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TO-LO splittings of glassy dielectrics

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The dielectric function of a glassy dielectric is shown to be expressed in terms of the local density of states and the average of the squared polarization vector. In this expression the Coulomb interaction between arbitrary distant points are taken into account through what we call the dipole approximation. We propose an effective Hamiltonian in which the long-wavelength optic modes are separated from the other vibrational modes, and from which we gain insight into the nature of TO and LO vibrational modes in glassy dielectrics.

I. INTRODUCTION

In 1976, Galeener and Lucovsky[1] experimentally showed that in glasses such as vitreous silica ($v-SiO_2$) or $v-GeO_2$, it is necessary to take account of the long-range Coulomb interaction for the explanation of the Raman-scattering data of those materials. They assigned the unexplained peaks in the Raman spectra as either transverse optic (TO) or longitudinal optic (LO) by comparing them with the peaks of ϵ_2 and $\mathrm{Im}(-1/\epsilon)$ ($\epsilon=\epsilon_1+i\epsilon_2$ is the dielectric constant) which were obtained from infrared (ir) reflection spectra of the same materials.

Since in these experiments the wavelength of the external electric field is much larger than the characteristic interatomic distance, we should treat the very large system in order to take account of the Coulomb interaction properly. Therefore it was a difficult problem to calculate, for instance, the ir response from the microscopic model of glassy dielectrics including the Coulomb interaction even in an approximate way. As far as we know, the only relevant attempt has been made by Pick and Yvinec[2] in the molecular dynamics method for a model of molecular glass.

In this paper we establish a connection between the dielectric properties of the isolated small part of the glassy system (that is, the part whose scale is much smaller than the wavelength of the external field considered) and the dielectric function $\epsilon(\Omega)$ of the whole infinite system. In doing so, the Coulomb interaction between arbitrary distant points is taken into account in an approximate way, and from the expression for $\epsilon(\Omega)$ we find a way to estimate the magnitude of the TO-LO splitting of the infinite system in terms of the data of small systems.

In Sec. II we give the model vibrational Hamiltonian of the infinite glassy system, from which we derive the expression for the dielectric function $\epsilon(\Omega)$. This procedure is in some respects an extension of Lines's[3] ideas on ferroelectric glasses into the dynamical case in the paraelectric phase.

Next in Sec. III we propose another method to get the same expression of $\epsilon(\Omega)$ by approximating the model Hamiltonian itself and transcribing it into what we may call the effective Hamiltonian for the long-wavelength modes. The form of this effective Hamiltonian leads us to consider the more general question as to the nature of optical vibrations in glassy dielectrics, which is the subject to be discussed in Sec. IV.

II. MODEL HAMILTONIAN AND THE DIELECTRIC FUNCTION

To begin with we consider instead of the infinite bulk system an isolated cube of glassy dielectrics of size $L\times L\times L$. The vibrational Hamiltonian of the system under the external field $\vec{E}^{(0)}$ is written in terms of their normal modes within the harmonic approximation as

$$H^{(0)}=\sum_f(\tfrac{1}{2}P_f^2+\tfrac{1}{2}\omega_f^2Q_f^2)-\sum_f\vec{p}_fQ_f\cdot\vec{E}^{(0)}\,, \quad (1)$$

where $\vec{p}_f$ is the electric dipole moment of the cube produced by the unit displacement of the mode f. The polarizability $\overleftrightarrow{\alpha}^{(0)}$ of this cube can be defined as

$$\vec{p}=\overleftrightarrow{\alpha}^{(0)}(\Omega)\cdot\vec{E}^{(0)} \quad (2)$$

through the relation between the total dipole moment $\vec{p}$ of the cube and the external field, both of which are assumed to vary with time as

$\exp(-i\Omega t)$. From Eq. (1) this polarizability can be expressed in the following form:

$$\overleftrightarrow{\alpha}^{(0)}(\Omega)=\sum_f \frac{\vec{p}_f\vec{p}_f}{\omega_f^2-\Omega^2} \ . \tag{3}$$

