

Disorder-induced light scattering in solids: Microscopic theory and applications to some model systems

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A microscopic approach to evaluate the disorder-induced light scattering spectra in solids is presented. A quite general theory is developed and then specialized to some model systems that can represent an extended class of real systems. The general features of the disorder-induced spectra of real systems can be predicted, once the microscopic disorder and the mechanism responsible for the induced polarizability are correctly taken into account.

I. INTRODUCTION

For many years a great deal of theoretical and experimental work has been devoted to the study of disorder-induced light-scattering (DILS) spectra, i.e., of those spectral components that are absent in perfect crystals and become important to the spectra of all solids that show some kind of microscopic disorder. In fact, because of the disorder, the \mathbf{k} -conservation rule breaks down and each mode of the system can couple with the radiation field, giving rise to a broad spectrum.

In the harmonic approximation the intensity of the DILS component $I_{\alpha\beta}(\omega)$ has been generally related to the overall density of states $\rho(\omega)$ and to the Bose population factor $n(\omega)$ as follows:¹

$$I_{\alpha\beta}(\omega) \propto \frac{n(\omega) + 1}{\omega} C_{\alpha\beta}(\omega) \rho(\omega). \quad (1)$$

Here, a frequency-dependent coupling coefficient $C_{\alpha\beta}(\omega)$ has been introduced and the indexes α and β (running over x , y , and z) represent the polarization components of the scattered and incident electric fields. Equation (1) can be formally compared with the expression of the one-phonon incoherent neutron scattering spectrum, $I_{\text{inc}}(\omega)$, which, in a simple Bravais cubic lattice, reads²

$$I_{\text{inc}}(\omega) \propto \frac{n(\omega) + 1}{\omega} \rho(\omega). \quad (2)$$

In this expression the density of states is simply multiplied by the step-up factor $n(\omega) + 1$ and by the normalization of the harmonic propagator $1/\omega$, while in the light scattering case [Eq. (1)] the same quantities are also multiplied by a frequency-dependent coupling coefficient

$C_{\alpha\beta}(\omega)$, which measures how much the modes with frequencies close to ω are active in scattering light. $C_{\alpha\beta}(\omega)$ strongly determines the DILS spectral shape and, in general, it may be a rather complicated function of ω .

In the past years many works have been devoted to the theoretical determination of the coupling coefficient $C_{\alpha\beta}(\omega)$ in a variety of disordered solids.

The pioneering work on this subject was done by Whalley and was concerned with orientationally disordered crystals.³ He showed that the randomly oriented molecules generate an "electrical" disorder that is responsible for the observed broad depolarized spectra. Assuming perfect lattice vibrations and no correlation between the anisotropic polarizabilities of different molecules, he derived an ω^2 behavior for $C_{\alpha\beta}(\omega)$ along the entire acoustic branch.

Some years later Shuker and Gamon⁴ claimed that the DILS spectrum in amorphous solids could originate from the mode localization produced by structural disorder. As a matter of fact, in their work the presence of "electrical disorder" was completely ignored and the DILS spectrum was described just as a coherent spectrum somewhat broadened because of the mode localization.

In 1974 Martin and Brenig⁵ developed a model for light scattering in amorphous films. They described this system in terms of fluctuating elasto-optic coefficients and strain tensors, assuming that modes could be represented as distorted plane waves. They used an empirical Gaussian ansatz for the spatial decay of the fluctuations correlation function, thus obtaining

$$C_{\alpha\beta}(\omega) = \omega^2 (A_{\text{L}} e^{-\omega^2/2(c_{\text{L}}\bar{k})^2} + A_{\text{T}} e^{-\omega^2/2(c_{\text{T}}\bar{k})^2}). \quad (3)$$

They made a distinction between longitudinal and trans-

verse excitations, contributing to the DILS spectrum with different Raman activities A_L and A_T , respectively. At low frequencies ($\omega \ll c_T \bar{k}$) the ω^2 dependence of $C_{\alpha\beta}(\omega)$ they found agrees with the Whalley's results, while, due to the finite range $1/\bar{k}$ of the correlation function, two different cutoff frequencies appear in the spectrum which are related to the longitudinal and transverse sound velocities c_L and c_T , respectively.

In 1979 some of us used a microscopic model to deal with the light scattering from disordered systems consisting of anisotropic molecules.⁶ It was shown that while the usual Brillouin doublet is not influenced by the electrical disorder, the anisotropic spectrum is essentially governed by the single molecule dynamics. The spatial correlation function of the anisotropic part of the molecular polarizability (which was empirically assumed to have an exponential decay) cancels the contribution of the high wave-vector modes from the disordered Raman spectrum. In this model the origin of the DILS spectrum was attributed to the rototranslational coupling.

In 1981 we performed experiments and built up a theory in order to extract the translational phonon density of states from the Raman spectra of ice.^{7,8} The density of states spectral shape was reconstructed by using the depolarization ratios as measured in the three independent scattering configurations and was found to be in good agreement with lattice dynamics calculations and specific heat behavior.

In this paper we will begin by establishing a general formalism to deal with DILS spectra in harmonic solids, avoiding any *a priori* hypothesis on the dynamics of the systems and on the origin of disorder. The scattering equation so obtained will hold for many different kinds of disordered solids, and most of the existing results can be derived by specializing our equations to a chosen physical system. The calculation will be applied to simple models which can represent an extended class of systems and then analytically solved for a linear chain. An interesting result which in some way contradicts the theoretical prediction of Whalley will be derived and discussed.

II. BASIC THEORY

For solid systems, either ordered or not, a general formulation of the DILS scattering can be developed from a microscopic point of view. This is the most natural and powerful procedure for those systems where one or more kinds of scattering units, having much smaller dimension than the light wavelength, can be identified. The DILS spectrum appears when the effective polarizability tensors of such units do not have the translational symmetry of the lattice.

