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Mean field approach to ferroelastic transitions in molecular crystals

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A mean field approach to the dynamics of structural phase transitions in molecular crystals is presented. The approach is based on a description of the rotational and translational molecular motions, and the coupling between them, in terms of generalized susceptibilities. Two models for the orientational susceptibility are used. One is a classical description in terms of two-dimensional rotors, the other a two-dimensional anharmonic oscillator model. The specific example considered is *sym*-triazine. In this crystal molecules experience a very strong orienting field which restricts the molecular rotational motion to libration. The coupling between the molecular rotations and translations is shown to lead to a softening of acoustic phonons. This softening has considerable anisotropy in reciprocal space. An approximate solution for the high temperature phase is shown to be in good agreement with experiments.

I. INTRODUCTION

Structural phase transitions in molecular crystals have been the subject of an increasing number of light scattering and neutron scattering experiments as well as theoretical studies. Examples of systems which have been studied recently are benzil,[1-4] chloranil,[5-8] and *sym*-triazine.[9,10] In the case of benzil the mechanism for the structural phase transition is assumed to proceed through a triggering of a Brillouin zone-boundary point instability by a zone-center one.[1] The softening of the zone-center optic mode is accompanied by a fourfold expansion of the crystal's unit cell at the transition.[2] In addition, a softening of several acoustic mode frequencies is observed.[3] For chloranil the transition results in the doubling of the unit cell along one axis of the crystal.[5] The order parameter corresponds to the staggered rotation of the molecules about one or more of the molecular axes.[8] Again, anomalies in the elastic constants occur as a consequence of the phase transition.[7] In the case of chloranil the soft mode occurs at the zone boundary rather than the zone center. In addition, a sharp central peak is observed. This critical scattering has considerable extent in q space.[5] In contrast to these fairly complex systems, in *sym*-triazine one observes no obvious optic soft modes, a softening of acoustic modes but no central peak.[9(a),9(b)]

In all cases changes in the molecular orientations, and in the case of benzil, internal configurations, occur along with the structural changes. A complete elucidation of the details of the coupling between the center-of-mass translations and molecular orientations, including its wave vector dependence, is beyond the scope of this paper. It is the purpose of this paper to examine the interaction between molecular orientations and center-of-mass translations and to determine its influence on the mechanics of structural phase transitions in molecular crystals. The type of rotation-translation coupling considered has the bilinear form $Ae\eta$, where e is a lattice strain and η the order parameter for the transition. The order parameter in such instances generally describes the change in the molecular orientation.

In particular, we wish to examine the effect of this type of coupling on the acoustic phonon spectrum and to provide a description of structural phase transitions for which this type of coupling is dominant. Although interaction terms of this nature seem to occur in both benzil and chloranil, they are the dominant coupling in the case of *sym*-triazine.

The instabilities of coupled rotor–phonon systems have recently been derived using the time-dependent Hartree approximation[10(a),10(b)] for the case of one-dimensional rotators.[11] In the present work the ideas developed there, and in the related approach of deRaedt and Michel,[12] are extended to treat molecular crystals with bilinear interaction terms. *Sym*-triazine is taken as an example.

The present approach differs from that of Michel and Naudts in the treatment of the statics[13(b)] and dynamics[13(c)] of ferroelastic phase transitions. The basic dynamic equations of the approach of the second paper are *a priori* more general than those derived from the Hartree approximation, as in the present approach. However, when it comes to the explicit evaluation of the orientational relaxation transport coefficients, approximations have to be made. An advantage of the present approach is that it leads in a straightforward way to the approximation of the orientational transport coefficient by the dynamic single particle susceptibility. The present approach takes advantage of this situation and uses the expressions for the single particle dynamic susceptibility developed by deRaedt and Michel.[12]

II. MEAN FIELD GENERALIZED SUSCEPTIBILITY

Consider a Hamiltonian for an interacting system

$$\mathcal{H}_0 = \sum_{i\alpha} \mathcal{H}_\alpha(Q_{i\alpha}) - \frac{1}{2} \sum_{\substack{i\alpha\\ j\beta}} W_{i\alpha,j\beta}\, Q_{i\alpha} Q_{j\beta} \,. \tag{1}$$

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Here $Q_{i\alpha}$ is the αth coordinate for the ith molecule and may represent either rotational or translational motion. The first term in Eq. (1) represents the sum of single particle terms such as kinetic energy or crystal field, and the second term represents the interactions which depend linearly on the coordinates of two molecules.

To examine the response to an external perturbation, one adds a small external disturbance $\sum_{i\alpha}\hat{\mathcal{H}}_{i\alpha}(t)$ to the Hamiltonian Eq. (1), where

$$\hat{\mathcal{H}}_{i\alpha}(t) = -U_{i\alpha}(t)\,Q_{i\alpha} \ . \tag{2}$$

The density matrix for the system is approximated by a product of single-particle density matrices:

$$\rho = \prod_{i=1}^{N}\prod_{\alpha=1}^{n}\rho_\alpha^i \ . \tag{3}$$

The index i runs over all unit cells and α denotes n degrees of freedom within a given cell. The single-particle density matrices ρ_α^i are assumed to be independent of the index i.

The perturbing term (2), when added to the Hamiltonian (1), will change the equilibrium density matrix by a small amount to

$$\rho_\alpha^i \to \rho_\alpha^i(t) = \rho_\alpha^i + \tilde{\rho}_\alpha^i(t) \ . \tag{4}$$

Using the perturbed density matrix (4) one defines the effective molecular field or Hartree potential for the coordinate $Q_{i\alpha}$ as

$$\mathcal{H}_{i\alpha}^{(H)}(t) = \mathcal{H}_{i\alpha} - W_{i\alpha}(t)\,Q_{i\alpha} \ , \tag{5}$$

where

$$\mathcal{H}_{i\alpha} = \mathcal{H}_\alpha(Q_{i\alpha}) - \sum_{j\beta} W_{i\alpha,j\beta}\,\mathrm{Tr}\{Q_{j\beta}\rho_\beta^j\}\,Q_{i\alpha} \tag{6}$$

and

$$W_{i\alpha}(t) = \sum_{j\beta} W_{i\alpha,j\beta}\,\mathrm{Tr}\{Q_{j\beta}\tilde{\rho}_\beta^j(t)\} + U_{i\alpha}(t) \ . \tag{7}$$

In Eqs. (6) and (7) the trace is taken over the indices j and β.

The equation of motion for the density matrix is,[14] in units with $\hbar = 1$,

$$i\frac{\partial}{\partial t}\rho_\alpha^j(t) = [\mathcal{H}_{j\alpha}^{(H)}(t),\ \rho_\alpha^j(t)] \ . \tag{8}$$

Using $[\mathcal{H}_{j\alpha}, \rho_\alpha^j] = 0$ and linearizing one obtains[14]

$$\tilde{\rho}_\alpha^j(t) = -i\int_{-\infty}^{t} dt'\,W_{j\alpha}(t')\,[\rho_\alpha^j,\ \tilde{Q}_{j\alpha}(t'-t)] \ , \tag{9}$$

where the operator $\tilde{Q}_{j\alpha}(t)$ is defined in the interaction representation by

$$\tilde{Q}_{j\alpha}(t) = \exp(i\mathcal{H}_{j\alpha}t)Q_{j\alpha}\exp(-i\mathcal{H}_{j\alpha}t) \ . \tag{10}$$

The response for the coordinate $Q_{i\alpha}$ is

$$Y_{j\alpha}(t) = \mathrm{Tr}\{\tilde{\rho}_\alpha^j(t)\,Q_{i\alpha}\} \ . \tag{11}$$

Using Eqs. (9) and (10) the response can be written as

$$Y_{i\alpha}(t) = \int_{-\infty}^{t} dt'\left\{\sum_{j\beta} W_{i\alpha,j\beta}\,Y_{j\beta}(t') + U_{i\alpha}(t')\right\}K_\alpha(t-t') \ , \tag{12}$$

where the linear response function $K_\alpha(t)$ is defined by

$$K_\alpha(t) = i\,\mathrm{Tr}\{\rho_\alpha^j[\tilde{Q}_{j\alpha}(t),\ \tilde{Q}_{j\alpha}(0)]\}_j \ . \tag{13}$$

Defining the transforms

$$\begin{aligned} Y_{j\alpha}(t) &= \frac{1}{2\pi N}\int_{-\infty}^{\infty} d\omega \sum_{\mathbf{q}} \exp[i(\mathbf{q}\cdot\mathbf{R}_j - \omega t)]\,\mathcal{Y}_\alpha(\mathbf{q},\omega) \ , \\ U_{j\alpha}(t) &= \frac{1}{2\pi N}\int_{-\infty}^{\infty} d\omega \sum_{\mathbf{q}} \exp[i(\mathbf{q}\cdot\mathbf{R}_j - \omega t)]\,\mathcal{U}_\alpha(\mathbf{q},\omega) \ , \end{aligned} \tag{14}$$

and the single-particle susceptibility

$$\chi_\alpha^0(\omega) = \int_0^{\infty} dt\,\exp(i\omega t)\,K_\alpha(t) \ , \tag{15}$$