If $L \gg a$ which we assume hereafter (a being a characteristic interatomic distance), we may replace $\overleftrightarrow{\alpha}^{(0)}$ by its configurational average defined below. When Ω is fixed, the dominant contribution in Eq. (3) comes from the modes with $\omega_f \cong \Omega$. Because there are many such terms when $L \gg a$, we can approximate $\vec{p}_f\vec{p}_f$ in these dominant terms by its ensemble average with fixed Ω

$$\langle \vec{p}_f\vec{p}_f \rangle_\Omega = \tfrac{1}{3}p^2(\Omega)\overleftrightarrow{1} \ , \tag{4}$$

where $\overleftrightarrow{1}$ is the unit 3×3 matrix and we have used the fact that in macroscopically isotropic glasses there are no preferred directions for $\vec{p}$'s except for the axis of the cubic block. On the same approximation, we can replace the density of eigenfrequency $N_L(\Omega)=\sum_f \delta(\Omega-\omega_f)$ with its ensemble average

$$\left\langle \sum_f \delta(\Omega-\omega_f) \right\rangle = N_L(\Omega) \ . \tag{5}$$

Therefore, in effect we approximate $\overleftrightarrow{\alpha}^{(0)}$ by the following averaged polarizability:

$$\begin{aligned} &\langle \overleftrightarrow{\alpha}^{(0)}(\Omega) \rangle = \alpha(\omega)\overleftrightarrow{1} \ , \\ &\alpha(\omega)=\int \frac{N_L(\omega)}{\omega^2-\Omega^2}\frac{p^2(\omega)}{3}d\omega \ . \end{aligned} \tag{6}$$

The detailed meanings of the $N_L(\Omega)$ and $p^2(\Omega)$ will be discussed in Sec. IV.

Next we consider an infinite glassy dielectric. This can be regarded formally as an assembly of $L\times L\times L$ cubic blocks stuck in a simple cubic array. The nature of each block was described above, and now the interaction between the normal modes of different blocks can be considered.

For the blocks that are not neighboring each other, the interblock interactions between them are the long-range elastic interaction and the Coulomb interaction. In the ir frequency range we can neglect the former, whereas the Coulomb interaction between them can be expanded into the multipole-multipole interactions between the centers of blocks, and we retain only the dipole-dipole interaction term which is the lowest order in the expansion with respect to the distance between the centers of blocks.

In contrast to this, the interblock interactions between neighboring blocks are complicated. These include the short-range part of the non-Coulombic force as well as the Coulomb interaction whose multipole expansion does not generally converge. Nevertheless, we keep here again only the dipole-dipole interaction term, expecting that as long as the response to the long-wavelength external field is concerned, this dipole-dipole term will especially yield the most dominant contribution in producing the TO-LO splitting.

Within these approximations the bulk Hamiltonian of the infinite system can be written in the following form:

$$\begin{aligned} H=&\sum_a H_a^{(0)}(\{P_{af}\},\{Q_{af}\},\vec{E}_a^{(0)}) \\ &+\tfrac{1}{2}\sum_{a\neq b}\vec{p}_a\cdot\overleftrightarrow{V}_{ab}\cdot\vec{p}_b \end{aligned} \tag{7}$$

with

$$\vec{p}_a=\sum_f^{(a)}\vec{p}_{af}Q_{af} \ , \tag{8}$$

$$\overleftrightarrow{V}_{ab}=R_{ab}^{-3}(\overleftrightarrow{1}-3\hat{R}_{ab}\hat{R}_{ab}) \ , \tag{9}$$

where $H_a^{(0)}$ describes the normal vibrations in block a that are coupled with the external field as given in Eq. (1), $\hat{R}_{ab}$ is the unit vector directing from the center of block a to that of block b, and R_{ab} is the distance between them. $\sum_f^{(a)}$ denotes summing over all the normal modes in block a. Within this approximation, the external field acting on block a can be replaced by a uniform field that has the same value as the true field at the center of block $\vec{R}_a$.