The instantaneous position of each unit of mass m_l is defined by the vector $\mathbf{R}^l(t)$:

$$\mathbf{R}^l(t) = \mathbf{x}^l + \mathbf{u}^l(t), \quad (4)$$

where \mathbf{x}^l is the equilibrium position and $\mathbf{u}^l(t)$ the displacement from equilibrium. In a solid system it is reasonable to assume the relation $\langle u^2 \rangle \ll a^2$, where a is the nearest-neighbors average distance. In the harmonic

approximation the Hamiltonian of such a system reads

$$H = \frac{1}{2} \sum_{l\alpha} \frac{(P_\alpha^l)^2}{m_l} + \frac{1}{2} \sum_{l\alpha} \sum_{l'\beta} \Phi_{\alpha\beta}(l'l) u_\alpha^l u_\beta^{l'}, \quad (5)$$

where $\mathbf{P}^l(t)$ is the momentum of the l th unit and $\Phi_{\alpha\beta}(l'l)$ are the force constants. Hamiltonian (5) can be diagonalized by writing

$$\mathbf{u}^l(t) = \left(\frac{\hbar}{2m_l} \right)^{1/2} \sum_p \frac{e(p|l)}{\sqrt{\omega_p}} \hat{A}_p(t), \quad (6)$$

where p is the mode index ($p = 1, 2, \dots, 3N - 6$), $\hat{A}_p(t)$ is the normal-mode field operator of eigenvalue ω_p and $e(p|l)$ represents the orthogonal set of eigenvectors.

The field operator is expressed in terms of boson creation $[\hat{a}_p^\dagger(t)]$ and annihilation $[\hat{a}_p(t)]$ operators as follows:

$$\hat{A}_p(t) = \hat{a}_p(0) e^{i\omega_p t} + \hat{a}_p^\dagger(0) e^{-i\omega_p t}. \quad (7)$$

The light-scattering spectral density $I(\mathbf{q}, \omega)$ (expressed in photon/sec for unit frequency) can be written in terms of the correlation function of the space Fourier transform of the macroscopic polarizability density tensor $P_{\alpha\beta}(\mathbf{r}, t)$ (Ref. 9)

$$\tilde{P}_{\alpha\beta}(\mathbf{q}, t) = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} P_{\alpha\beta}(\mathbf{r}, t) \quad (8)$$

and reads

$$I(\mathbf{q}, \omega) = \mathcal{A} \sum_{\alpha\beta\gamma\delta} \hat{m}_\alpha \hat{n}_\beta \hat{m}_\gamma \hat{n}_\delta I_{\alpha\beta\gamma\delta}(\mathbf{q}, \omega), \quad (9)$$

where

$$I_{\alpha\beta\gamma\delta}(\mathbf{q}, \omega) = \frac{1}{2\pi N} \int dt e^{i\omega t} \langle \tilde{P}_{\alpha\beta}(\mathbf{q}, t) \tilde{P}_{\gamma\delta}^*(\mathbf{q}, 0) \rangle \quad (10)$$

and

$$\mathcal{A} = J_i \rho V \frac{\omega_i \omega_s^3}{c^4} \Delta\Omega.$$

In Eq. (9) $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$ are the polarization unit vectors of the scattered and incoming radiation, ρ the number density, J_i the photon flux of the incident light, $\Delta\Omega$ the collected solid angle, and V the scattering volume. $\hbar\omega_i$ and $\hbar\omega_s$ are the energies of the incoming and the scattered photons, respectively; $\hbar\omega = \hbar\omega_i - \hbar\omega_s$, and $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$ are the exchanged energy and wave vector.

In atomic and/or molecular systems $\tilde{P}_{\alpha\beta}(\mathbf{q}, t)$ can be described microscopically in a general way by using the effective microscopic polarizability tensor $\pi_{\alpha\beta}^l(t)$.¹⁰ Following the procedure adopted in Ref. 11 we may write

$$\tilde{P}_{\alpha\beta}(\mathbf{q}, t) = \sum_l \pi_{\alpha\beta}^l(t) e^{-i\mathbf{q}\cdot\mathbf{R}^l(t)}. \quad (11)$$

In solid systems the time dependence of $\pi_{\alpha\beta}^l(t)$ can be well approximated by its first-order expansion in $\mathbf{u}^l(t)$

$$\pi_{\alpha\beta}^l(t) = \pi_{\alpha\beta}^l + \sum_{m\mu} V_{\alpha\beta,\mu}^{lm} u_\mu^m(t), \quad (12)$$

where both

$$\pi_{\alpha\beta}^l = [\pi_{\alpha\beta}^l(t)]_{\text{eq}} \quad (13)$$

and

$$V_{\alpha\beta,\mu}^{lm} = \left(\frac{\partial \pi_{\alpha\beta}^l(t)}{\partial u_{\mu}^m} \right)_{\text{eq}} \quad (14)$$

are relative to the equilibrium configuration of the system. The time dependence of $\tilde{P}_{\alpha\beta}(\mathbf{q}, t)$ can be obtained by using Eqs. (11) and (12) and the normal mode representation for $\mathbf{u}^l(t)$, i.e.,

$$\begin{aligned} \tilde{P}_{\alpha\beta}(\mathbf{q}, t) = & \sum_l \left(\frac{\hbar}{2m_l} \right)^{1/2} e^{-i\mathbf{q}\cdot\mathbf{x}^l} \\ & \times \sum_p \sum_{\mu} e_{\mu}(p|l) L_{\alpha\beta,\mu}^l(\mathbf{q}) \frac{\hat{A}_p(t)}{\sqrt{\omega_p}}, \end{aligned} \quad (15)$$

where

$$L_{\alpha\beta,\mu}^l(\mathbf{q}) = -iq_{\mu} \pi_{\alpha\beta}^l + Q_{\alpha\beta,\mu}^l(\mathbf{q}) \quad (16)$$

and

$$Q_{\alpha\beta,\mu}^l(\mathbf{q}) = \sum_m V_{\alpha\beta,\mu}^{ml} e^{-i\mathbf{q}\cdot[\mathbf{x}^m - \mathbf{x}^l]}. \quad (17)$$

Equation (15) shows that the local polarizability is modulated through a coupling amplitude $L_{\alpha\beta,\mu}^l(\mathbf{q})$ by the oscillation amplitude produced by mode p on the l unit [$e(p|l)/\sqrt{m_l}$].