Eq. (12) leads to

$$\sum_\beta \{\delta_{\alpha\beta} - W_{\alpha\beta}(\mathbf{q})\,\chi_\alpha^0(\omega)\}\,\mathcal{Y}_\beta(\mathbf{q},\omega) = \chi_\alpha^0(\omega)\,\mathcal{U}_\alpha(\mathbf{q},\omega) \ , \tag{16}$$

where

$$W_{\alpha\beta}(\mathbf{q}) = \sum_l W_{j\alpha,l\beta}\exp[i\mathbf{q}\cdot(\mathbf{R}_l - \mathbf{R}_j)] \ . \tag{17}$$

The coupled system susceptibilities $\chi_{\alpha\beta}$ are defined by

$$\chi_{\alpha\beta}(\mathbf{q},\omega) = \left.\frac{\partial\mathcal{Y}_\alpha(\mathbf{q},\omega)}{\partial\mathcal{U}_\beta(\mathbf{q},\omega)}\right|_{\mathcal{U}_1=\mathcal{U}_2=\cdots=0} \ . \tag{18}$$

If we set

$$M_{\alpha\beta}(\mathbf{q},\omega) = \delta_{\alpha\beta} - W_{\alpha\beta}(\mathbf{q})\,\chi_\alpha^0(\omega) \ , \tag{19}$$

the definition (18) leads to

$$\chi_{\alpha\beta}(\mathbf{q},\omega) = (M^{-1})_{\alpha\beta}\,\chi_\beta^0(\omega) \ , \tag{20}$$

where M^{-1} is the inverse of the matrix M whose elements are defined in Eq. (19).

This result is equivalent to that obtained by other authors[11,15] using the time-dependent Hartree approximation.[10(a),10(b)] Several examples illustrate the utility of Eq. (20). For a single mode, $\alpha = \beta = 1$, one finds

$$\chi_{11}(\mathbf{q},\omega) = \{[1/\chi_1^0(\omega)] - W_{11}(\mathbf{q})\}^{-1} \ . \tag{21}$$

For two interacting modes, $\alpha, \beta = 1, 2$, one has, e.g., if

$W_{11}(\mathbf{q}) = W_{22}(\mathbf{q}) = 0$, $W_{12}(\mathbf{q}) = w(\mathbf{q})$ and $W_{21}(\mathbf{q}) = w(\mathbf{q})^*$:

$$\chi_{11}(\mathbf{q},\omega) = \{[1/\chi_1^0(\omega)] - |w(\mathbf{q})|^2\chi_2^0(\omega)\}^{-1} \ . \tag{22}$$

Expressions similar to Eq. (22) are found for χ_{22}, χ_{12}, and χ_{21}. Equivalent expressions involving more coordinates are easily derived from Eq. (20). Expressions like Eq. (21) have been used to calculate the generalized susceptibility of interacting rotors,[15,16] while equations of the type (22) are utilized when calculating the susceptibility of coupled spin-phonon[17,18] or translation-rotation[11,13(a)-13(d)] systems.

III. MEAN FIELD DESCRIPTION

For the Landau mean field approach to the structural phase transition in *sym*-triazine[9] the order parameter was chosen as the doubly degenerate molecular rotation (R_x, R_y) belonging to the E_g irreducible representation of D_{3d}. There are, of course, other sets of basis functions for this representation: strains (e_4, e_5) and $(e_6, e_1 - e_2)$ and higher order rotation terms $[R_xR_y, \frac{1}{2}(R_x^2 - R_y^2)]$. Because of the bilinear coupling between the rotations and strains, the choice of order parameter is not unique. The Landau free energy expansion in terms of the lattice strains and molecular rotations has the form[9]

$$F=\tfrac{1}{2}a_0(T-T_0)(R_x^2+R_y^2)+\tfrac{1}{3}b(R_y^3-3R_x^2R_y)+\tfrac{1}{4}c(R_x^2+R_y^2)^2+\frac{1}{2}\,\frac{c_{11}^0+c_{12}^0}{2}(e_1+e_2)^2+\tfrac{1}{2}c_{33}^0e_3^2+c_{13}^0(e_1+e_2)e_3+\tfrac{1}{2}c_{44}^0(e_4^2+e_5^2)$$
$$+\frac{1}{2}\,\frac{c_{11}^0-c_{12}^0}{2}(e_6^2+e_7^2)+c_{14}^0(e_5e_7-e_4e_6)+A(e_4R_x-e_5R_y)+B(e_6R_x+e_7R_y)+C\left(e_4R_xR_y-e_5\frac{R_x^2-R_y^2}{2}\right)$$
$$+D\left(e_6R_xR_y+e_7\frac{R_x^2-R_y^2}{2}\right)+\cdots\ , \qquad (23)$$

where we have set $e_7 \equiv e_1 - e_2$.

Instead of the molecular rotations R_x and R_y one can express the free energy [Eq. (23)] in terms of tesseral harmonics S_{LM}. Approximate relationships valid for $x \ll z$ and $y \ll z$ are

$$R_x \cong -\frac{1}{\sqrt{3}}S_{2-1} = -yz\ ,$$
$$R_y \cong \frac{1}{\sqrt{3}}S_{21} = xz\ ,$$
$$R_xR_y \cong -\frac{1}{\sqrt{3}}S_{2-2} = -xy\ ,$$
$$\tfrac{1}{2}(R_x^2-R_y^2) \cong -\frac{1}{\sqrt{3}}S_{22} = -\tfrac{1}{2}(x^2-y^2)\ , \qquad (24)$$

where $x=\sin\theta\cos\phi$, $y=\sin\theta\sin\phi$, and $z=\cos\theta$.

The origin of the orientation-dependent terms of the free energy [Eq. (23)] has been discussed in detail.[9] *Ab initio* calculations[19] have shown that long-range interactions between *sym*-triazine molecules include dispersion and induction contributions as well as multipole–multipole terms. The octupole–octupole interactions seem to dominate the latter because the molecular quadrupole moment is comparatively small.[19] When the octupole–octupole interactions between neighboring molecules form the dominant multipolar coupling one must specify the orientation of each molecule by three degrees of freedom. Therefore, one expands the interactions between two *sym*-triazine molecules in terms of the rotation matrices $D^L_{MM'}(\alpha\beta\gamma)$. The angular variables (α,β,γ) are the Euler angles representing the orientation of one molecule relative to the intermolecular axis connecting the molecules.

In our treatment of the structural phase transition in *sym*-triazine we ignore librations or reorientations about the threefold molecular axis.[9] In that case an expansion of the multipole–multipole potential in terms of the spherical harmonics $Y_{LM}(\theta,\phi)$ is adequate. The orientation of a given molecule is then specified by the angles (θ,ϕ) only. Instead of the spherical harmonics it is instead convenient to use the tesseral harmonics, as defined by Eqs. (24), or equivalently,

$$S_{21} = -\sqrt{\frac{2\pi}{5}}\,(Y_{21}-Y_{2-1})\ ,$$
$$S_{2-1} = i\sqrt{\frac{2\pi}{5}}\,(Y_{21}+Y_{2-1})\ ,$$
$$S_{22} = \sqrt{\frac{2\pi}{5}}\,(Y_{22}+Y_{2-2})\ ,$$
$$S_{2-2} = -i\sqrt{\frac{2\pi}{5}}\,(Y_{22}-Y_{2-2})\ . \qquad (25)$$

The anisotropic dispersion, induction, and repulsion interactions between *sym*-triazine molecules can also be approximately represented by an expansion in terms of the orientational functions S_{LM}, but with a radial dependence which differs from the above. The total interaction potential between two molecules i and j has the form

$$V(i,j) = \sum_{\substack{LM\\L'M'}} C^{LL'}_{MM'}(\mathbf{r}_{ij})\,S_{LM}(\theta_i,\phi_i)\,S_{L'M'}(\theta_j,\phi_j)\ . \qquad (26)$$

Here (θ_i,ϕ_i) defines the orientation of molecule i. The coefficients $C^{LL'}_{MM'}(\mathbf{r}_{ij})$ consist of contributions from multipolar, induction, dispersion, and repulsive interactions. Atom–atom representations of the interaction potential (26) have been developed.[20,21] However the coefficients $C^{LL'}_{MM'}(\mathbf{r}_{ij})$ are probably not sufficiently well specified to allow us to calculate the susceptibility of the interacting molecular rotors with sufficient accuracy, using an expression like Eq. (21), where $W_{11}(\mathbf{q})$ represents the Fourier transform of the two-molecule interaction (26). With these constraints in mind it is reasonable to define an effective single-particle potential for each molecule which represents the orienting field in which each molecule moves. This approach is consistent with the mean field methods introduced in Sec. II.

