a closed chain). The potential energy is given by (1) with

$$\begin{aligned} \langle n|\mathbf{D}|n+1\rangle &= -[k_0 + (-1)^n k_1] \\ \langle n|\bar{\mathbf{D}}|n\rangle &= -\sum_{n' \neq n} \langle n|\bar{\mathbf{D}}|n'\rangle. \end{aligned} \tag{93}$$

It is necessary to choose a model for the dissipation matrix Γ_0. Dissipation can be introduced by considering the macroscopic equations of hydrodynamics. In such equations, the dissipative term corresponds to the viscous force and is taken to be proportional to the Laplacian of the velocity field. If we develop a discrete form of motion equation, an imaginary matrix that represents the dissipation of energy is obtained. For instance, in one-dimensional systems it is well known that, for a regular lattice, the Laplacian of the velocity is represented by

$$\Delta v = [v(n+1) + v(n-1) - 2v(n)]/a^2 \tag{94}$$

where $v(n)$ is the velocity of the nth atom and a the lattice parameter (here $a = 1$). This equation corresponds to a dissipation matrix with dissipation forces between first neighbours. Note that it is necessary to consider all elements of the matrix to obtain a correct physical description. For instance, a positive sign of the diagonal elements does not mean that energy is created in the material. So we now assume that the dissipation matrix Γ_0 is proportional to the Laplacian of the velocity field

$$\Gamma_0 = \gamma \Delta v \tag{95}$$

and we study the infrared absorption of the chain. Let us suppose that the chain is ionic with two ions per unit cell. It is well known that only the optical mode of the centre of the Brillouin zone is infrared-active. We have determined the imaginary part $\chi''(\omega)$ of the susceptibility by the moments method and by direct diagonalization. The results are shown in figures 1 and 2 for two values of the damping γ. We note that results obtained by both methods are in excellent agreement. Values of coefficients a_n and b_n for both models are reported in table 1. In figure 3, we give the dispersion curves, obtained by both methods, from the differential scattering cross section of the same chain. Results obtained by direct diagonalization and by moments method are in complete agreement.

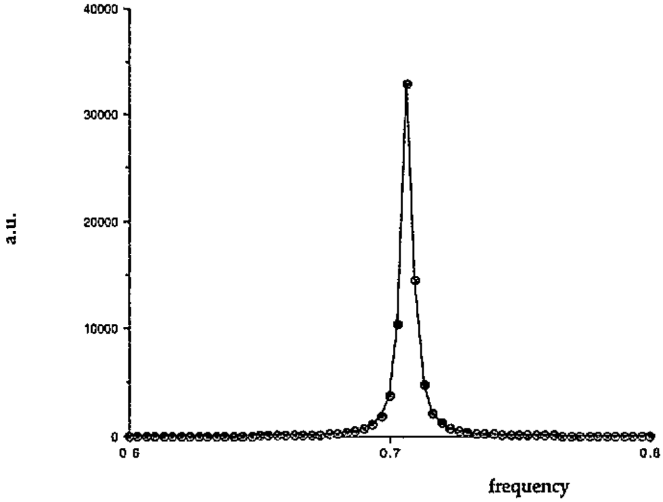

Figure 1. Dielectric susceptibility of a damped chain with $k_0 = 0.125$, $k_1 = 0.025$ and $\gamma = 0.001\,25$ obtained by diagonalization (——) and with the moments method (O).