Equation (15) is a good starting point for light-scattering calculations in all solid systems: its application to a monatomic perfect Bravais lattice is straightforward and somewhat useful for further steps. In fact, in this case, due to the total translational invariance of the lattice, the electrical quantity $L_{\alpha\beta,\mu}^l(\mathbf{q})$ is site independent since both $\pi_{\alpha\beta}^l$ and $Q_{\alpha\beta,\mu}^l(\mathbf{q})$ are site independent. Moreover, the normal modes are perfect plane waves with polarization unit vectors $\mathbf{e}(\mathbf{k}, \chi)$, where χ is the branch index and \mathbf{k} the wave vector of the normal mode (\mathbf{k}, χ) . The relation between the general eigenvector $\mathbf{e}(p|l)$ and $\mathbf{e}(\mathbf{k}, \chi)$ is therefore

$$\mathbf{e}(p|l) = \frac{\mathbf{e}(\mathbf{k}, \chi)}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{x}_l}. \quad (18)$$

It follows that, by replacing \sum_p with $\sum_{\mathbf{k}} \sum_{\chi}$ in Eq. (15), and considering that

$$\sum_l e^{-i(\mathbf{q}-\mathbf{k})\cdot\mathbf{x}^l} = N \Delta_{(\mathbf{k}-\mathbf{q})} \quad (19)$$

(here $\Delta_{\mathbf{k}} = 1$ if \mathbf{k} is zero or a reciprocal lattice vector, otherwise $\Delta_{\mathbf{k}} = 0$) we obtain

$$\tilde{P}_{\alpha\beta}(\mathbf{q}, t) = \left(\frac{N\hbar}{2m} \right)^{1/2} \sum_{\chi} \sum_{\mu} e_{\mu}(\mathbf{q}, \chi) L_{\alpha\beta,\mu}(\mathbf{q}) \frac{\hat{A}_{\mathbf{q}\chi}(t)}{\sqrt{\omega_{\chi}(\mathbf{q})}}. \quad (20)$$

Equation (20) states that the time dependence of $\tilde{P}_{\alpha\beta}(\mathbf{q}, t)$ is due only to those modes with $\mathbf{k} = \mathbf{q}$ (\mathbf{q} -conservation rule) belonging to any branch χ , for which the term $\mathbf{e}(\mathbf{q}, \chi) \cdot \mathbf{L}_{\alpha\beta}(\mathbf{q})$ does not vanish. This is the well-known result which gives the Brillouin spectrum: the intensity of the polarized longitudinal mode is essentially due to $q_{\mu} \pi_{\alpha\beta}$, while in the depolarized configurations, transverse and longitudinal intensities are governed by the $Q_{\alpha\beta,\mu}(\mathbf{q})$ term [see Eq. (16)].¹¹

On the other hand, as we have stressed, if some kind of electrical disorder exists the DILS spectrum appears, and all modes of the system contribute to it because the quantity $L_{\alpha\beta,\mu}^l(\mathbf{q})$ becomes site dependent. The whole spectrum will contain the Brillouin as well as the DILS contribution; however the first (which comes from the $\mathbf{k} = \mathbf{q}$ modes) is confined in the very-low-frequency range, while the second will extend on a very-large-frequency range (up to some hundred wave numbers) because of the contributions from all \mathbf{k} values.

In the following, disregarding the effect of the disorder in the Brillouin spectrum, we will calculate the DILS contribution from (10) and (15) just assuming $\mathbf{q} \simeq 0$, i.e., by taking the $\mathbf{q} = 0$ limit of $\tilde{P}_{\alpha\beta}(\mathbf{q}, t)$ in Eq. (10). As far as the scattering amplitude is concerned this is justified because only the local fluctuation of $L_{\alpha\beta,\mu}^l(\mathbf{q})$ will contribute to the DILS spectrum because of the small $|\mathbf{q}|$ value exchanged by radiation, so that only the $Q_{\alpha\beta,\mu}^l(0)$ term will be relevant in Eq. (16).

If the Hamiltonian of the crystal is independent on the electrical disorder, the dynamical variables $\hat{A}_{\mathbf{k}\chi}(t)$ and the equilibrium quantities $Q_{\alpha\beta,\mu}^l(0)$ are statistically independent. Furthermore, the translational invariance of the lattice ensures that the eigenvectors $\mathbf{e}(p|l)$ in Eq. (15) can be expressed through Eq. (18). Therefore, by substituting Eq. (18) into (15) we obtain

$$\begin{aligned} I_{\alpha\beta}(\omega) = & I_{\alpha\beta\alpha\beta}^{\text{DILS}}(\mathbf{0}, \omega) = \frac{\hbar}{2N^2 m} \sum_{\mathbf{k}\chi} \sum_{\mathbf{k}'\chi'} \sum_{l'l'} e^{i\mathbf{k}\cdot\mathbf{x}_l} e^{-i\mathbf{k}'\cdot\mathbf{x}_{l'}} \\ & \times \sum_{\mu\nu} \frac{e_{\mu}(\mathbf{k}, \chi) e_{\nu}^*(\mathbf{k}', \chi')}{\sqrt{\omega_{\chi}(\mathbf{k}) \omega_{\chi'}(\mathbf{k}')}} < Q_{\alpha\beta,\mu}^l(0) Q_{\alpha\beta,\nu}^{l'}(0) > \\ & \times \frac{1}{2\pi} \int dt e^{i\omega t} < \hat{A}_{\mathbf{k}\chi}(t) \hat{A}_{\mathbf{k}'\chi'}(0) >. \end{aligned} \quad (21)$$

Since for the Stokes side we have

$$\frac{1}{2\pi} \int dt e^{i\omega t} \langle \hat{A}_{\mathbf{k}\chi}(t) \hat{A}_{\mathbf{k}'\chi'}(0) \rangle = \Delta_{(\mathbf{k}-\mathbf{k}')\delta_{\chi\chi'}} [n(\omega) + 1] \delta(\omega - \omega_{\chi}(\mathbf{k}))$$

we get for the scattered intensity

$$I_{\alpha\beta}(\omega) = \frac{\hbar}{2m} \sum_{\mathbf{k}\chi} C_{\alpha\beta}(\mathbf{k}, \chi) \frac{n(\omega) + 1}{\omega} \delta(\omega - \omega_{\chi}(\mathbf{k})), \quad (22)$$

where

$$C_{\alpha\beta}(\mathbf{k}, \chi) = \frac{1}{N^2} \sum_{l'l''} e^{i\mathbf{k}\cdot(\mathbf{x}_l - \mathbf{x}_{l'})} \sum_{\mu\nu} e_{\mu}(\mathbf{k}, \chi) e_{\nu}^*(\mathbf{k}, \chi) \langle Q_{\alpha\beta,\mu}^l(0) Q_{\alpha\beta,\nu}^{l'}(0) \rangle. \quad (23)$$

Equation (22) is the same as Eq. (1) if

$$C_{\alpha\beta}(\omega) = \frac{\sum_{\mathbf{k}\chi} C_{\alpha\beta}(\mathbf{k}, \chi) \delta(\omega - \omega_{\chi}(\mathbf{k}))}{\sum_{\mathbf{k}\chi} \delta(\omega - \omega_{\chi}(\mathbf{k}))}. \quad (24)$$