IV. ROTATIONAL SUSCEPTIBILITY

For trigonal symmetry[22] the effective orienting potential seen by each *sym*-triazine molecule has the form[23]

$$V(\theta,\phi) = a_{00} + a_{20}S_{20}(\theta,\phi) + a_{40}S_{40}(\theta,\phi) + a_{43}S_{43}(\theta,\phi) + \cdots\ , \qquad (27)$$

where the $S_{LM}(\theta,\phi)$ are the tesseral harmonics and the a_{LM} are expansion coefficients. Here we specify the molecular orientations by only the angles (θ,ϕ), that is, we are ignoring rotations about the threefold axis of symmetry of the molecule. Using the definitions of Sec. III, Eq. (27) can be rewritten as

$$V(\theta,\phi) = \mathrm{const} + \tfrac{1}{2}a(x^2+y^2) + \tfrac{1}{3}b(x^3-3xy^2)z + \tfrac{1}{4}c(x^2+y^2)^2 + \cdots \qquad (28)$$

with a suitable choice of the potential parameters a, b, and c, Eq. (28) does not only represent the conventional crystal field but, within the framework of the mean field approximation, can also approximate the effective orienting field. When considering a limited range of temperatures in the neighborhood of the phase transition it is reasonable to use the values of the potential parameters obtained from the Landau description, evaluated at the transition temperature $T_c = 198$ K. This approach yields

$$a \cong a_0(T-T_0)\big|_{T=198\,\mathrm{K}} = 1.23\times 10^4\ \mathrm{cm}^{-1}\ ,$$

$$b = -3.11\times 10^3\ \mathrm{cm}^{-1}\ ,$$

$$c = 3.53\times 10^4\ \mathrm{cm}^{-1}\ .$$

The calculation of the generalized susceptibility of a two-dimensional rotor in a crystal has been described by deRaedt and Michel.[12] Although these calculations apply to cubic crystal fields, they are easily extended to crystal fields of trigonal symmetry. Using their second-order approximation the orientational susceptibility is calculated from

$$\chi_Q^0(\omega) = -\frac{\beta(\langle Q^2\rangle - \langle Q\rangle^2)\,\Omega_A^2(\omega + i\Omega_B)}{\omega(\omega^2-\Omega_B^2) + i(\omega^2-\Omega_A^2)\,\Omega_B}\ , \tag{29}$$

where Q is an orientational coordinate, that is, one of the $Q_{i\alpha}$, as defined in Sec. II. For trigonal symmetry, D_{3d}, the functions Q to be considered have E_g symmetry. We choose the tesseral harmonics S_{2-1}, S_{21}, S_{2-2}, and S_{22}, as defined in Eqs. (25). Using the notation of Ref. 12:

$$\Omega_A^2 = -\frac{\langle\{\dot{Q}, Q\}\rangle}{\beta(\langle Q^2\rangle - \langle Q\rangle^2)} \tag{30}$$

and

$$\Omega_B^2 = \frac{\langle\{\ddot{Q}, \mathring{Q}\}\rangle}{\langle\{\dot{Q}, Q\}\rangle}\ . \tag{31}$$

Here $\{,\}$ indicates a Poisson bracket, $\beta = 1/T$ (we use units with $\hbar = k_B = 1$), the dot indicates a time derivative and the classical average, denoted by the angular brackets $\langle\cdots\rangle$ is calculated as

$$\langle f\rangle = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_{-\infty}^{\infty} dp_\phi \int_{-\infty}^{\infty} dp_\theta f(\theta,\phi,p_\theta,p_\phi)$$

$$\times\exp[-\beta(K+V)] \Big/ \int_0^{2\pi} d\phi \int_0^{\Pi} d\theta \int_{-\infty}^{\infty} dp_\phi \int_{-\infty}^{\infty} dp_\theta$$

$$\times\exp[-\beta(K+V)]\ , \tag{32}$$

where the rotational kinetic energy is given by

$$K = \frac{1}{2I}(p_\theta^2 + p_\phi^2/\sin^2\theta)\ , \tag{33}$$

and the effective field V is specified by Eq. (28). In Eq. (33) I is the moment of inertia about either the molecular x or y axes. With these definitions the calculation of the moments Ω_A^2 and Ω_B^2 follows in the manner of previous work.[12]

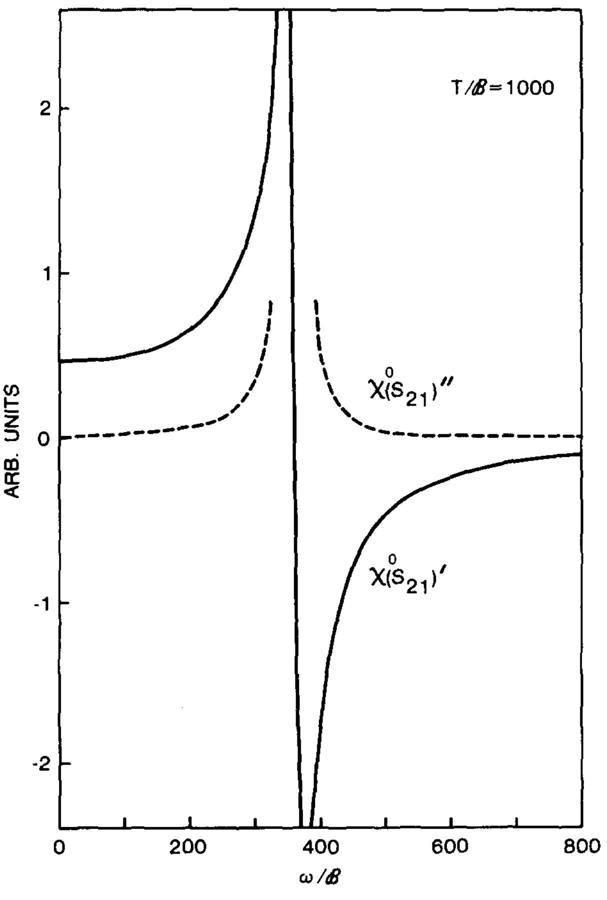

FIG. 1. Real and imaginary parts of the rotational susceptibility $\chi^0(S_{21}) = \chi^0(S_{21})' + i\chi^0(S_{21})''$, as calculated in Sec. IV.

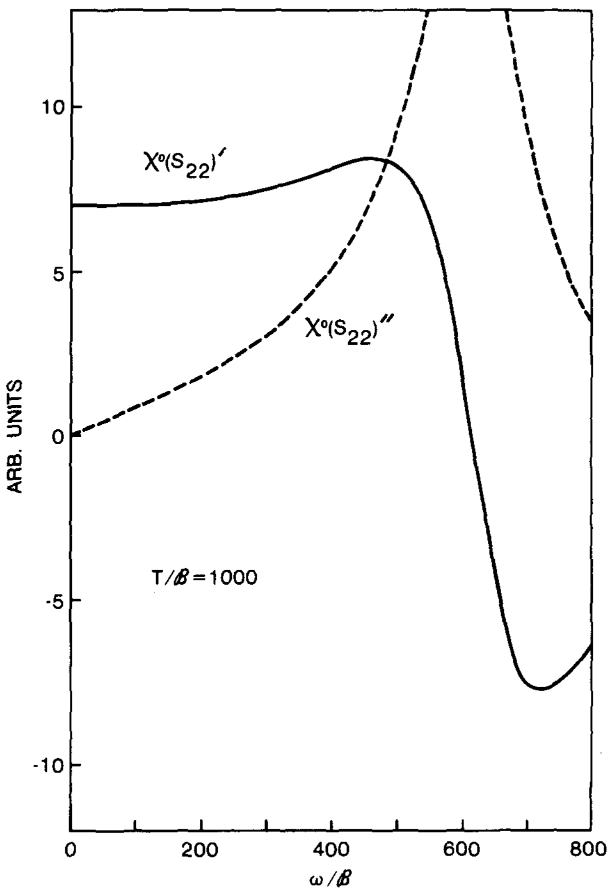

FIG. 2. Real and imaginary parts of the rotational susceptibility $\chi^0(S_{22}) = \chi^0(S_{22})' + i\chi^0(S_{22})''$, as calculated in Sec. IV.

Examples of the frequency dependence of the generalized rotational susceptibility, as calculated from Eq. (29), are shown in Figs. 1 and 2. The real and imaginary parts of the susceptibility are calculated from $\chi_Q^0 = \chi_Q^{0'} + i\chi_Q^{0''}$, with Q equal to S_{2-1}, S_{21}, S_{2-2}, and S_{22}. Only the results for S_{21} and S_{22} are shown because the results for S_{2-1} and S_{2-2} are identical to those for S_{21} and S_{22}, respectively. From Figs. 1 and 2 it is apparent

TABLE I. Coefficients $-i\sqrt{3m}\,G_{\alpha M}(\mathbf{q})$ in the long wavelength limit $qa_h \ll 1$. Here m is the molecular mass. The coefficients A, B, C, and D are the same as those of the Landau free energy expansion (23).