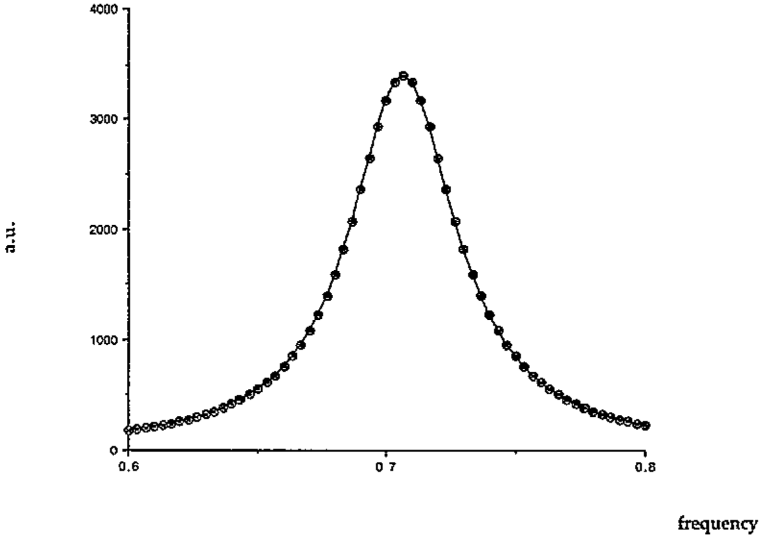

Figure 2. Dielectric susceptibility of a damped chain with $k_0 = 0.125$, $k_1 = 0.025$ and $\gamma = 0.0125$ obtained by diagonalization (——) and with the moments method (O).

5.2. Systems with coupling between oscillators and relaxation modes

Many aspects of a phase transition can be understood on the basis of the phenomenological theory: the so-called Landau theory of phase transitions. However, it is important to take into account the discreteness effects and microscopic origin of the phenomenological parameters. Anharmonic interactions are believed to be responsible for these structural phase transitions. If the phonon frequency reaches zero at some temperature, the phonon is regarded as condensing into the lattice to give a transition. In contrast, many physical

Table 1. Coefficients of the 'continued' fraction a_n and b_n for the perfectly dimerized chain. Only the first coefficients differ from zero. Recall that, for the harmonic chain, a_1 differs from zero but $b_1 = 0$.

γ	a_1	b_1
0.0125	0.05	−0.5
0.001 25	0.005	−0.5

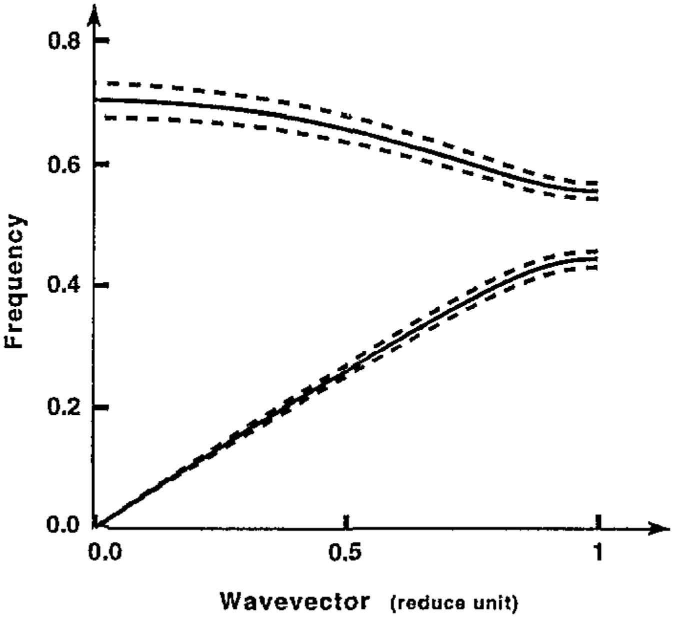

Figure 3. Dispersion curves obtained from the differential scattering cross section of a damped chain with $k_0 = 0.125$, $k_1 = 0.025$ and $\gamma = 0.0125$ obtained by diagonalization and with moments method. The upper and lower curves give the halfwidth of the phonon peaks.

properties have been explained by supposing the presence of relaxation modes in these materials.

So we consider a system of interacting oscillators and relaxation modes. We shall show how to determine the linear response and present some illustrations.

Let us consider the following equations:

$$m_n \frac{\mathrm{d}^2 u_\alpha(n)}{\mathrm{d}t^2} = -\sum_{\beta n'} \Phi_{\alpha\beta}(n, n')u_\beta(n') - \sum_{\beta n'} A_{\alpha\beta}(n, n')z_\beta(n') \tag{96}$$

and

$$\frac{\mathrm{d}z_\alpha(n)}{\mathrm{d}t} = -\sum_{\beta n'} G_{\alpha\beta}(n, n')u_\beta(n') - \sum_{\beta n'} T_{\alpha\beta}(n, n')z_\beta(n') \tag{97}$$