We wish to stress that the procedure used to derive the scattered intensity [i.e., Eq. (22)] from Eqs. (10) and (15) is valid only if the electrical disorder does not influence the dynamical properties of the system. In other words, the obtained results will hold only for those media, if any, which are ordered from a mechanical point of view but electrically disordered. As a matter of fact this model can be a good approximation in describing the translational contribution of systems such as orientationally disordered crystals³ and some mixed crystals, while it becomes unrealistic for amorphous solids and glasses. The calculation of DILS spectra in the last classes of disordered media requires a different approach because both electrical and mechanical disorder, and their mutual correlation, need to be taken into account.¹²

III. MODEL SYSTEMS

In this section we will apply the relation introduced in the previous section to the calculation of both $C_{\alpha\beta}(\mathbf{k}, \chi)$ and $C_{\alpha\beta}(\omega)$ in the case of some simple systems. In order to proceed we need to know the explicit dependence of the effective molecular polarizability on the coordinates of all the molecules of the system.

In general a number of different mechanisms (like dipole induced dipole, overlap and exchange effects, dipole-quadrupole interaction, dispersion forces, bond polarizabilities, etc.,^{13,14}) can contribute to the induced polarizability in real systems. Among them, the dipole-induced-dipole (DID) mechanism is always present and it cannot be neglected being responsible, for example, for the Lorentz-Lorenz relation. Because all of the previously mentioned effects can be formally treated like DID,¹⁵ in the following we will restrict ourselves to the treatment

of the latter without any loss of generality.

In the short-range approximation of DID,^{16,17} the effective atomic polarizability tensor for the i th scattering unit, $\pi_{\alpha\beta}^i$, can be expressed in terms of its bare polarizability $p_{\alpha\beta}^i$ as follows:

$$\pi_{\alpha\beta}^i(t) = p_{\alpha\beta}^i + \sum_{j \neq i} \sum_{\gamma\delta} p_{\alpha\gamma}^i T_{\gamma\delta}^{(2)}(\mathbf{R}^{ij}(t)) p_{\delta\beta}^j, \quad (25)$$

where $T_{\alpha\beta}^{(2)}(\mathbf{r})$ is the short-range dipole propagator:

$$T_{\alpha\beta}^{(2)}(\mathbf{r}) = \nabla_{\alpha} \nabla_{\beta} \frac{1}{|\mathbf{r}|} = \frac{[3\hat{r}_{\alpha}\hat{r}_{\beta} - \delta_{\alpha\beta}]}{|\mathbf{r}|^3} \quad (26)$$

and $\mathbf{R}^{ij}(t) = \mathbf{R}^i(t) - \mathbf{R}^j(t)$. We wish to stress that for the model system we want to treat, the DILS spectrum will be entirely due to the derivatives of the induced term [the second term in Eq. (25)]; these are site dependent even in a mechanically perfect lattice if the bare polarizabilities of the units are disordered (electrical disorder). As a consequence, the quantity $Q_{\alpha\beta\mu}^i(0)$ will be nonzero and site dependent, and can be explicitly evaluated together with its correlation function.

A. Disordered cubic lattice of isotropic units

For the sake of simplicity and without loss of generality, in the following we will consider a monatomic cubic Bravais lattice with harmonic interaction potentials.¹⁸ The electrical disorder is produced by randomly assigning to each atom a different isotropic, pointlike polarizability α^i , i.e., $p_{\alpha\beta}^i = \alpha^i \delta_{\alpha\beta}$. From a mathematical point of view the polarizability α^i is a random, spatially uncorrelated variable with a site-dependent single-site probability distribution $P(\alpha^i)$. The assumed lack of correlation among the polarizability values at different sites implies that the n -site joint probability distribution is given by

$$P^{(n)}(\alpha^1, \alpha^2, \dots, \alpha^n) = \prod_{k=1}^n P(\alpha^k). \quad (27)$$

Using Eqs. (14), (17), and (25), Eq. (23) becomes

$$C_{\alpha\beta}(\mathbf{k}, \chi) = \frac{1}{N^2} \sum_{ij} \sum_{l \neq i} \sum_{m \neq j} (\langle \alpha^i \alpha^j \alpha^l \alpha^m \rangle - \langle \alpha \rangle^4) \times \sum_{\gamma} T_{\alpha\beta\gamma}^{(3)}(\mathbf{x}^{il}) e_{\gamma}(\mathbf{k}, \chi) (e^{i\mathbf{k}\cdot\mathbf{x}^l} - e^{i\mathbf{k}\cdot\mathbf{x}^i}) \sum_{\gamma} T_{\alpha\beta\gamma}^{(3)}(\mathbf{x}^{jm}) e_{\gamma}^*(\mathbf{k}, \chi) (e^{i\mathbf{k}\cdot\mathbf{x}^m} - e^{i\mathbf{k}\cdot\mathbf{x}^j})^*, \quad (28)$$

where $T_{\alpha\beta\gamma}^{(3)}(\mathbf{x}^i) = -[\nabla_\alpha \nabla_\beta \nabla_\gamma (1/|\mathbf{r}|)]$.

The explicit evaluation of the configurational average $\langle \alpha^i \alpha^j \alpha^l \alpha^m \rangle$ yields (see Appendix A)

$$\begin{aligned} \langle \alpha^i \alpha^j \alpha^l \alpha^m \rangle &= (M_1)^4 + (M_1)^2 [M_2 - (M_1)^2] \\ &\quad \times (\delta_{ij} + \delta_{im} + \delta_{jl} + \delta_{lm}) \\ &\quad + [M_2 - (M_1)^2]^2 (\delta_{ij} \delta_{lm} + \delta_{im} \delta_{jl}), \end{aligned} \quad (29)$$

where M_n are the moments of the single-site probability distribution function:

$$M_n = \int_0^\infty (\alpha)^n P(\alpha) d\alpha. \quad (30)$$

Inserting Eq. (29) into (28) we have

$$\begin{aligned} C_{\alpha\beta}(\mathbf{k}, \chi) &= \frac{1}{N} [M_2 - (M_1)^2]^2 g_{\alpha\beta}(\mathbf{k}, \chi) \\ &\quad + \frac{1}{N} (M_1)^2 [M_2 - (M_1)^2] f_{\alpha\beta}(\mathbf{k}, \chi) \end{aligned} \quad (31)$$

with

$$g_{\alpha\beta}(\mathbf{k}, \chi) = 8 \sum_i \sin^2 \left(\frac{\mathbf{k} \cdot \mathbf{x}^i}{2} \right) \left(\sum_\gamma T_{\alpha\beta\gamma}^{(3)}(\mathbf{x}^i) e_\gamma(\mathbf{k}, \chi) \right)^2, \quad (32)$$

$$f_{\alpha\beta}(\mathbf{k}, \chi) = 4 \left(\sum_i \sin(\mathbf{k} \cdot \mathbf{x}^i) \sum_\gamma T_{\alpha\beta\gamma}^{(3)}(\mathbf{x}^i) e_\gamma(\mathbf{k}, \chi) \right)^2. \quad (33)$$