$\alpha \backslash M$	-1	$+1$	-2	$+2$
1	Bq_y	$Bq_x - Aq_z$	Dq_y	$Dq_x - Cq_z$
2	$Bq_x + Aq_z$	$-Bq_y$	$Dq_x + Cq_z$	$-Dq_y$
3	Aq_y	$-Aq_x$	Cq_y	$-Cq_x$

that S_{21} and $S_{2\text{-}1}$ give rise to modes of mainly propagating character. On the other hand, S_{22} and $S_{2\text{-}2}$ seem to have characteristics of both diffusive and propagating modes, or equivalently more heavily damped propagating modes.

V. ROTATION-TRANSLATION COUPLING

The form of the rotation-translation coupling for molecular crystals with D_{3d} symmetry has been derived earlier.[9,24,25] It is however convenient to summarize the results. The rotation-translation interaction Hamiltonian has the form

$$\mathcal{H}_{RT} = \sum_{\mathbf{q}} \sum_{j} \sum_{M} g_{jM}(\mathbf{q})\, Q(\mathbf{q}j) S_{2M}(\mathbf{q})^* \; . \tag{34}$$

Here $Q(\mathbf{q}j)$ represents the coordinate for a "bare" acoustic phonon with wave vector $\mathbf{q}$ and polarization index j. The index M runs over $M = \pm 1$, ± 2. The Fourier transforms of the tesseral harmonics S_{LM} are defined by

$$S_{LM}(\mathbf{q}) = N^{-1/2} \sum_{l} S_{LM}(\theta_l, \phi_l) \exp(-i\mathbf{q} \cdot \mathbf{R}_l) \; . \tag{35}$$

The coefficients $g_{jM}(\mathbf{q})$ for $M = \pm 1$, ± 2 and values of the polarization index $j = 1, 2, 3$ are specified by the relation

$$g_{jM}(\mathbf{q}) = \frac{1}{\sqrt{3}} \sum_{\alpha=1}^{3} G_{\alpha M}(\mathbf{q}) \exp(\alpha)(\mathbf{q}j) \; . \tag{36}$$

In Eq. (36) the factor of $\sqrt{3}$ has been introduced to accomodate the definitions [Eq. (24)]. In the long wavelength limit $qa_h \ll 1$, the coefficients $G_{\alpha M}(\mathbf{q})$ are given in Table I.

For $\mathbf{q}$ along [001] the polarization vectors are

$$\hat{e}(q_z 1) = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad \hat{e}(q_z 2) = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \hat{e}(q_z 3) = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} .$$

Equation (36), together with Table I, then yields

$$\mathbf{g}(q_z) = \frac{iq_z}{\sqrt{3m}} \begin{bmatrix} 0 & -A & 0 & -C \\ A & 0 & C & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} . \tag{37}$$

In the long wavelength limit the frequencies of the bare transverse acoustic (TA) phonons are given by

$$\rho[\omega_1^0(q_z)]^2 = \rho[\omega_2^0(q_z)]^2 = c_{44}^0 q_z^2 \; , \tag{38}$$

where $\rho = m/v$ is the density, with m the molecular mass and v the volume per molecule, and c_{44}^0 is the bare elastic constant. Using Eq. (38), two of the elements of the matrix $\mathbf{g}$ of Eq. (37) are

$$\begin{aligned} g_{1,+1}(q_z) &= -iA\omega_1^0(q_z)/\sqrt{3vc_{44}^0} \; , \\ g_{1,+2}(q_z) &= -iC\omega_1^0(q_z)/\sqrt{3vc_{44}^0} \; . \end{aligned} \tag{39}$$

It follows from Table I that for $\mathbf{q}$ along [001] the bare TA phonon polarized along [100] is coupled only to the orientational coordinates S_{21} and S_{22}, while the bare T phonon polarized along [010] is coupled only to $S_{2\text{-}1}$ and $S_{2\text{-}2}$. The longitudinal acoustic (LA) phonon, with bare elastic constant c_{33}^0, is not coupled to the orientational coordinates at all. Hence the elastic constant c_{33}^0 is unaffected by the coupling to the molecular orientations.

The situation is more complicated for $\mathbf{q}$ in the (x, y) plane. For $\mathbf{q}$ along [100] the phonon polarization vectors have the form

$$\hat{e}(q_x 1) = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \hat{e}(q_x 2) = \begin{bmatrix} \sqrt{1-\xi^2} \\ 0 \\ -\xi \end{bmatrix}, \quad \hat{e}(q_x 3) = \begin{bmatrix} \xi \\ 0 \\ \sqrt{1-\xi^2} \end{bmatrix} .$$

Here ξ is expected to be small. If it can be assumed that the quasilongitudinal and quasitransverse bare acoustic phonon modes, specified by the polarization vectors $\hat{e}(q_x 2)$ and $\hat{e}(q_x 3)$ are approximately polarized along [100] and [001], respectively, then $\xi \cong 0$. This assumption is equivalent to neglecting the bare elastic constant c_{14}^0 compared with c_{11}^0, c_{66}^0, and c_{44}^0. The approximation $\xi \cong 0$ yields

$$\mathbf{g}(q_x) = \frac{iq_x}{\sqrt{3m}} \begin{bmatrix} B & 0 & D & 0 \\ 0 & B & 0 & D \\ 0 & -A & 0 & -C \end{bmatrix} . \tag{40}$$

Equation (40) indicates that the coordinate $S_{2\text{-}1}(q_x)$ is coupled to the TA phonon polarized along [010] ($j = 1$) with coupling coefficient B. $S_{2\text{-}2}(q_x)$ is coupled to the $j = 1$ TA phonon with coupling coefficient D. $S_{21}(q_x)$ and $S_{22}(q_x)$ are coupled to both the quasi-LA phonon ($j = 2$) and the quasi-TA phonon ($j = 3$). The coupling coefficients are B and D in the first case and A and C in the second.

For the [010] direction the bare acoustic phonon polarization vectors are

$$\hat{e}(q_y 1) = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \hat{e}(q_y 2) = \begin{bmatrix} \sqrt{1-\eta^2} \\ 0 \\ -\eta \end{bmatrix}, \quad \hat{e}(q_y 3) = \begin{bmatrix} \eta \\ 0 \\ \sqrt{1-\eta^2} \end{bmatrix} .$$

Making the approximation $\eta \cong 0$, which is again equivalent to neglecting c_{14}^0 in comparison with the other bare elastic constants, one obtains

$$\mathbf{g}(q_y) = \frac{iq_y}{\sqrt{3m}} \begin{bmatrix} 0 & -B & 0 & -D \\ B & 0 & D & 0 \\ A & 0 & C & 0 \end{bmatrix} . \tag{41}$$

A similar interpretation to that for the [100] direction follows from Eq. (41). If one neglects c_{14}^0 in comparison with c_{11}^0, c_{66}^0, and c_{44}^0 the frequency of the bare LA phonon in the (x, y) plane is given by

$$\rho(\omega_{\mathrm{LA}}^0)^2 \cong c_{11}^0 q^2 \; . \tag{42}$$

The two bare TA phonon frequencies are

$$\rho(\omega^0_{\mathrm{TA1}})^2 \cong c^0_{44} q^2 , \tag{43}$$

and

$$\rho(\omega^0_{\mathrm{TA2}})^2 \cong c^0_{66} q^2 , \tag{44}$$

where $q^2 = q_x^2 + q_y^2$.

The form of the rotation-translation coupling in the three symmetry directions, as given by Eqs. (37), (40), and (41), indicate that the bare elastic constant c^0_{44} will be renormalized by coupling to the orientational coordinates S_{21} and S_{22}, or equivalently S_{2-1} and S_{2-2}. The pertinent coupling coefficients are A and C. On the other hand, the bare elastic constants c^0_{66} and c^0_{11} are also renormalized by coupling to the same pairs of orientational coordinates, but the pertinent coupling coefficients are B and D. Experiments for *sym*-triazine[10] and benzil[3,4] indicate that c_{44} shows the most dramatic softening. Hence previous assumptions that for both systems A and C are larger than B and D are probably reasonable. It should be pointed out that the assumption of neglecting c^0_{14} reduces the complexity of the problem. The actual results for the effective elastic constants in the various symmetry directions for $c^0_{14} \neq 0$ are of course more complicated.[3,4] The details are given in Ref. 4 for the case of benzil.