where $z_\alpha(n)$ represents the α component of the nth relaxation mode. Equations (96) and (97) are the generalization of the Vacher and Boyer (1978) equations developed to study propagation of acoustic waves in viscoelastic anisotropic media, and then they include the model of Christensen (1971) developed for isotropic solids. It is easy to show that relaxation modes introduce self-energy in phonon propagators, such that

$$\Pi(\omega) = \bar{\mathbf{A}}\mathbf{T}\mathbf{G} - \mathrm{i}\bar{\mathbf{A}}\mathbf{T}^{-1}\bar{\mathbf{A}}^{-1}(\mathbf{D}\omega + \mathbf{I}\omega^3) \tag{98}$$

where

$$D_{\alpha\beta}(n,n') = \Phi_{\alpha\beta}(n,n')/m_n^{1/2}m_{n'}^{1/2} \tag{99}$$

$$\bar{A}_{\alpha\beta}(n,n') = A_{\alpha\beta}(n,n')/m_n^{1/2} \tag{100}$$

$$\bar{G}_{\alpha\beta}(n,n') = G_{\alpha\beta}(n,n')/m_{n'}^{1/2} \tag{101}$$

which is equivalent to (26) with $\mathbf{H} = \bar{\mathbf{A}}\mathbf{T}\mathbf{G}$, $\mathbf{K} = 0$, $\mathbf{L} = \bar{\mathbf{A}}\mathbf{T}^{-1}\bar{\mathbf{A}}^{-1}\mathbf{D}$ and $\mathbf{M} = \bar{\mathbf{A}}\mathbf{T}^{-1}\bar{\mathbf{A}}^{-1}$. Recall that we consider the response of the system, i.e. that ω is a real variable. In order to compute with constant matrices, we now follow the same formalism developed in section 3. Equations (96) and (97) can be written in matrix form with

$$|R\rangle = \begin{pmatrix} |X\rangle \\ |V\rangle \\ |Z\rangle \end{pmatrix}. \tag{102}$$

We obtain

$$\mathrm{d}|R\rangle/\mathrm{d}t = -\bar{\mathbf{D}}|R\rangle \tag{103}$$

with

$$\bar{\mathbf{D}} = \begin{pmatrix} 0 & -\mathbf{I} & 0 \\ \mathbf{D} & 0 & \bar{\mathbf{A}} \\ \bar{\mathbf{G}} & 0 & \mathbf{T} \end{pmatrix}. \tag{104}$$

The response function can be obtained by using the expressions (53) and (54) but with

$$\mathbf{Q}^{\mathrm{A}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mathbf{Q} & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{Q}^{\mathrm{R}} = \begin{pmatrix} \mathbf{Q} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{105}$$

$\mathbf{Q}$ being the charge matrix $[q_{\alpha\beta}(n)/m_n^{1/2}]\delta_{nn'}$ for determination of dielectric susceptibility and $(b_n/m_n^{1/2})Q_{\mathrm{d}\alpha}\exp(-W_n)\exp(-\mathrm{i}\mathbf{Q}_{\mathrm{d}}\cdot r_n)$ for determination of the inelastic scattering cross section.

To illustrate the method, we consider, as a physical example, the phonon dispersion of the soft branch in $\mathrm{K_2SeO_4}$ (Axe *et al* 1980). The microscopic origin of the instability has been discussed in detail by Haque and Hardy (1980) and Bussman-Holder *et al* (1981): competition between long-range Coulomb interactions and short-range overlap forces are believed to be responsible for the occurrence of instability in ionic crystals. However, physical discussion of the origin of instability is beyond the scope of this paper.