Note that the phonon-radiation coupling coefficient naturally splits into two terms, the first of which is proportional to the square of the variance of the polarizability distribution ($M_2 - (M_1)^2$), while the second to the variance itself multiplied by the squared mean polarizability (M_1^2). As expected, $C_{\alpha\beta}(\mathbf{k}, \chi)$ vanishes for electrically ordered systems [i.e., $M_2 = (M_1)^2$].

It is worth noting that the two terms appearing in $C_{\alpha\beta}(\mathbf{k}, \chi)$ have a different \mathbf{k} dependence. Actually while

both are proportional to $|\mathbf{k}|^2$ near the Brillouin zone center, they behave differently when \mathbf{k} approaches the zone boundary. A first idea of the ω dependence of these two terms in the high- $|\mathbf{k}|$ region can be had by taking into account only the effect of the nearest-neighbor atoms in the sums of Eqs. (32) and (33). In this approximation, because of the different periodicity of the argument of the sine, $g_{\alpha\beta}(\mathbf{k}, \chi)$ attains its maximum value at zone boundary where $f_{\alpha\beta}(\mathbf{k}, \chi)$ is expected to have a minimum. Therefore the ω behavior produced by $f_{\alpha\beta}(\mathbf{k}, \chi)$ will show a cutoff frequency.

In order to evidence the relevance of the results obtained we will first restrict ourselves to a one-dimensional system.

1. Analytic results for a linear chain of disordered isotropic units

In the case of a linear chain with only nearest-neighbor longitudinal interaction (force constant Φ), the radiation-phonon coupling coefficient $\mathcal{C}(\omega)$ can be analytically evaluated as a function of phonon frequency.

The eigenvalues of such a system are

$$\omega^2(k) = \omega_0^2 \sin^2 \left(\frac{ka}{2} \right), \quad (34)$$

where $\omega_0 = 2(\Phi/m)^{1/2}$, and a is the nearest-neighbor distance. Phonons are always polarized along the chain, like the incident and scattered electric field that we choose. From Eqs. (32) and (33) and taking into account only the DID contribution coming from the nearest neighbor, we obtain

$$f(k) = \frac{9}{4} \left(\frac{2}{a} \right)^8 \sin^2(ka), \quad (35)$$

$$g(k) = \frac{9}{4} \left(\frac{2}{a} \right)^8 \sin^2 \left(\frac{ka}{2} \right), \quad (36)$$

and therefore

$$C(k) = \left(\frac{2}{a} \right)^8 \frac{9}{4N} (M_2 - (M_1)^2) \left[(M_1)^2 \sin^2(ka) + (M_2 - (M_1)^2) \sin^2 \left(\frac{ka}{2} \right) \right]. \quad (37)$$

From Eq. (34) it is easy to get

$$\sin^2 \left(\frac{ka}{2} \right) = \left(\frac{\omega(k)}{\omega_0} \right)^2, \quad (38)$$

$$\sin^2(ka) = 4 \left(\frac{\omega(k)}{\omega_0} \right)^2 \left[1 - \left(\frac{\omega(k)}{\omega_0} \right)^2 \right]. \quad (39)$$

Therefore we obtain

$$g(k) = \frac{9}{4} \left(\frac{2}{a} \right)^8 \left(\frac{\omega(k)}{\omega_0} \right)^2 \quad (40)$$

and

$$f(k) = 9 \left(\frac{2}{a} \right)^8 \left[1 - \left(\frac{\omega(k)}{\omega_0} \right)^2 \right] \left(\frac{\omega(k)}{\omega_0} \right)^2. \quad (41)$$

Finally, $\mathcal{C}_{\alpha\beta}(\omega)$ is given by

$$\begin{aligned} C_{\alpha\beta}(\omega) &= \left(\frac{2}{a} \right)^8 \frac{27}{2N} [M_2 - (M_1)^2] \\ &\quad \times \left\{ (M_1)^2 \left(\frac{2\omega}{\omega_0} \right)^2 \left[1 - \left(\frac{\omega}{\omega_0} \right)^2 \right] \right. \\ &\quad \left. + (M_2 - (M_1)^2) \left(\frac{\omega}{\omega_0} \right)^2 \right\}. \end{aligned} \quad (42)$$

In this equation the disorder of the polarizability is completely accounted for by (M_1) and $[M_2 - (M_1)^2]$, which represent the mean value of the polarizability and the mean-squared polarizability fluctuation, respectively. Thus Eq. (42) states that the ω behavior of the phonon-radiation coupling depends on the ratio between $(M_1)^2$ and $[M_2 - (M_1)^2]$.

It is interesting to consider the particular case of a system where only two atomic species of polarizabilities α_A and α_B are present. Assuming x to be the concentration of species A , the single-site probability distribution for the polarizability may be written as

$$P(\alpha) = x\delta(\alpha - \alpha_A) + (1 - x)\delta(\alpha - \alpha_B), \quad (43)$$

and defining

$$\bar{\alpha} = \frac{\alpha_A + \alpha_B}{2} \quad (44)$$

and

$$\Delta\alpha = \frac{\alpha_A - \alpha_B}{2} \quad (45)$$

we obtain

$$M_1 = \bar{\alpha} + (2x - 1)\Delta\alpha \quad (46)$$

and

$$M_2 - (M_1)^2 = 4x(1 - x)(\Delta\alpha)^2. \quad (47)$$

The maximum contribution to the spectrum due to the polarizability fluctuation is then reached for $x=0.5$, where

$$\frac{(M_1)^2}{M_2 - (M_1)^2} \Big|_{\max} = \left(\frac{\bar{\alpha}}{\Delta\alpha} \right)^2. \quad (48)$$

For some real mixed crystals (i.e., those for which the two different species can be reasonably treated from a dynamical point of view as an average particle¹⁹) this ratio largely exceeds unity ($\alpha_A \simeq \alpha_B$). The behavior of $\mathcal{C}(\omega)$ is therefore dominated by the term which cuts the density of states in the high-frequency range.