VI. COUPLED SUSCEPTIBILITIES

The calculation of the generalized susceptibilities for the bare rotational coordinates has been outlined in Sec. IV. The susceptibility for the translational motion can be approximated by that for a damped harmonic oscillator with frequency $\omega^0_j(\mathbf{q})$,

$$\chi_{\mathrm{osc}}(\omega) = \frac{1}{m}\, \chi^0_j(\mathbf{q}, \omega) , \tag{45}$$

where

$$\chi^0_j(\mathbf{q}, \omega) = \{[\omega^0_j(\mathbf{q})]^2 - (\omega + i\lambda)^2\}^{-1} . \tag{46}$$

Here the harmonic oscillator damping constant λ is introduced as an adjustable parameter. The bare phonon frequencies $\omega^0_j(\mathbf{q})$ follow from the bare elastic constants $c^0_{\rho\sigma}$.[9] The latter are not known for either *sym*-triazine or benzil, but can be estimated from a comparison of the predicted and observed temperature dependences of the elastic constants. In Sec. V the rotation-translation coupling was defined in terms of $\mathbf{q}$-space coordinates. Because there is a factor of $\sqrt{m}$ difference in the conventional definitions of the phonon coordinate $Q(\mathbf{q}j)$ and its Fourier transform, the molecular displacement, it is convenient to use Eq. (46) as the bare phonon susceptibility, rather than Eq. (45).

The temperature dependent elastic constants follow from the phonon–phonon susceptibilities. This calculation has been detailed for the case of the cubic alkali cyanides.[13(d)] However, in view of the approximations made already in arriving at Eqs. (42) through (44) it perhaps suffices to assume that the dispersion relations involving the temperature dependent elastic constants c_{44} and c_{66} can be calculated from the same simplified equations as the bare elastic constants in Eqs. (43) and (44). The matrix problem involved in determining the renormalized elastic constants is then simplified considerably.

For example, for $\mathbf{q}$ along the [010] direction the phonon–phonon susceptibility for the TA phonon with polarization index $j = 3$ follows from Eq. (22) where the subscript 1 indicates a translational coordinate and the subscript 2 a rotational coordinate. The coupling strength $w(q_y)$ differs from $g(q_y)$ by a factor of $iq_y/\sqrt{m}$, as is seen from Eq. (41). With these considerations in mind one finds

$$\chi_{33}(q_y, \omega) = \{1/\chi^0_3(q_y, \omega) - [\,|g_{3,-1}(q_y)|^2 \chi^0(S_{2-1}) + |g_{3,-2}(q_y)|^2 \chi^0(S_{2-2})]\}^{-1} . \tag{47}$$

Here $\chi^0_3(q_y, \omega)$ is the bare phonon susceptibility, as given by Eq. (46) with $j = 3$ and $\omega^0_3(q_y)$ specified by Eq. (43). The orientational single-particle susceptibilities $\chi^0(S_{2-1})$ and $\chi^0(S_{2-2})$ are assumed to be independent of $\mathbf{q}$ and have a frequency dependence as illustrated in Figs. 1 and 2. The assumption of wave vector independence is equivalent to the assumption of Einstein modes for the librational oscillations. Hence $\chi^0(S_{2-1})$ and $\chi^0(S_{2-2})$ are calculated from Eq. (29) with Q equal to S_{2-1} and S_{2-2}, respectively. Expressions similar to Eq. (47) are found for the phonon–phonon susceptibilities $\chi_{33}(q_x, \omega)$ for $\mathbf{q}$ along [100] and $\chi_{11}(q_z, \omega)$ and $\chi_{22}(q_z, \omega)$ for $\mathbf{q}$ along [001].

The rotation-translation coupling coefficients $g_{jM}(q_y)$ can be rewritten in the manner of Eqs. (39). Then Eq. (47) becomes

$$\chi_{33}(q_y, \omega) = \{1/\chi^0_3(q_y, \omega) - A^2 \{[\omega^0_3(q_y)]^2/(3vc^0_{44})\} [\chi(S_{2-1}) + (C/A)^2 \chi(S_{2-2})]\}^{-1} . \tag{48}$$

The renormalized elastic constant c_{44} is calculated by taking the limit $\omega \to 0$ in Eq. (48) and defining

$$\rho[\omega_3(q_y)]^2 = c_{44} q_y^2 = \rho/\chi_{33}(q_y, 0) . \tag{49}$$

The result is

$$c_{44}/c^0_{44} = 1 - [A^2/(3vc^0_{44})][\chi(S_{2-1}) + (C/A)^2 \chi(S_{2-2})]\big|_{\omega=0} . \tag{50}$$

The calculations outlined in Sec. IV indicate that $\chi(S_{2-2})|_{\omega=0}$ is about a factor of 10^{-2} smaller than $\chi(S_{2-1})|_{\omega=0}$. The ratio C/A can be estimated from an earlier mean field theory as $C/A \cong -1.4$.[25] Unless that estimate is incorrect by at least an order of magnitude we can assume that the contribution of the S_{2-2} term to the renormalization of c_{44} is negligible. An examination of the temperature dependence of $\chi(S_{2-1})|_{\omega=0}$, as calculated using Eq. (29), shows that the representation

$$\chi(S_{2-1}) \propto (T - T_0)^{-1} \tag{51}$$

is a reasonably accurate representation over the temperature range of interest. If we ignore the S_{2-2} contribution and make the assumption [Eq. (51)] then one obtains the result

$$c_{44}/c^0_{44} = (T - T_1)/(T - T_0) . \tag{52}$$

The temperature dependence of the elastic constant c_{44} in *sym*-triazine, as measured by Brillouin scattering,[10] follows relation (52) with $T_1 = 180$ K and $T_0 = -759$ K. Other methods[9,26] seem to indicate a somewhat larger value of T_1. In the previous mean-field treatment of *sym*-triazine[9] the proportionality constant in Eq. (51) is $3/a_0$ and $T_1 = T_0 + A^2/(a_0/vc^0_{44})$. In the present calculations we calculate the rotational susceptibilities from Eq. (29). The volume per molecule v is introduced to allow the free energy [Eq. (23)] to have units of energy, rather, as is done conventionally, energy density. This is accomplished by letting $c^0_{\rho\sigma} \rightarrow vc^0_{\rho\sigma}$ in Eq. (23). The factor of 3 follows from the definitions (24). A similar result to Eq. (50) is obtained for c_{66},

$$c_{66}/c^0_{66} = 1 - [B^2/(3vc^0_{66})]\,[\chi(S_{21}) + (D/B)^2\,\chi(S_{22})]\big|_{\omega=0} \; . \qquad (53)$$

Neglecting the $\chi(S_{22})$ contribution results in

$$c_{66}/c^0_{66} = (T - T_2)/(T - T_0) \; . \qquad (54)$$

Brillouin scattering measurements[10] give $T_2 = 17$ K. The result $T_1 > T_2$ implies that $A^2/c^0_{44} > B^2/c^0_{66}$.

The most detailed measurement on *sym*-triazine to date is the temperature dependence of the neutron scattering intensity for TA phonons propagating along a^*_h and polarized along c^*_h.[22,26] Following previous approaches[13] it makes at least qualitative sense to compare the measured temperature dependence for these phonon groups with that calculated for the phonon–phonon correlation function

$$\mathcal{S}_{33}(\mathbf{q}, \omega) = 2\chi''_{33}(\mathbf{q}, \omega)/[1 - \exp(-\beta\omega)] \; . \qquad (55)$$

Here χ''_{33} is the imaginary part of the phonon–phonon susceptibility [Eq. (50)]. In the calculation of the correlation function (55) we treat the combination of parameters $A^2/(3vc^0_{44})$ as a single adjustable constant. This approach ensures that the effective elastic constant, as given by Eq. (50), has a temperature dependence in reasonable agreement with experiment,[10] i.e., Eq. (52). This is the only adjustable parameter in this model as the ratio C/A is estimated from previous work.[25]

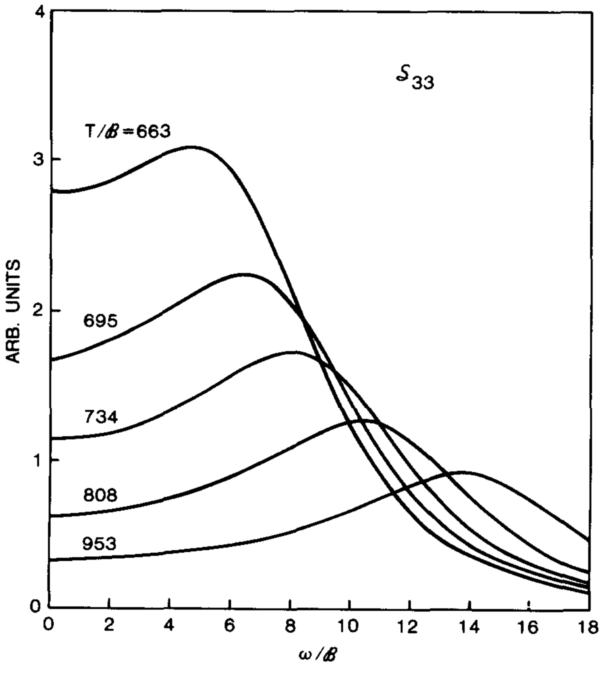

FIG. 3. Temperature and frequency dependence of the phonon–phonon correlation functions $\mathcal{S}_{33}$, as calculated in Sec. IV.