On the basis of the equation of motion derived from Eq. (7), we have the following stationary solution subjected to $\vec{E}_a^{(0)}[\propto\exp(-i\Omega t)]$:

$$\vec{p}_a=\overleftrightarrow{\alpha}_a^{(0)}(\Omega)\cdot\vec{E}_a \ , \tag{10}$$

$$\vec{E}_a=\vec{E}_a^{(0)}-\sum_{b(\neq a)}\overleftrightarrow{V}_{ab}\cdot\vec{p}_b \ . \tag{11}$$

$\overleftrightarrow{\alpha}_a^{(0)}(\Omega)$ is defined in Eq. (3) with a subscript a to both $\vec{p}_f$ and ω_f. Upon adopting the same approximation that leads to Eq. (6) we replace $\overleftrightarrow{\alpha}_a^{(0)}(\Omega)$ by its configuration average $\langle\overleftrightarrow{\alpha}^{(0)}(\Omega)\rangle$. Then the averaged polarization $L^{-3}\vec{p}_a$ of block a under the external field

$$\vec{E}_a^{(0)}=\vec{E}^{(0)}(\vec{k},\Omega)\exp(i\vec{k}\cdot\vec{R}_a-i\Omega t)$$

is written as

$$L^{-3}\vec{p}_a=\vec{P}(\vec{k},\Omega)\exp(i\vec{k}\cdot\vec{R}_a-i\Omega t) \ , \tag{12}$$

$$\vec{P}(\vec{k},\Omega)=\frac{\alpha(\Omega)/L^3}{1+\overleftrightarrow{\Gamma}(\vec{k}L)\alpha(\Omega)/L^3}\vec{E}^{(0)}(\vec{k},\Omega)\ . \tag{13}$$

Here we have introduced a function

$$\overleftrightarrow{\Gamma}(\vec{q})=\sum_{n_1}\sum_{n_2}\sum_{n_3}|\vec{n}|^{-3}\left[\overleftrightarrow{1}-3\frac{\vec{n}}{|\vec{n}|}\frac{\vec{n}}{|\vec{n}|}\right]\times\exp(-i\vec{q}\cdot\vec{n}) \tag{14}$$

with

$$\vec{n}=(n_1,n_2,n_3)\ , \tag{15}$$

the sum being extended over all integers.

We are now in a position to derive the dielectric function $\epsilon(\Omega)$. Taking proper care of the long-wavelength limit $\vec{q}\to 0$ of $\overleftrightarrow{\Gamma}(\vec{q})$ which depends on the direction of $\vec{q}$, we have for the transverse response ($\vec{k}\perp\vec{E}^{(0)}$),

$$\vec{P}(\vec{0},\Omega)=\frac{\alpha(\Omega)/L^3}{1-4\pi\alpha(\Omega)/3L^3}\vec{E}^{(0)}(\vec{0},\Omega) \tag{16}$$

and for the longitudinal response ($\vec{k}\|\vec{E}^{(0)}$),

$$\vec{P}(\vec{0},\Omega)=\frac{\alpha(\Omega)/L^3}{1+8\pi\alpha(\Omega)/3L^3}\vec{E}^{(0)}(\vec{0},\Omega)\ . \tag{17}$$

It is straightforward to show either from Eq. (16) or (17) that the dielectric function takes the form

$$\epsilon(\Omega)=\frac{1+8\pi\alpha(\Omega)/3L^3}{1-4\pi\alpha(\Omega)/3L^3}\ . \tag{18}$$

This function approximately describes the dielectric properties of the bulk system much larger than the wavelength of the electric field. In this expression the effect of the long-range part of the Coulomb interaction is taken into account in the dipole approximation. The magnitude of the TO-LO splitting can be estimated from this expression as will be discussed later in the next section.

III. EFFECTIVE HAMILTONIAN FORMALISM

In this section we rederive Eqs. (16)–(18) by transforming the model Hamiltonian (7) itself into an effective Hamiltonian. This procedure tells us how to deal with a group of modes attributed to one molecular mode when we calculate the macroscopic response of the system. It is shown that in the derived effective Hamiltonian the optical activity of each block can be represented in the form of a set of effective masses of the coupled oscillators.