2. Numerical results for a three-dimensional lattice

Since an analytical solution is impossible for the three-dimensional simple cubic case, we carried out a numerical computation for both $f_{\alpha\beta}(\omega)$ and $g_{\alpha\beta}(\omega)$ [whose definition in term of $f_{\alpha\beta}(\mathbf{k}, \chi)$ and $g_{\alpha\beta}(\mathbf{k}, \chi)$ is obvious, see Eq. (24)] in a perfect lattice with disordered isotropic polarizabilities. The calculation was performed by introducing only first neighbor stretching and bending force constants, with a strength ratio of 3. A grid of about 3×10^4 points was used for sampling the irreducible part of the Brillouin zone which, for the light-scattering problem we are considering, is $\frac{1}{8}$ of the full zone. For each \mathbf{k} value, both eigenfrequencies and eigenvectors were calculated and subsequently used to evaluate the scattering coefficients in Eqs. (32) and (33). In Fig. 1 the overall density of states $\rho(\omega)$ is shown, while in Figs. 2 and 3 we report the functions $g_{\alpha\beta}(\omega)$ and $f_{\alpha\beta}(\omega)$, respectively,

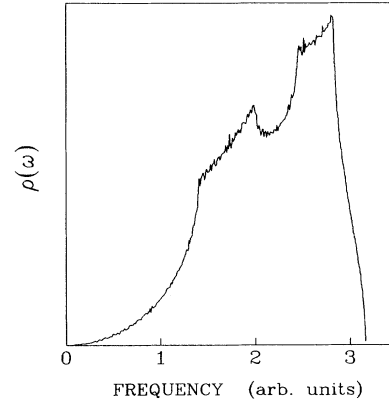


FIG. 1. Vibrational density of states for a simple cubic lattice.

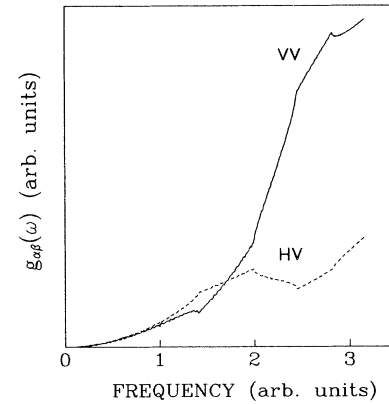


FIG. 2. $g_{\alpha\beta}(\omega)$ (see text) in two different scattering configurations. Solid line: polarized configuration (VV). Broken line: depolarized configuration (HV).

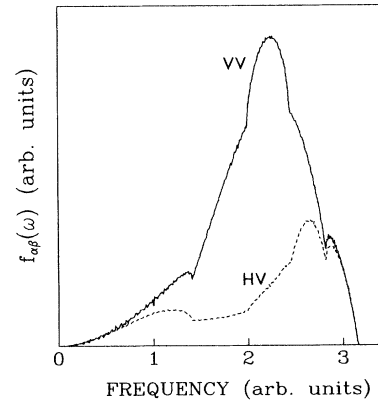


FIG. 3. $f_{\alpha\beta}(\omega)$ (see text) in two different scattering configurations. Solid line: polarized configuration (VV). Broken line: depolarized configuration (HV).

in both polarized (VV) and depolarized (HV) scattering configurations. Once the first and the second moments M_1 and M_2 of the polarizability distribution are known, the Raman scattering coefficient $C_{\alpha\beta}(\mathbf{k}, \chi)$ can be completely reconstructed following Eq. (31). In our calculation the DID contribution was truncated to the second coordination shell; in fact, since the $T_{\alpha\beta\gamma}^{(3)}(\mathbf{r})$ tensor rapidly decays with increasing the interatomic distance, the contributions from more distant atoms are completely negligible. The difference in shape between $f_{\alpha\beta}(\omega)$ and $g_{\alpha\beta}(\omega)$, as well as their ω dependence for different scattering configurations, clearly show that neither the spectral shapes nor the depolarization ratios as a function of fre-

quency can be predicted if the details of the microscopic mechanism involved in the polarizability modulation are unknown.

B. Orientationally disordered crystals

For orientationally disordered crystals the electrical disorder is due to the random orientation of anisotropic molecules. Therefore in our model we assign to each site of the perfect lattice an anisotropic polarizability tensor $p_{\alpha\beta}^i$ which is randomly oriented in space. The Raman coupling coefficient may be written as

$$C_{\alpha\beta}(\mathbf{k}\chi) = \frac{1}{N^2} \sum_{ij} \sum_{m \neq i} \sum_{l \neq j} \sum_{\mu\nu} \sum_{\mu'\nu'} \langle p_{\alpha\mu}^i p_{\beta\nu}^m p_{\alpha\mu'}^j p_{\beta\nu'}^l \rangle - \langle p_{\alpha\beta} \rangle^4 \delta_{\alpha\mu} \delta_{\beta\nu} \delta_{\alpha\mu'} \delta_{\beta\nu'} \\ \times \sum_{\gamma} T_{\mu\nu\gamma}^{(3)}(\mathbf{x}^{im}) e_{\gamma}(\mathbf{k}, \chi) (e^{i\mathbf{k}\cdot\mathbf{x}_m} - e^{i\mathbf{k}\cdot\mathbf{x}_i}) \sum_{\gamma} T_{\mu'\nu'\gamma}^{(3)}(\mathbf{x}^{jl}) e_{\gamma}(\mathbf{k}, \chi) (e^{-i\mathbf{k}\cdot\mathbf{x}_l} - e^{-i\mathbf{k}\cdot\mathbf{x}_j}). \quad (49)$$