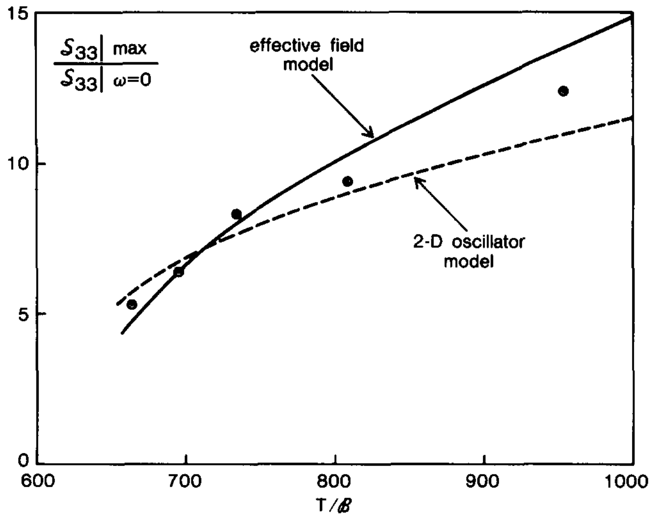

FIG. 4. Comparison of the temperature dependencies of the ratio: Neutron intensity maximum/neutron intensity at $\omega = 0$ from Ref. 26 (dots), $\mathcal{S}_{33}|_{\max}/\mathcal{S}|_{\omega=0}$ as calculated in Sec. VI (solid line), and as calculated in Sec. VII (dashed line).

Figure 3 shows the changes of the phonon–phonon correlation function $\mathcal{S}_{33}(q_y, \omega)$, as calculated from Eqs. (48) and (55) as the transition temperature is approached. Reduced frequency and temperature units are used. For *sym*-triazine the rotational constant is $\mathcal{B} = \hbar^2/(2I) \cong 0.2$ cm^{-1}. The reduced temperatures are equivalent to the temperatures of Fig. 2 of Ref. 26. Comparison of that figure with Fig. 3 of the present paper shows that good agreement in both the frequency and temperature dependences of $\mathcal{S}_{33}$ and the measured phonon groups is found. The calculated spectra at low frequencies clearly show a softening of this TA phonon with no central peak. This implies that at low frequencies one is in a regime of fast relaxation of orientations.[17] Another way to compare the theoretical and neutron scattering results is to plot the temperature dependence of the ratio of the maximum in the neutron intensity to its value at $\omega = 0$ with the ratio $\mathcal{S}_{33}|_{\max}/\mathcal{S}_{33}|_{\omega=0} = 0$. The results are shown in Fig. 4. Again, good agreement is found.

The other coupled correlation functions are calculated in the same manner. As examples we show plots of $\mathcal{S}(S_{21}, S_{21})$ and $\mathcal{S}(S_{22}, S_{22})$ for two temperatures in Figs. 5 and 6, respectively. For *sym*-triazine $T/\mathcal{B} = 1000$ corresponds to $T = 309$ K. It is seen that the peaks of the correlation functions shift only very slightly over a rather large temperature range. This is in agreement with the relative temperature independence of the Raman-active librational modes.[27,28] These librational modes are represented by Einstein modes in the present model. It should be kept in mind that the present approach makes no corrections for thermal expansion. This latter effect tends to produce a decrease in the librational frequencies with increasing temperatures apart from any effect due to orientational anharmonicities as specified in Eq. (23). The measured librational frequencies include both the influence of thermal expansion and anharmonicity in the orienting potential. These competing contributions are of opposite sign and can lead to observed Raman frequencies which are almost

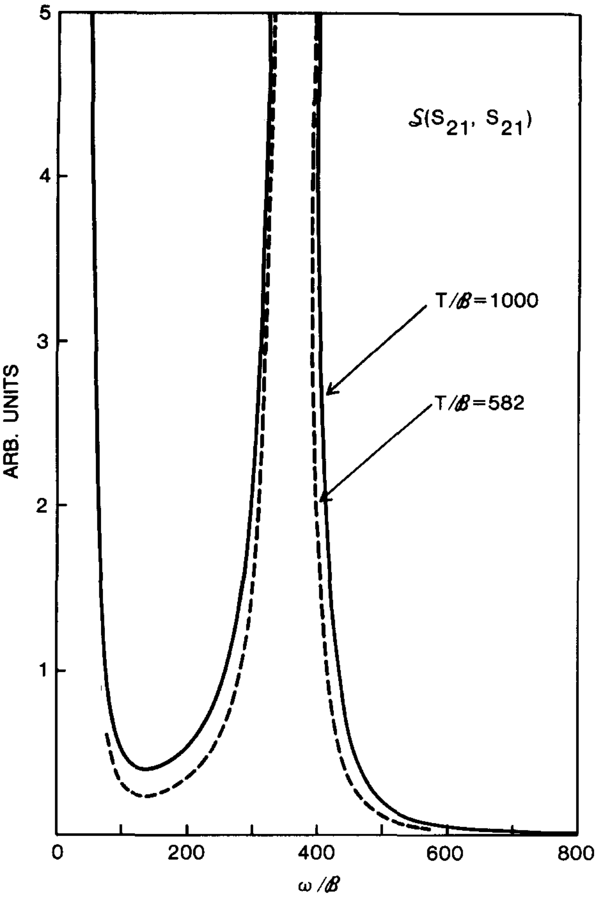

FIG. 5. Temperature and frequency dependence of the correlation function $s(S_{21}, S_{21})$, as calculated in Sec. VI.

independent of temperature. This seems to occur in both chloranil[6] and *sym*-triazine.[27,28]

VII. TWO-DIMENSIONAL OSCILLATOR MODEL

In contrast to the alkali cyanides,[13-16] for which the potential wells are fairly shallow when compared to k_BT, the orienting potential (28) in *sym*-triazine is extremely strong. Hence the orientational motions are librations about well-defined equilibrium orientations rather than hindered rotations. Thus, an alternative approach to the classical model of Sec. IV is to treat the librations as anharmonic oscillations. The Raman spectrum of *sym*-triazine in the high temperature phase shows two E_g modes.[27,28] The lower frequency modes, around 67.5 cm^{-1} at $T = 300$ K, are mainly rotational and the higher frequency modes, around 91.4 cm^{-1} at $T = 300$ K, are mainly translational in character.[20] For the coupling between these optic modes and the acoustic phonon modes we propose the following model: The coupling to the lower frequency optic modes is essentially the same as the rotation-translation coupling described in Sec. V. We neglect the coupling of the acoustic phonons to the higher optic mode, but use the average phonon frequency as an adjustable parameter. Einstein modes with no **q** dispersion are assumed for the lower E_g modes.

The energy level of an anharmonic librational oscillator in a trigonal field have been worked out within the framework of first-order perturbation theory by Smith.[23] The result is

$$E(n_1, n_2) = E_0 + \omega_0(n_1 + n_2 + 1) + \Delta(3n_1^2 + 3n_2^2 + 4n_1n_2 + 5n_1 + 5n_2 + 4) ,$$

$$n_1, n_2 = 0, 1, 2, \ldots \; . \tag{56}$$

In terms of the trigonal potential coefficients, as defined in Eq. (28) one has

$$\omega_0 = \sqrt{2\mathcal{B}a} \tag{57}$$

and

$$\Delta = \tfrac{1}{2}(\mathcal{B}/\omega_0)^2 c \; . \tag{58}$$

Using the values of the parameters chosen in Secs. IV and VI one obtains $\omega_0/\mathcal{B} = 338$ and $\Delta/\mathcal{B} = 0.72$. Here again we are using units with $\hbar = 1$.