Let us consider a linear chain of oscillators coupled to a linear chain of relaxation modes. The chain consists of identical atoms with first-neighbour interaction only

$$\langle n|\mathbf{D}|n+1\rangle = -k_0. \tag{106}$$

In this simple example, suppose that

$$\langle n|\bar{\mathbf{G}}|n+m\rangle = \langle n|\bar{\mathbf{A}}|n+m\rangle = \tau\langle n|\dot{\mathbf{T}}|n+m\rangle = -g_m \qquad m = 1, 2, \ldots, 5 \tag{107}$$

i.e. long-range interactions are included until the fifth neighbour. Experimental and calculated phonon branches are reported in figure 4 for four temperatures. The theoretical results can be obtained by three different methods. In the first two methods we used the transitional invariance of the system and the solutions have been developed in Bloch representation $|k\rangle$. In this representation, the dynamic matrix is a 3 × 3 complex non-symmetric matrix. The response functions are obtained either by direct diagonalization, or by the moments method as described in previous section, but now in Fourier space. It is also possible to use the moments method directly on the large system with cyclic boundary conditions. The three methods give exactly the same result. In this example, we have used a chain with 360 atoms corresponding to a 1080 × 1080 dynamic matrix. The values of the parameters τ and g_m are reported in table 2. In the fitting process, we have used the 130 K and 250 K phonon branches and supposed linear dependence with temperature for the coefficients g_m; τ is adjusted for every temperature. The dependence of τ with temperature is reported in figure 5. One notes that τ varies linearly with temperature. We observe general qualitative agreement with the experiment.

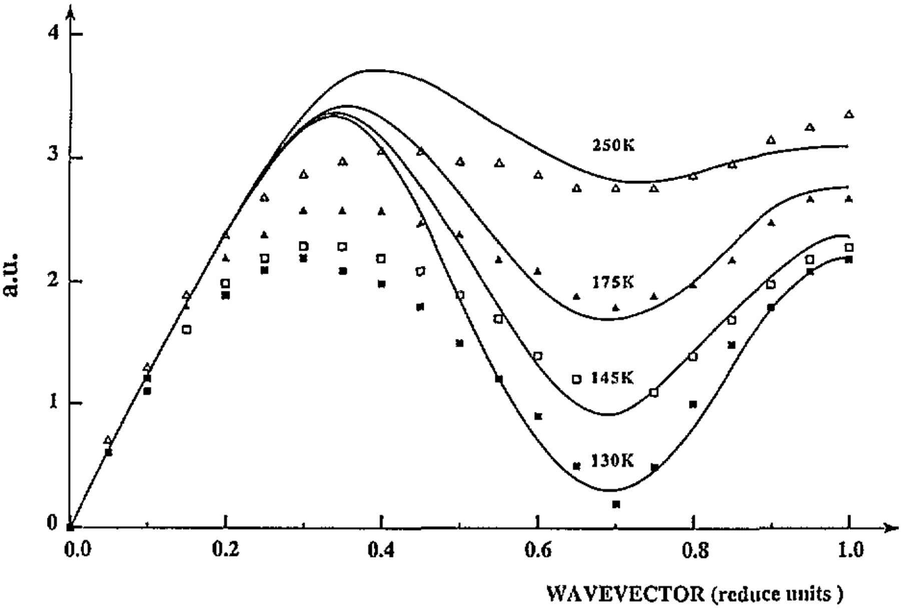

Figure 4. Dispersion curves obtained in K_2SeO_4 for four temperatures: full curves represent the experimental results and symbols the theoretical results. Parameters of the model are reported in table 2. The system is perfectly ordered.

Let us now consider a disordered system. Here we assume that the coupling constants are given by

$$\langle n|\bar{\mathbf{G}}|n+m\rangle = \langle n|\bar{\mathbf{A}}|n+m\rangle = \tau\langle n|\mathbf{T}|n+m\rangle = -g_m(1+\gamma_n). \tag{108}$$

Table 2. Parameters of the long-range interaction between the relaxation modes. We used the 130 K and 250 K phonon branches to adjust these parameters and supposed linear dependence with temperature for the g_m coefficients. Parameter τ is adjusted for every temperature.