Taking for simplicity a symmetric-top molecule, the bare polarizability tensor may be written as

$$p_{\alpha\beta}^i = \alpha \delta_{\alpha\beta} + \beta \hat{y}_{\alpha\beta}^i = \alpha \delta_{\alpha\beta} + \beta (\hat{y}_{\alpha}^i \hat{y}_{\beta}^i - \frac{1}{3} \delta_{\alpha\beta}), \quad (50)$$

where \hat{y}^i is the unit vector parallel to the symmetry axis of the i th molecule, and α and β are the isotropic and anisotropic parts of the polarizability, respectively. Considering that only the terms with $m \neq i$ and $l \neq j$ contribute to the sums appearing in the expression for $C_{\alpha\beta}(\mathbf{k}, \chi)$, and that for fully uncorrelated molecular orientations the relation

$$\langle \beta_{\alpha\beta}^m \beta_{\gamma\delta}^l \rangle = \delta_{ml} \langle \beta_{\alpha\beta} \beta_{\gamma\delta} \rangle \quad (51)$$

holds, we obtain

$$\langle p_{\alpha\mu}^i p_{\beta\nu}^m p_{\alpha\mu'}^j p_{\beta\nu'}^l \rangle - \langle p_{\alpha\beta} \rangle^4 \delta_{\alpha\mu} \delta_{\beta\nu} \delta_{\alpha\mu'} \delta_{\beta\nu'} \\ = \langle (\alpha \delta_{\alpha\mu} + \beta_{\alpha\mu}^i) (\alpha \delta_{\beta\nu} + \beta_{\beta\nu}^m) (\alpha \delta_{\alpha\mu'} + \beta_{\alpha\mu'}^j) (\alpha \delta_{\beta\nu'} + \beta_{\beta\nu'}^l) \rangle - \alpha^4 \delta_{\alpha\mu} \delta_{\beta\nu} \delta_{\alpha\mu'} \delta_{\beta\nu'} \\ = \alpha^2 \delta_{\alpha\mu} \delta_{\alpha\mu'} \delta_{ml} \langle \beta_{\beta\nu} \beta_{\beta\nu'} \rangle + \alpha^2 \delta_{\beta\nu} \delta_{\beta\nu'} \delta_{ij} \langle \beta_{\alpha\mu} \beta_{\alpha\mu'} \rangle \\ + \alpha^2 \delta_{\beta\nu} \delta_{\alpha\mu'} \delta_{il} \langle \beta_{\alpha\mu} \beta_{\beta\nu'} \rangle + \alpha^2 \delta_{\alpha\mu} \delta_{\beta\nu'} \delta_{mj} \langle \beta_{\beta\nu} \beta_{\alpha\mu'} \rangle \\ + \delta_{ij} \delta_{ml} \langle \beta_{\alpha\mu} \beta_{\alpha\mu'} \rangle \langle \beta_{\beta\nu} \beta_{\beta\nu'} \rangle + \delta_{il} \delta_{jm} \langle \beta_{\alpha\mu} \beta_{\beta\nu'} \rangle \langle \beta_{\beta\nu} \beta_{\alpha\mu'} \rangle. \quad (52)$$

In terms of the molecular anisotropy we have

$$\langle \beta_{\alpha\beta} \beta_{\gamma\delta} \rangle = \frac{\beta^2}{45} [3(\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) - 2\delta_{\alpha\beta} \delta_{\alpha\gamma} \delta_{\beta\delta}] \quad (53)$$

thus obtaining

$$C_{\alpha\beta}(\mathbf{k}, \chi) = \frac{1}{N} \frac{\beta^4}{(45)^2} g'_{\alpha\beta}(\mathbf{k}, \chi) + \frac{1}{N} \frac{\alpha^2 \beta^2}{45} f'_{\alpha\beta}(\mathbf{k}, \chi), \quad (54)$$

where

$$f'_{\alpha\beta}(\mathbf{k}, \chi) = (1 - 2\delta_{\alpha\beta}) f_{\alpha\beta}(\mathbf{k}, \chi) + 3\sqrt{f_{\alpha\alpha}(\mathbf{k}, \chi) f_{\beta\beta}(\mathbf{k}, \chi)} \\ + \frac{3}{2}(1 + \delta_{\alpha\beta}) \sum_{\gamma} [f_{\alpha\gamma}(\mathbf{k}, \chi) + f_{\beta\gamma}(\mathbf{k}, \chi)], \quad (55)$$

$$g'_{\alpha\beta}(\mathbf{k}, \chi) = (5 - 4\delta_{\alpha\beta}) g_{\alpha\beta}(\mathbf{k}, \chi) + \frac{3}{2}(1 + \delta_{\alpha\beta}) \\ \times \sum_{\gamma} [g_{\alpha\gamma}(\mathbf{k}, \chi) + g_{\beta\gamma}(\mathbf{k}, \chi)] \\ + \frac{3}{2}(1 + \delta_{\alpha\beta}) \sum_{\gamma\delta} g_{\gamma\delta}(\mathbf{k}, \chi), \quad (56)$$

and the functions $f_{\alpha\beta}(\mathbf{k}, \chi)$ and $g_{\alpha\beta}(\mathbf{k}, \chi)$ are defined in

Eqs. (32) and (33).

Note that in this case also the phonon-radiation coupling coefficient splits into two terms, whose \mathbf{k} dependence is the same as for disordered crystals of isotropic molecules. The tensorial character of the polarizability for anisotropic molecules produces a complicated tensorial expression for $f'_{\alpha\beta}(\mathbf{k}, \chi)$ and $g'_{\alpha\beta}(\mathbf{k}, \chi)$, but their weight in the spectrum will be again given by

$$[M_2 - (M_1)^2]^2 = \frac{\beta^4}{(45)^2} \quad (57)$$

and

$$(M_1)^2[M_2 - (M_1)^2] = \frac{\alpha^2\beta^2}{45}. \quad (58)$$

The relative weight of the two terms will be therefore related to the ratio

$$\frac{(M_1)^2}{M_2 - (M_1)^2} = 45 \left(\frac{\alpha}{\beta} \right)^2. \quad (59)$$

Since usually $\alpha > \beta$, the main contribution to the spectrum is expected to come from $f'_{\alpha\beta}(\mathbf{k}, \chi)$ in the case of orientationally disordered systems as well.

IV. SUMMARY AND CONCLUSIONS

In this paper we have shown that the mode-radiation coupling coefficient for DILS spectra can be successfully evaluated (without any empirical ansatz) once a microscopic approach to the phenomenon is adopted.

The DILS contribution has been written in terms of the induced molecular polarizability derivatives, i.e., quantities which can be site dependent even in topologically perfect crystals because of the irregularity of some electrical variables. In particular we have calculated the DID contribution to the DILS spectra of a perfect lattice consisting of scattering units bearing a random polarizability. We have assumed that the polarizabilities of different sites are completely uncorrelated and that this electrical disorder does not influence the dynamics of the crystal. We have found that under these hypotheses the coupling coefficient $C_{\alpha\beta}(\mathbf{k}, \chi)$ strongly depends on the polarizability distribution.

A general expression for $C_{\alpha\beta}(\mathbf{k}, \chi)$ has been obtained for two kind of polarizability, i.e., (i) a perfect lattice consisting of isotropic scatterers randomly distributed on the sites and (ii) a perfect lattice consisting of identical anisotropic molecules randomly oriented in their equilibrium configurations.