The generalized susceptibility of the two-dimensional oscillator with energy levels defined by Eq. (56) can be calculated from Eqs. (13) and (15), where Q stands for S_{2-1}, S_{21}, S_{2-2}, and S_{22}. The linear response function (13) is

$$K(t) = \frac{i}{Z} \sum_{n_1n_2} \exp[-\beta E(n_1, n_2)] \langle n_1n_2 | \exp(i\mathcal{H}t)Q \exp(-i\mathcal{H}t)Q - Q \exp(i\mathcal{H}t)Q \exp(-i\mathcal{H}t) | n_1n_2 \rangle , \tag{59}$$

where the partion function is

$$Z = \sum_{n_1n_2} \exp[-\beta E(n_1, n_2)] \; . \tag{60}$$

Two cases are of interest here. The first is $Q = S_{21} = \sqrt{3}\, xz$. For small amplitude librational oscillations $x \ll z \cong 1$. Hence we may approximate $S_{21} \cong \sqrt{3}\, x$. The approach outlined in Sec. II then gives for the orientational susceptibility to first order

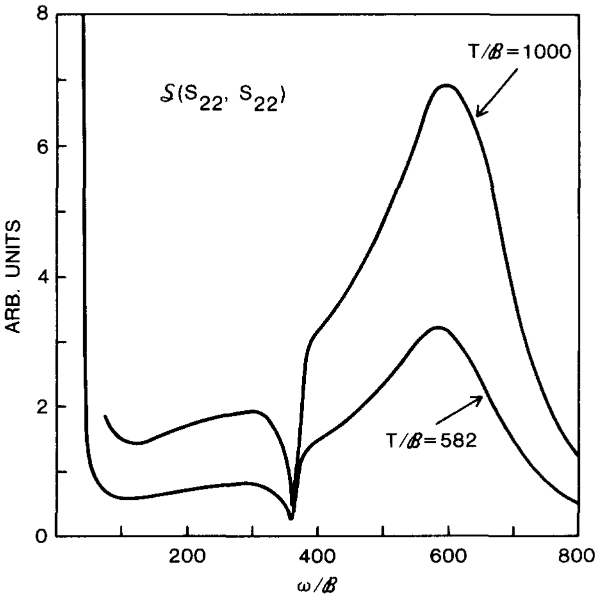

FIG. 6. Temperature and frequency dependence of the correlation function $s(S_{22}, S_{22})$, as calculated in Sec. VI.

$$\chi^0(\sqrt{3}\ x) = -6(2I\omega_0 Z)^{-1} \sum_{n_1 n_2} \exp[-\beta E(n_1, n_2)] \times \sum_{j=1}^{2} N_j(n_1, n_2)\, \Delta\omega_j / [(\Delta\omega_j)^2 - (\omega + i\gamma)^2] , \qquad (61)$$

where $N_1(n_1, n_2) = n_1 + 1$, $N_2(n_1, n_2) = n_1$ and

$$\Delta\omega_1 = -\omega_0 - 2\Delta(3n_1 + 2n_2 + 4) , \quad \Delta\omega_2 = \omega_0 + 2\Delta(3n_1 + 2n_2 + 1) ,$$

and γ is a librational damping constant. A similar result is obtained for $\chi^0(\sqrt{3}\ y)$. The other case of interest has $Q = \sqrt{3}\ xy$. Here the result for the orientational susceptibility is, again to first order,

$$\chi^0(\sqrt{3}\ xy) = -6(4I^2\omega_0^2 Z)^{-1} \sum_{n_1 n_2} \exp[-\beta E(n_1, n_2)] \times \sum_{j=1}^{4} N_j(n_1, n_2)\, \Delta\omega_j / [(\Delta\omega_j)^2 - (\omega + i\gamma)^2] , \qquad (62)$$

where

$$N_1(n_1, n_2) = (n_1 + 1)(n_2 + 1) , \quad N_2(n_1, n_2) = n_1(n_2 + 1) ,$$

$$N_3(n_1, n_2) = (n_1 + 1) n_2 , \quad N_4(n_1, n_2) = n_1 n_2 ,$$

and

$$\Delta\omega_1 = -2\omega_0 - 10\Delta(n_1 + n_2 + 2) , \quad \Delta\omega_2 = -2\Delta(1 - n_1 + n_2) ,$$

$$\Delta\omega_3 = -2\Delta(1 + n_1 - n_2) , \quad \Delta\omega_4 = 2\omega_0 + 10\Delta(n_1 + n_2) .$$

The calculation for $\chi^0[\frac{1}{2}\sqrt{3}\ (x^2 - y^2)]$ follows in the same manner.

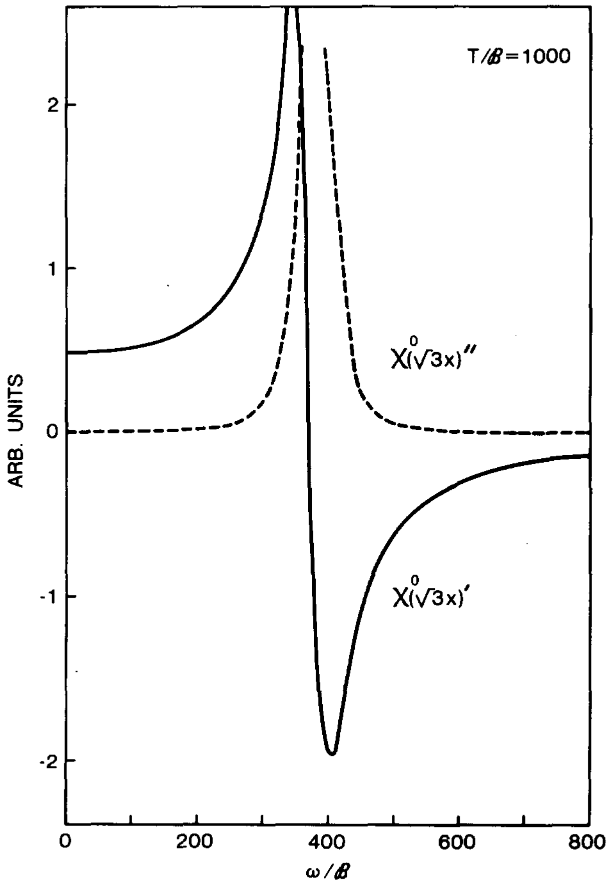

FIG. 7. Real and imaginary parts of the librational oscillator susceptibility $\chi^0(\sqrt{3}\ x) = \chi^0(\sqrt{3}\ x)' + i\chi^0(\sqrt{3}\ x)''$, as calculated in Sec. VII.

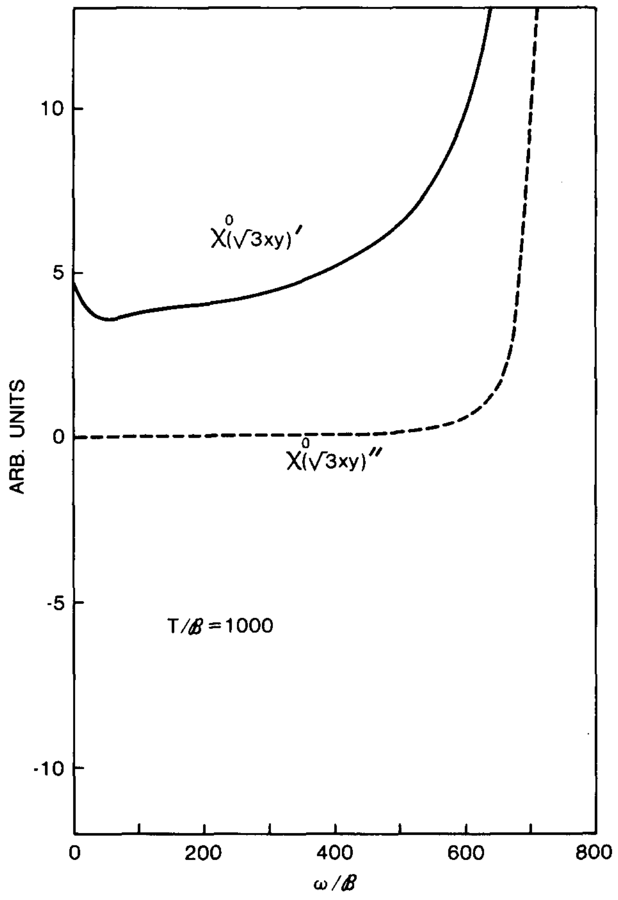

FIG. 8. Real and imaginary parts of the librational oscillator susceptibility $\chi^0(\sqrt{3}\ xy) = \chi^0(\sqrt{3}\ xy)' + i\chi^0(\sqrt{3}\ xy)''$, as calculated in Sec. VII.

The frequency dependence of the calculated orientational susceptibilities $\chi^0(\sqrt{3}\ x)$ and $\chi^0(\sqrt{3}\ xy)$ are shown in Figs. 7 and 8. Comparison with Figs. 1 and 2 show that the behavior of these generalized susceptibilities are very similar to $\chi^0(S_{21})$ and $\chi^0(S_{22})$, respectively, as calculated using the classical methods of Sec. IV. The coupled susceptibilities are calculated in the same manner as in Sec. VI, except that $\chi^0(\sqrt{3}\ x)$ and $\chi^0(\sqrt{3}\ xy)$ are substituted for $\chi^0(S_{2-1})$ and $\chi^0(S_{2-2})$ in expressions such as Eq. (48). The phonon–phonon correlation $\mathcal{S}_{33}$ calculated in this manner is shown in Fig. 9 for the same range of temperatures as in Fig. 3. In the calculation of the rotational susceptibilities we use the same value of $A^2/(3vc_{44}^0)$ as in Sec. VI and choose $\omega_0/\mathcal{B} = 338$, $\Delta/\mathcal{B} = 0.84$, and $\gamma = 12\Delta$. It is seen from a comparison of Figs. 3 and 9 that although the behavior of $\mathcal{S}_{33}$ is slightly different for the two approaches, the fit of the neutron scattering results[26] is reasonably good. The results for the ratio $\mathcal{S}_{33}|_{\max}/\mathcal{S}_{33}|_{\omega=0}$ are shown in Fig. 4 together with the predictions of Sec. VI and the experimental results.