T (K)	g_1	g_2	g_3	g_4	g_5	τ
130	0.340	0.00	0.0935	0.00	0.0153	0.357
145	0.346	0.0187	0.0914	0.00	0.0153	0.364
175	0.359	0.0374	0.0871	0.00	0.0153	0.391
250	0.391	0.0595	0.0765	0.00	0.0153	0.437

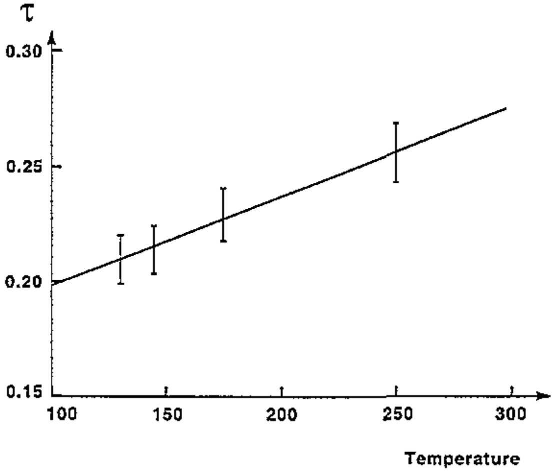

Figure 5. Variation of parameter τ with temperature.

The γ_n are independent random variables distributed according to the continuous bounded probability density function $P(\gamma)$, which is zero except in the region $-1 < \gamma < 1$ where $P(\gamma) = 0.5$. We computed the phonon branches for different values of the temperature with a chain of 360 atoms. The results are reported in figure 6. We observe that the disorder enlarges the region of unstable phonons.

We note also that the method is not so well conditioned as in the case of pure harmonic systems and some difficulties may occur. For instance, the position of point $Q_\mathrm{d} = 0.75$ ($T = 130$ K, figure 6) is certainly wrong. This problem could be due to the choice of the form of the infinite tail of the continued fraction.

5.3. Systems with electron–phonon coupling

It is well known that the one-dimensional (1D) metal is intrinsically unstable to the formation of charge-density waves (Peierls 1955). For instance, TTF-TCNQ (tetrathiafulvalene tetracyanoquinodimethane) is a one-dimensional metal at high temperature that undergoes a metal–insulator transition at 54 K (Heeger and Garito 1975). Inelastic neutron studies of the phonon spectrum reveal a giant Kohn anomaly at room temperature, which becomes stronger at low temperature (Comès *et al* 1976). One method involves viewing Peierls instability in terms of the electronic dielectric response function, which is related to the Lindhard function (Heeger 1977). It is also possible to study Peierls instability using the Green function (Schultz 1978) in Fourier space. To illustrate the moments method, we shall study Peierls instability in direct space with the help of the SSH Hamiltonian (21). In the presence

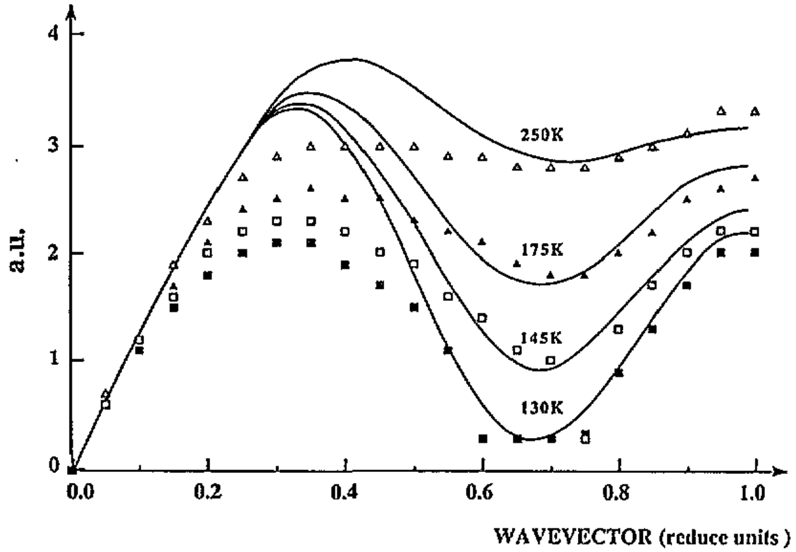

Figure 6. Dispersion curves obtained with the same model as reported in figure 4 in the presence of disorder for four temperatures: symbols represent the theoretical results. Experimental results are reported for comparison with the ordered model.