In both cases $C_{\alpha\beta}(\mathbf{k}, \chi)$ turns out to be a linear combination of two functions which are very different in the high- $|\mathbf{k}|$ region. We have shown that the relative weights of these two terms depend on the square of the ratio between the average polarizability and its fluctuation. Therefore the coupling coefficients for a given (\mathbf{k}, χ) mode can be determined only if the details of the polarizability distribution are known.

The evaluation of the frequency-dependent coefficient has been analytically performed for a linear chain. For a three-dimensional simple cubic crystal consisting of

isotropic scatterers the calculation has been performed numerically.

In the case of a one-dimensional lattice, Whalley's result³ for orientationally disordered crystals [i.e., $C_{\alpha\beta}(\omega) \propto \omega^2$] has been recovered in the limit of small isotropic polarizabilities ($\alpha \ll \beta$) which, nevertheless, is unrealistic for an extended class of molecular solids. If, on the contrary, $\alpha \gg \beta$ the behavior of $C_{\alpha\beta}(\omega)$ deviates from Whalley's result because the contribution from the high-frequency modes rapidly drops to zero.

In the case of isotropic disorder the two different behaviors (previously obtained for $\alpha \ll \beta$ and $\beta \ll \alpha$) can be achieved assuming $\bar{\alpha} \ll \Delta\alpha$ or $\bar{\alpha} \gg \Delta\alpha$, respectively.

We want to stress again that for real systems $\alpha \gg \beta$ (or $\bar{\alpha} \gg \Delta\alpha$) is the most common case, and that therefore a falling down of $C_{\alpha\beta}(\omega)$ at high ω may be expected. This behavior is similar to that found by Martin and Brenig⁵ by introducing a finite correlation length for the fluctuating quantities. It is worth stressing that the drop of the high-frequency part of the DILS spectra has been obtained here without introducing any correlation between the disordered electrical variables. In other words, the high-frequency shape of DILS spectra changes just changing by the ratio $(M_1)^2/M_2$, even if the microscopic variable involved is completely uncorrelated.

This result is not produced by the particular induction mechanism we are considering, but rather from the general structure of the induced term, which is a multi-particle property and depends (assuming pairwise additivity) on the relative position of all pairs of molecules. As a consequence, the correlation function appearing in the general expression of $C_{\alpha\beta}(\mathbf{k}, \chi)$ has a nonzero spatial correlation length even in the absence of any microscopic correlation. In the DID theory this is mathematically expressed by the presence of a four-site polarizability correlation function in Eqs. (28) and (51).

It follows that even in simple physical systems (like those we have treated in this paper) one has to be very careful in extracting information on the correlation properties of microscopic quantities (as, for example, molecular orientations) from the DILS spectral shape.

APPENDIX A: EVALUATION OF $\langle \alpha^i \alpha^j \alpha^l \alpha^m \rangle$

In order to evaluate $\langle \alpha^1 \alpha^2 \alpha^3 \alpha^4 \rangle$ the following properties of the single-site probability distribution have to be taken into account:

$$\int P(\alpha) d\alpha = 1, \quad P(\alpha^1, \alpha^2, \dots, \alpha^n) = \prod_{k=1}^n P(\alpha^k).$$

Further we have defined the n th moment of the single-site probability distribution as

$$M_n = \int_0^\infty (\alpha)^n P(\alpha) d\alpha.$$

Therefore the configurational average $\langle \alpha^1 \alpha^2 \alpha^3 \alpha^4 \rangle$ may be written as

$$\begin{aligned}
\langle \alpha^1 \alpha^2 \alpha^3 \alpha^4 \rangle = & (M_1)^4 (1 - \delta_{12})(1 - \delta_{13})(1 - \delta_{14})(1 - \delta_{23})(1 - \delta_{24})(1 - \delta_{34}) \\
& + (M_1)^2 M_2 [\delta_{12}(1 - \delta_{13})(1 - \delta_{14})(1 - \delta_{34}) + \delta_{13}(1 - \delta_{12})(1 - \delta_{14})(1 - \delta_{24}) \\
& + \delta_{14}(1 - \delta_{12})(1 - \delta_{13})(1 - \delta_{23}) + \delta_{23}(1 - \delta_{21})(1 - \delta_{24})(1 - \delta_{14}) \\
& + \delta_{24}(1 - \delta_{21})(1 - \delta_{23})(1 - \delta_{13}) + \delta_{34}(1 - \delta_{31})(1 - \delta_{32})(1 - \delta_{12})] \\
& + M_1 M_3 [\delta_{12} \delta_{13}(1 - \delta_{14}) + \delta_{12} \delta_{14}(1 - \delta_{13}) + \delta_{13} \delta_{14}(1 - \delta_{12}) + \delta_{23} \delta_{24}(1 - \delta_{12})] \\
& + (M_2)^2 [\delta_{12} \delta_{34}(1 - \delta_{13}) + \delta_{13} \delta_{24}(1 - \delta_{12}) + \delta_{14} \delta_{23}(1 - \delta_{12})] + M_4 \delta_{12} \delta_{13} \delta_{14} .
\end{aligned}$$

Remembering that in Eq. (28) only the terms with $i \neq l$ and $j \neq m$ will contribute, this reduces to

$$\begin{aligned}
\langle \alpha^1 \alpha^2 \alpha^3 \alpha^4 \rangle = & (M_1)^4 (1 - \delta_{12})(1 - \delta_{14})(1 - \delta_{23})(1 - \delta_{34}) \\
& + (M_1)^2 M_2 [\delta_{12}(1 - \delta_{14})(1 - \delta_{34}) + \delta_{14}(1 - \delta_{12})(1 - \delta_{23}) \\
& + \delta_{23}(1 - \delta_{12})(1 - \delta_{14}) + \delta_{34}(1 - \delta_{23})(1 - \delta_{12})] + (M_2)^2 (\delta_{12} \delta_{34} + \delta_{14} \delta_{23})
\end{aligned}$$

and finally trivial algebra yields

$$\langle \alpha^1 \alpha^2 \alpha^3 \alpha^4 \rangle = (M_1)^4 + (M_1)^2 [M_2 - (M_1)^2] (\delta_{12} + \delta_{14} + \delta_{23} + \delta_{34}) + [(M_1)^2 - M_2]^2 (\delta_{12} \delta_{34} + \delta_{14} \delta_{23}) .$$

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