VIII. DISCUSSION

Two mean field approaches to the structural phase transition in *sym*-triazine have been described. The first approach is based on a classical description of an orienting molecule in an anharmonic effective field,

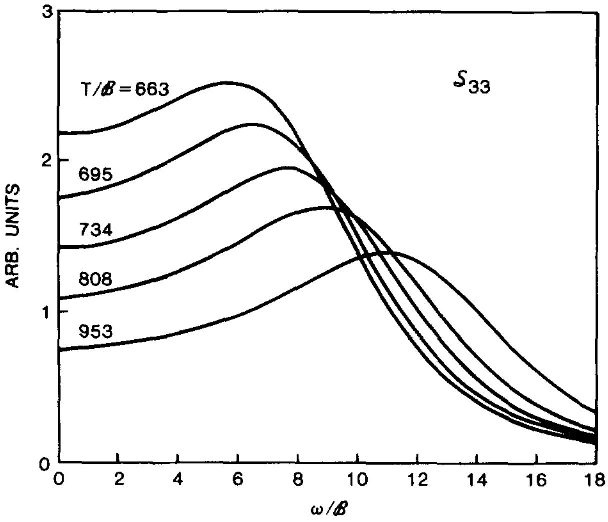

FIG. 9. Temperature and frequency dependence of the phonon-phonon correlation function s_{33}, as calculated in Sec. VII.

first developed by de Raedt and Michel.[12] The other is based on a two-dimensional harmonic oscillator model developed by Smith for linear molecules in a trigonal field.[23] A third approach, which would use a quantum mechanical description of the hindered rotator levels in terms of symmetry-adapted spherical harmonics,[23] was not used, although many of the details have been worked out.[29]

The advantage of the present approach over the more general theories of ferroelastic transitions[13(a)–13(d)] is that the mean field methods introduced in Sec. II lead in a straightforward manner to an approximate expression for the coupled susceptibilities in terms of the single particle rotational and translational susceptibilities. An approach developed by de Raedt and Michel[12] is central to the calculation of the single particle susceptibility in one approach and a coupled oscillator model is used for another. These different methods are shown to lead to very similar results and are found to be consistent with Brillouin[10] and neutron scattering[26] measurements.

Our approach basically assumes a very strong but slightly anharmonic orientational potential well for *sym*-triazine. The orientational motions of the molecules are then essentially librations. The temperature dependence of the librational frequencies observed in Raman scattering[27,28] is a consequence of both the anharmonicity of the orienting potential and the thermal expansion of the lattice. In the case of *sym*-triazine it is reasonable to assume that a slight softening of the Raman frequencies due to the anharmonicity of the orienting potential is more or less cancelled by a stiffening due to lattice contraction as the temperature is decreased.

The assumption of anharmonicity of the orientational potential together with a coupling between the molecular orientations and lattice strains explains the q dependence of the observed softening of the acoustic phonon modes.[10] In addition, it gives a qualitative explanation of the frequency and temperature dependence of the TA phonon groups observed with inelastic neutron scattering.[26]

This approach to the structural transition in *sym*-triazine has been criticized by Rae who has offered an alternative approach based on the quasiharmonic approximation.[30] Nonetheless, Rae's method has been shown by two of us[31] to give the same results as the previous Landau theory approach,[9] although there may be some differences in the definitions of the bare coordinates. The present approach, as well as the previous Landau theory,[9] have the advantage of being able to describe the coupling of the molecular orientations to more than just a single strain. On the other hand, Rae's theory, in its present form, can only describe the temperature dependence of a single acoustic soft mode.

Finally, a comment on Rae's last criticism of our approach relating to paragraph (iii) of his Appendix.[30] While the practice of expressing the orientational order parameters in terms of a power series in the strains, the principal order parameters, will probably not always lead to exact results, it is nonetheless reasonably common practice when approaching rather clumsy, nonlinear problems of this type.[32] This is especially true when the coefficients of this expansion are accessible to experiment, as is the case for *sym*-triazine. Hence, rather than solve a system of nonlinear equations,[32] it is often preferable to consider such a relation as established and to introduce it into the equilibrium conditions to obtain relations between the expansion coefficients.

[1] J. C. Toledano, Phys. Rev. B 20, 1147 (1979).

[2] J. Sapriel, A. Boudou, and A. Perigaud, Phys. Rev. B 19, 1484 (1979).

[3] R. Vacher, M. Boissier, and J. Sapriel, Phys. Rev. B 23, 215 (1981).

[4] A. Yoshihara, W. D. Wilber, E. R. Bernstein, and J. C. Raich, J. Chem. Phys. 76, 2064 (1982).

[5] W. D. Ellenson and J. K. Kjems, J. Chem. Phys. 67, 3619 (1977).

[6] A. Girard, Y. Delugeard, C. Ecolivet, and H. Cailleau, J. Phys. C 15, 2127 (1982).

[7] C. Ecolivet, Solid State Commun. 40, 503 (1981).

[8] J. L. Baudour, Y. Delugeard, H. Cailleau, and M. Sanquer, Acta Crystallogr. B 37, 1553 (1981).

[9] (a) J. C. Raich and E. R. Bernstein, J. Chem. Phys. 73, 1955 (1980); (b) A. Yoshihara, C. L. Pan, E. R. Bernstein, and J. C. Raich, *ibid.* 76, 3218 (1982).

[10] (a) D. R. Fredkin and N. R. Werthamer, Phys. Rev. A 138, 1527 (1965); (b) W. Brenig, Z. Phys. 171, 60 (1963).

[11] A. Hüller and J. C. Raich, J. Chem. Phys. 77, 2038 (1982).

[12] B. de Raedt and K. H. Michel, Phys. Rev. B 19, 767 (1979).

[13] (a) E. Courtens, J. Phys. Lett. 37, 21 (1976); (b) K. H. Michel and J. Naudts, Phys. Rev. Lett. 39, 212 (1977); J. Chem. Phys. 67, 547 (1977); (c) K. H. Michel and J. Naudts, *ibid.* 68, 216 (1978); (d) B. deRaedt, K. Binder, and K. H. Michel, *ibid.* 75, 2977 (1981).

[14] S. W. Lovesey, *Dynamic Correlations* (Benjamin, New York, 1980).

[15] D. Sahu and S. D. Mahanti, Phys. Rev. Lett. 48, 936 (1982).

[16] D. Sahu and S. D. Mahanti, Phys. Rev. B 26, 2981 (1982).

[17] Y. Yamada, H. Takatera, and D. L. Huber, J. Phys. Soc. Jpn. 36, 641 (1974).

[18] Y. Yamada, J. Phys. Soc. Jpn. 50, 2996 (1981).

[19] F. Mulder, G. van Dijk, and C. Huiszoon, Mol. Phys. 38,

577, 1497 (1979).

[20] T. Luty (unpublished work).

[21] Z. Gamba and H. Bonadee, J. Chem. Phys. 75, 5059 (1981).

[22] In Ref. 9 the twofold axis of symmetry is chosen along the y axis. This choice agrees with the conventional choice of axes for the *sym*-triazine molecule. It, however, does not agree with the conventional choice of axes for the elastic constant matrix, as, for example, in J. F. Nye, *Physical Properties of Crystals* (Oxford, 1957) where the twofold axis of symmetry is chosen along x. Here we follow the convention of Ref. 9.

[23] D. Smith, J. Chem. Phys. 76, 1445 (1982).

[24] J. C. Raich and E. R. Bernstein, Chem. Phys. Lett. 82, 138 (1981).

[25] J. C. Raich, A. Yoshihara, and E. R. Bernstein, Mol. Phys. 45, 197 (1982).

[26] I. U. Heilman, W. D. Ellenson, and J. Eckert, J. Phys. C 12, L185 (1979).

[27] S. J. Daunt, H. F. Shurvell, and L. Pazdernik, J. Raman Spectrosc. 4, 205 (1975).

[28] G. R. Elliot and Z. Iqbal, J. Chem. Phys. 63, 1914 (1975).

[29] H. Yasuda and J. C. Raich, Mol. Phys. 47, 647 (1982).

[30] A. I. M. Rae, J. Phys. C 15, 1883 (1982); 287 (1982).

[31] J. C. Raich and E. R. Bernstein, J. Phys. C 15, 283 (1982).

[32] See, for example, E. Courtens and R. W. Gammon, Phys. Rev. B 24, 3890 (1981).