of electron–phonon coupling, the phonon Green function is given by expression (16) with self-energy given by (23). To study Peierls instability or Kohn anomaly, we computed the dispersion curve. The differential scattering cross section is calculated for different values of the momentum transfer inside the first Brillouin zone. However, with value (23) for the self-energy, it is not possible to reduce the matrices to frequency-independent elements as we did for constant damping and for systems with coupling between relaxation modes and oscillators. To evaluate the differential scattering cross section, it is interesting to work with real matrices and separate the real part $\Delta(\omega)$ and the imaginary part $\Gamma(\omega)$ of $\Pi(\omega)$. The equation (28), without the external field, can be written as:

$$\mathrm{d}|R\rangle/\mathrm{d}t = -\bar{\mathbf{D}}(\omega)|R\rangle \tag{109}$$

with

$$\bar{\mathbf{D}}(\omega) = \begin{pmatrix} 0 & -\mathbf{I} \\ \mathbf{D} + \Delta(\omega) & \Gamma(\omega)/\omega \end{pmatrix}. \tag{110}$$

To compute the response of the system, we follow exactly the same procedure as for the system with constant damping. For a given value of the frequency in the self-energy, we evaluate the differential scattering cross section and memorize the value obtained for this frequency. The dispersion curves obtained for a chain of 120 atoms by this method and by direct diagonalization, with $K = 0.0011$ eV Å^{-2}, $t_0 = 1$ eV, $\alpha = 0.003\,56$ eV Å^{-1}, $T = 40$ K, are reported in figure 7 for a half-filled band (Fermi wavevector $k_F = \pi/2a$). We note excellent agreement between both results. With this system, the Kohn anomaly appears for the phonon $q = 2k_F$ at the first Brillouin zone boundary. Our result is in agreement with the theory. We also compute the dispersion curves with the help of the Lindhard function. This method does take into account the imaginary part of the phonon frequency. However, the results are in general agreement with those obtained by direct diagonalization or the moments method.

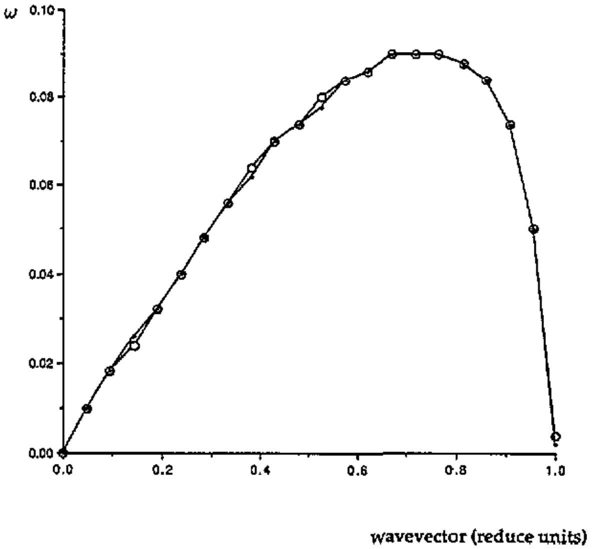

Figure 7. Dispersion curves obtained with a linear chain in the presence of electron–phonon coupling for a half-filled band ($T = 40$ K) with direct diagonalization (O) and by the moments method (·). The number of calculated coefficients a_n and b_n depends on the point of the Brillouin zone and varies from 4 to 35. Recall that the iterations stop when one coefficient b_n is lower than a given value.

6. Discussion and conclusion

The work presented here concerns the first step in developing a general computing method to evaluate physial properties of very large disordered systems with damping. In fact, the response function (12) is a bilinear combination of the Green functions of the system, and the problem involves determining these Green functions. To compute these functions directly, it is necessary first to determine the self-energy and then the Green function itself. Determination of the self-energy and response function requires the computation of all eigenvalues and eigenvectors of a general non-symmetric matrix, which is actually impossible in very large disordered systems. The same problem exists for harmonic materials and it is known that, in this case, research on solutions by developing the Green function in continued fractions is particularly well adapted: every step of the development represents an approximation of the genuine Green function. For instance, if we stop development of the continued fraction of the first order, the Green function obtained corresponds to an Einstein (one-body) material with a frequency that is a mean value of the frequencies of the real system. At the next step (second order), the Green function corresponds to a two-body system (for example, two interacting atoms in a well) with frequencies that are related to the entire real material and thus take the disorder into account. With 200 (or more) generalized moments, one obtains a 200-body (or more) Green function, which represents a very good approximation of the exact Green function of the whole system. It was thus very interesting to look for this type of solution for damped materials. However, to simplify the problem, in this first paper, we supposed that the self-energy is a known function.