First we divide the frequency range over which ω_{af}'s are distributed into sections such that I_ω, the total range of the ω_{af}'s, is given by

$$I_\omega=\bigcup_s I_s\ , \tag{19}$$

$$I_s=[\omega_s,\omega_{s+1}),\quad \cdots<\omega_{s-1}<\omega_s<\omega_{s+1}<\cdots\ . \tag{20}$$

Here it should be noted that I_s's are independent of the block suffices a, b, etc. We now regard the eigenfrequencies within the same section as effectively degenerate at the frequency $\bar{\omega}_s$ ($\omega_s\le\bar{\omega}_s<\omega_{s+1}$), that is, we replace each $H_a^{(0)}$ in Eq. (7) with the following function:

$$H_a^{(0)}=\sum_s\left[\frac{1}{2}\left[\sum_{\substack{f\\ \omega_{af}\in I_s}}P_{af}^2\right]+\tfrac{1}{2}\bar{\omega}_s^2\left[\sum_{\substack{f\\ \omega_{af}\in I_s}}Q_{af}^2\right]-\vec{p}_a^{(s)}\cdot\vec{E}_a^{(0)}\right]\ , \tag{21}$$

where

$$\vec{p}_a^{(s)}=\sum_{\substack{f\\ \omega_{af}\in I_s}}\vec{p}_{af}Q_{af}\ . \tag{22}$$

After the suitable averaging procedure which will be discussed later, we will formally let the width of the I_s of every section vanish.

Now we define the three vectors $\tilde{U}_{ax}^{(s)},\tilde{U}_{ay}^{(s)},\tilde{U}_{az}^{(s)}$ in the subspace of the normal coordinates of the block a whose eigenfrequencies are in the range I_s

$$(\tilde{U}_{a\mu}^{(s)})_f=(\vec{p}_{af})_\mu,\quad \mu=x,y,z,\quad \omega_{af}\in I_s\ . \tag{23}$$

If the inner products of these vectors satisfy the following orthogonality conditions:

$$(\tilde{U}_{a\mu}^{(s)},\tilde{U}_{a\nu}^{(s)})=\sum_{\substack{f\\ \omega_{af}\in I}}(\tilde{U}_{a\mu}^{(s)})_f(\tilde{U}_{a\nu}^{(s)})_f \tag{24}$$

$$=(1/m^{(s)})\delta_{\mu\nu}\ , \tag{25}$$

where $m^{(s)}$ is a constant, then it is easily shown that we can find the orthogonal transformation in this subspace which has the following properties:

$$Q_{af}^{(s)}=\sum_g(T_a^{(s)})_{fg}Q_{ag}'^{(s)}\ , \tag{26}$$

$$\tilde{T}_a^{(s)}T_a^{(s)}=T_a^{(s)}\tilde{T}_a^{(s)}=1\ , \tag{27}$$

$$(T_a^{(s)})_{fg}=(m^{(s)})^{1/2}(U_{a\mu}^{(s)})_f\ , \tag{28}$$

with $g=1,2,3$ for $\mu=x,y,z$, respectively. Equation (27) is the general definition of the orthogonal transformation $T_a^{(s)}$ and its transpose $\tilde{T}_a^{(s)}$, and Eq. (26) gives the new orthogonal coordinates $\{Q'^{(s)}_{ag}\}$ introduced by this transformation. Using these conditions, we can write Eq. (22) as

$$\vec{\mathrm{P}}_a^{(s)}=(m^{(s)})^{-1/2}(Q'^{(s)}_{a1},Q'^{(s)}_{a2},Q'^{(s)}_{a3})\ . \tag{29}$$

This means that in the new coordinate system only three of these coordinates are optically active. In fact, Eq. (25) holds only when we take the configurational average of the left-hand side of the equation as discussed in Sec. II, and in that case, $(m^{(s)})^{-1}$ can be shown to be given by

$$(m^{(s)})^{-1}=\int_{\omega_s}^{\omega_{s+1}}N_L(\omega)\frac{p^2(\omega)}{3}d\omega\ . \tag{30}$$

When the number of modes $\{Q_{af}\}$ within the section I_s is very large so that the components of the vectors $\tilde{U}_{a\mu}^{(s)}$'s can be regarded as fairly random, we may assume that Eq. (25) holds. We shall adopt this approximation. Then we can rewrite the model Hamiltonian H into the following form:

$$H_{\mathrm{eff}}=\sum_a\sum_s[(\vec{\pi}_a^{(s)})^2/2m^{(s)}+\tfrac{1}{2}m^{(s)}\bar{\omega}_s^2(\vec{\mathrm{p}}_a^{(s)})^2-\vec{\mathrm{p}}_a^{(s)}\cdot\vec{\mathrm{E}}_a^{(0)}]+\tfrac{1}{2}\sum_{a\neq b}\sum\left[\sum_s\vec{\mathrm{p}}_a^{(s)}\right]\cdot\vec{\mathrm{V}}_{ab}\cdot\left[\sum_{s'}\vec{\mathrm{p}}_b^{(s')}\right]$$

$$+\sum_a\sum_s\left[\frac{1}{2}\left[\sum_{g\geq 4}^{(a)}(P'^{(s)}_{ag})^2\right]+\tfrac{1}{2}\bar{\omega}_s^2\left[\sum_{g\geq 4}^{(a)}(Q'^{(s)}_{ag})^2\right]\right]\ . \tag{31}$$

In this effective Hamiltonian, $\vec{\pi}_a^{(s)}=m^{(s)}\dot{\vec{\mathrm{p}}}_a^{(s)}$ and $P'^{(s)}_{ag}$ are the momenta conjugate to $\vec{\mathrm{p}}_a^{(s)}$ and $Q'^{(s)}_{ag}$, respectively. The first group of terms can be regarded as the Hamiltonian of the simple cubic array of multi-mode oscillators having masses $\{m^{(s)}\}$ and eigenfrequencies $\{\bar{\omega}_s\}$, and these oscillators are coupled with those of the different sites (blocks) through the dipole-dipole interaction indicated by the second group of terms in Eq. (31). The remaining terms represent the Einstein oscillators which are optically inactive and isolated from each other. This result reminds us of the work done by Fano[4] who has studied the nature of the Hamiltonian similar to (31) as a model of the collective excitations of electrons in condensed materials.

It is a straightforward task to derive the dielectric function on the basis of the reformulation so far given. Following the well-known procedure for dealing with the periodic system, we get from Eq. (31) the response of the system to the external field for the transverse case:

$$\vec{\mathrm{P}}(\vec{0},\Omega)=\frac{L^{-3}\sum_s\dfrac{1}{m^{(s)}(\bar{\omega}_s^2-\Omega^2)}}{1-\dfrac{4\pi}{3}L^{-3}\sum_s\dfrac{1}{m^{(s)}(\bar{\omega}_s^2-\Omega^2)}}\vec{\mathrm{E}}^{(0)}(\vec{0},\Omega) \tag{32}$$

and for the longitudinal case

$$\vec{\mathrm{P}}(\vec{0},\Omega)=\frac{L^{-3}\sum_s\dfrac{1}{m^{(s)}(\bar{\omega}_s^2-\Omega^2)}}{1+\dfrac{8\pi}{3}L^{-3}\sum_s\dfrac{1}{m^{(s)}(\bar{\omega}_s^2-\Omega^2)}}\vec{\mathrm{E}}^{(0)}(\vec{0},\Omega)\ , \tag{33}$$

which yield the dielectric function in the form

$$\epsilon(\Omega)=\frac{1+\dfrac{8\pi}{3}L^{-3}\sum_s\dfrac{1}{m^{(s)}(\bar{\omega}_s^2-\Omega^2)}}{1-\dfrac{4\pi}{3}L^{-3}\sum_s\dfrac{1}{m^{(s)}(\bar{\omega}_s^2-\Omega^2)}}\ . \tag{34}$$

Since we regard $N_L(\Omega)$ and $p^2(\Omega)$ as smooth functions of Ω, Eqs. (32)–(34) become Eqs. (16)–(18), respectively, in the limit of $\max_s|\omega_{s+1}-\omega_s|\to 0$. Note that the final results are not sensitive to the size of each block ($L\times L\times L$) because for $L\gg a$, $N_L(\Omega)/L^3$ and $p^2(\Omega)$ are to be the intensive quantities.