Following the method developed in Benoit (1987), we introduced an auxiliary distribution function (72). We have shown that, on the one hand, the transform (73) of this function can be expanded in a continued fraction and, on the other, (72) is related to the response function. From a mathematical point of view, the positiveness of the Hankel determinants is connected to the existence of a d-dimensional distribution function. In this work, the auxiliary function (72) is a two-dimensional density function with complex weight and so the Hankel determinants, and then the coefficients b_n, can be negative. However, development in the continued fraction exists and is convergent. Note that a sufficient condition for the d-dimensional moments problem to be determined is that the series of power $-1/2n$ of the sum of the two-dimensional moments $\mu_{2n,0}$ and $\mu_{0,2n}$ goes to infinity (Shohat and Tamarkin (1963)). The distribution function (72) being bounded, it is clear that this condition is satisfied here.

The next step now concerns determination of the self energy (17) or (23) using the moments method. For anharmonic systems, evaluation of (17), without explicit determination of the eigenfrequencies and eigenvectors, is a very difficult problem. However, an approximate method developed for determination of second-order processes has been proposed in Benoit (1987) and could allow evaluation of (17). For systems with electron–phonon coupling, evaluation of (23) can be obtained by determination of the one-electron Green functions, using for instance the Kubo–Greenwood formula (Mayou 1988), which is easy with the moments method (Benoit *et al* 1992b). Finally, it is necessary, as for the usual moments method, to study in detail the behaviour of the infinite tail of the continued fraction in order to improve the convergence.

The method does not depend on the type of potential or structure of the material and so can be used to compute the response functions of any type of system, fractal, disordered,. . . , in d-dimensional space. The reported examples show that this method is a powerful tool.

Appendix

Let us define $|M\rangle$ such that, in the dipolar approximation,

$$\langle \alpha n \mid M\rangle = M_\alpha(n) = \sum_\beta \frac{q_{\alpha\beta}(n)}{m_n^{1/2}} \bar{u}_\alpha(n) \tag{A1}$$

and the total electric dipole moment is given by

$$M_\alpha = \sum_n M_\alpha(n) = \sum_n \langle \alpha n \mid M\rangle. \tag{A2}$$

With the help of (2), (A1) and the **Q** matrix, equation (11) can be written

$$|M(t)\rangle = \mathbf{Q}|X(t)\rangle. \tag{A3}$$

The solution of (28), with the help of (29) and (30), is given by

$$|X(t)\rangle = \beta \int \mathbf{G}(t-t')\mathbf{Q}|E(t')\rangle\, \mathrm{d}t'. \tag{A4}$$

From (A3) and (A4) we obtain

$$|M(t)\rangle = \mathbf{Q}|X(t)\rangle = \beta \int \mathbf{QG}(t-t')\mathbf{Q}|E(t')\rangle\, \mathrm{d}t'. \tag{A5}$$

From (A2) and (A5) we obtain

$$M_\alpha = \sum_n \langle \alpha n \mid M \rangle = \beta \int \sum_{\beta n n'} \langle \alpha n | \mathbf{QG}(t-t')\mathbf{Q} | \beta n' \rangle \langle \beta n' \mid E(t') \rangle \, \mathrm{d}t'$$

$$= \beta \sum_\beta \int \sum_{nn'} \langle \alpha n | \mathbf{QG}(t-t')\mathbf{Q} | \beta n' \rangle E_\beta(t') \, \mathrm{d}t' \qquad \text{(A6)}$$

and the susceptibility tensor being given by

$$|M(t)\rangle = \int \chi(t-t') |E(t')\rangle \, \mathrm{d}t' \qquad \text{(A7)}$$

from (A6) and (A7) we obtain

$$\chi_{\alpha\beta} = \beta \sum_{nn'} \langle \alpha n | \mathbf{QGQ} | \beta n' \rangle \qquad \text{(A8)}$$

identical to expression (12).

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