Bearing these properties of the relevant quantities involved in $\epsilon(\Omega)$ in mind, Eq. (34) allows us to estimate the magnitude of the TO-LO splitting which is seen in the difference in the peak positions of $\Omega\epsilon_2(\Omega)$ and Im $[-\epsilon(\Omega)^{-1}]$ or in the reduced Raman intensity on the assumption that we know the ir absorption data $\Omega\epsilon_2(\Omega)$ from experiments or the function $N_L(\Omega)P^2(\Omega)/L^3$ from the model calculation of the small system. For example, consider the case that $\Omega\epsilon_2(\Omega)$ is known to have a single well-isolated peak at $\Omega=\omega_{\mathrm{T}}$ with the

width Δ and the integrated intensity i_0. Then as an approximation we can choose that

$$\bar{\omega}_{s_0}^2=\omega_T^2+2i_0/3\pi\ , \tag{35}$$

$$\omega_{s_0}<\bar{\omega}_{s_0}<\omega_{s_0+1}\equiv\omega_{s_0}+\Delta\ , \tag{36}$$

$$(L^3 m^{(s_0)})^{-1}=i_0/2\pi^2\ , \tag{37}$$

and for the s other than s_0, we set $m^{(s)}=\infty$. Then we get from Eq. (34)

$$\Omega\epsilon_2(\Omega)=i_0[\delta(\omega_T-\Omega)+\delta(\omega_T+\Omega)]\ , \tag{38}$$

$$\mathrm{Im}[-\epsilon^{-1}(\Omega)]=(i_0/\Omega)[\delta(\omega_L-\Omega)+\delta(\omega_L+\Omega)]\ , \tag{39}$$

where

$$\omega_L^2-\omega_T^2=2i_0/\pi \tag{40}$$

$$=(4\pi/L^3)\int_{\omega_{s_0}}^{\omega_{s_0}+\Delta} N_L(\omega)\frac{p^2(\omega)}{3}d\omega\ . \tag{41}$$

In order to have the more detailed results such as the width of the longitudinal response, or to treat the more complicated form of $N_L(\Omega)p^2(\Omega)/L^3$, we should evaluate Eq. (18) numerically.

Here one might ask the following questions: If we assume $L\gg a$, are not then the above mentioned TO-LO splittings also *in* the $N_L(\Omega)/L^3$ itself? If this is the case, do those splittings lead to undesired splittings, for instance, in $\Omega\epsilon_2(\Omega)$? We will discuss these questions in the next section.

IV. SUMMARY AND DISCUSSION

We constructed a model Hamiltonian for the vibrational modes in glassy dielectrics by replacing any kind of disorder in the original glassy system with the "cellular" disorder in the cubic "lattice." The expression for the dielectric response of the infinite bulk was obtained from this Hamiltonian by a method similar to the virtual crystal approximation in the disordered systems. Then we rederived the same results by transcribing the above Hamiltonian in terms of the induced dipole moments of the cubic blocks and the other optically inactive modes along with their conjugate momenta. The underlying idea is that so far as the response to the long-wavelength external field is concerned, we can construct an effective Hamiltonian which consists of only the macroscopic variables of the blocks independent of the details of the randomness involved in the systems. Thereby, the selection rules such as k-selection rule or TO-LO selection rule should be recovered approximately. In our treatment, the short- and middle-range ($\lesssim L$) character of the microscopic Hamiltonian of a glassy system were shown to be reflected through the factor

$$N_L(\Omega)p^2(\Omega)=(\Omega/\pi)\mathrm{Im}\langle\alpha_{\nu\nu}^{(0)}(\Omega+i0)\rangle\ . \tag{42}$$

Up to the present, we have considered only the long-wavelength optic modes ($\lambda\gg L$) and have expected implicitly that the quantity $N_L(\Omega)p^2(\Omega)$, which should be given by the microscopic model calculation, does not have the TO-LO splittings. Now we turn our attention to the modes other than the long-wavelength modes and discuss whether the above expectation is actually realized or not.

In order to clarify the essential nature of the normal modes of each block, it is instructive to consider the following simple model. Take two identical oscillators with an eigenfrequency ω_0 separated from each other by a distance $|\vec{R}_{12}|$. We assume that these two oscillators are mutually coupled through the induced dipole-dipole force, and hence their Hamiltonian can be written as

$$H=\sum_{i=1}^{2}(\vec{\pi}_i^2/2+\tfrac{1}{2}\omega_0^2\vec{p}_i^2)+\gamma R_{12}^{-5}[R_{12}^2(\vec{p}_1\cdot\vec{p}_2)-3(\vec{p}\cdot\vec{R}_{12})(\vec{p}_2\cdot\vec{R}_{12})]\ . \tag{43}$$

The normal modes of this system are easily analyzed and can be classified into two types, i.e., ir-active modes and ir-inactive modes. The latter bring about only the higher-order electric moments (quadrupole moments), inducing only the short-ranged electric field. The ir-inactive modes are further classified according to the angle between the $\vec{p}_i$'s and the vector connecting the two oscillators, $\vec{R}_{12}$. One mode satisfies $\vec{p}_1,\vec{p}_2\|\vec{R}_{12}$ and may be called an LO-like mode, whereas the other modes satisfy $\vec{p}_1\|\vec{p}_2\perp\vec{R}_{12}$ and may be called TO-like modes which have doubly degenerate and lower frequency. Summing up, we can say that if the two oscillators are coupled in the form of Eq. (43), the normal modes which do not expose their total dipole moment (i.e., $\vec{p}_1+\vec{p}_2=0$) are necessarily separated into two types according to the manner in which the two dipoles cancel out.

These results are the consequence of the anisotropic nature of the dipole-dipole interaction.

Next we consider the case in which there are many "dimers" (pairs of oscillators, each pair of which consists of two-coupled oscillators as described above) and we also assume the dipole-dipole interaction between the oscillators belonging to the different dimers. According to the above results, the ir-inactive modes of these dimers are mutually coupled only through the weak-and short-ranged interactions. Therefore, these modes are only weakly perturbed by other pairs and approximately conserve their *own* character such as TO-like or LO-like nature. This is in contrast to the ir-active modes which are coupled with each other through the long-range dipole-dipole interaction giving rise to either new ir-active or ir-inactive (or weakly active) modes in greater extent.

Although these models are too simple and the arguments given above are too qualitative to extend them directly to the general dielectric system, they are still helpful to gain insight into the relationship among $N_L(\Omega)$, $N_L(\Omega)p^2(\Omega)$, and the total density of states of the infinite system. We expect the following argument to hold: Among the normal modes of block a, a large part of them will be the modes with small $|\vec{p}_{af}|$, that is, only weakly ir-active, and these may have either TO-like or LO-like nature according to the manner in which the local dipole moments are canceled within the block. These modes may lead to the TO-LO peak splittings in $N_L(\Omega)$, but due to the smallness of their $|\vec{p}_{af}|$'s they will make relatively small contributions to $N_L(\Omega)p^2(\Omega)$. On the other hand, those modes with large $|\vec{p}_{af}|$ which do not yet have clear-cut TO or LO nature, couple strongly with the similar modes of other blocks and constitute the long-wavelength ($\lambda = 2\pi k^{-1} \geq L$) TO or LO modes described in Secs. II and III. Roughly speaking, the total density of states of the infinite system is the sum of the contributions from the modes of each block with small $|\vec{p}_{af}|$ and from the long-wavelength TO and LO modes. If we wish to have improved results, however, we will have to take account of the other interblock interactions which we have neglected in the above arguments.

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