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Correlation-function description of the ac orientational Kerr susceptibility of plastic crystals

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An expression is derived for the optical-field-induced birefringence due to molecular reorientations in cubic plastic crystals. The effect is described by a nonlinear susceptibility tensor shown to be proportional to a tensorial correlation function. For most cubic point groups this correlation function has only two independent components. A decomposition into irreducible tensorial sets leads to the two physically meaningful quantities. One is labeled the tensor strength. It measures the short-range angular correlation of molecular pairs. It is a susceptibility that increases as this range increases, i.e., as the plastic-solid phase transition is approached. The second quantity is labeled the tensor anisotropy. It measures the long-range cubic anisotropy of the molecular orientations. It is related to an orientational order parameter of the plastic-liquid transition.

I. INTRODUCTION

Plastic crystals are molecular solids in which the molecules are arranged in a regular lattice but have a great freedom of orientational motion.[1] These substances can easily be plastically deformed, which justifies their name.[2] This phase of matter is intermediate between the liquid phase, which has translational freedom, and the true solid phase, in which molecules are rigidly and regularly positioned (except for the effect of phonons, of course). Plastic mesophases are characterized by a low entropy of fusion (typically of the order of $2k_B$ per molecule, or even smaller),[3] a relatively high melting point, small elastic constants,[4] and, for those substances composed of polar molecules, by a large dielectric constant and a rapid dielectric relaxation time more characteristic of liquids than of solids.[5] The plastic-crystal lattice is usually of high symmetry.[6] Though the molecular point group can be of rather low symmetry, there is most often only one molecule per lattice point. All this is made possible by the constant reorientation of the constituent molecules. This motion is exhibited in x-ray diffraction patterns, which are extremely diffuse because of the large Debye-Waller factor.[6,7] It is also seen in NMR through the motional narrowing of resonance lines, very much like in liquids.[8] The plastic mesophase is common for organic substances composed of "globular" molecules. If these molecules, in spite of being globular, are also optically anisotropic, a depolarized wing is observed in Rayleigh scattering due to anisotropy fluctuations.[9] This component of the scattered light can be rather large. In those cases, a large ac Kerr effect is also expected, and this was recently confirmed experimentally.[10]

The purpose of the present paper is to describe the properties of the orientational contribution to the ac Kerr susceptibility tensor $\tilde{\chi}^{\mathrm{NL}}$. This tensor is defined in terms of the dielectric tensor $\tilde{\epsilon}$ by

$$\epsilon_{ij} = \epsilon_p \delta_{ij} + 4\pi\chi^{\mathrm{NL}}_{ijkl} F_k F_l + \cdots . \tag{1}$$

Here ϵ_p is the linear dielectric constant at the frequency of the probing field $\vec{E}$, δ_{ij} is the Kronecker symbol, and $\vec{F}$ is the strong, orienting laser field. It is assumed from the outset that the crystal has cubic symmetry, as this is by far the most common occurrence. In Eq. (1), the magnitude of the linearly polarized field $\vec{F}$ can be taken as $1/\sqrt{2}$ times the field amplitude. This is justified, as the treatment applies to systems whose orientational response times are much slower than the optical period. The same remark applies to all expressions in Sec. II. Using a formalism in the spirit of that developed by Kubo for the study of response functions,[11] the nonlinear susceptibility is expressed in terms of a correlation function of the anisotropic part of the molecular polarizabilities. This tensorial correlation function is then decomposed into irreducible tensorial sets.[12] For crystals with fourfold symmetry axes, two such sets are found. One can be designated as the tensor strength; it measures the amount of short-range angular correlation of the molecules. This cooperative ordering is being probed by the application of the orienting optical field $\vec{F}$. The response is a generalized susceptibility which is expected to become large near the plastic-solid phase transition, since the transition to the true solid is accompanied by the onset of long-range orientational order. The other irreducible tensorial set is shown to be related to the long-range anisotropy of molecular orientations in the plastic phase. This emphasizes that there is a certain form of orientational order in that phase. The liquid-plastic transition must in fact be characterized both by long-range translational order and by long-range anisotropic ordering of the molecular orientations. These are two distinct order parameters. Measurements, available so far on one substance, show considerable pretransitional effects on the long-range anisotropy, and suggest that this order is essential to the stability of the plastic phase.[10]

The measurement of the ac Kerr effect is a new tool for the investigation of the plastic crystalline mesophase and of its transitions to the liquid and to the solid. It is able to yield important information that was not so far acquired by other techniques. Inasmuch as there is great current interest in the understanding of melting, studies of plastic crystals and of their phase transitions are very apropos. Indeed these are systems in which the two processes of orientational and translational melting occur sequentially, at least in first approximation. This is similar to the situation in liquid crystals, except that in the latter case the sequential order is reversed. The fact that properties related to long-range orientational ordering are usually more dramatic than those related to long-range translational ordering might explain why so much attention has been given to liquid crystals as opposed to the plastic ones. The point of the present technique is to measure short-range orientational order and long-range anisotropy of this order.

The remainder of the paper is organized as follows. In Sec. II, general thermodynamical arguments are used to derive an expression for the orientational part, and for the nonlinear polarizability part, of the Kerr susceptibility tensor. The orientational part is found to be proportional to a tensorial correlation function. The symmetries of the distribution function entering this correlation function are analyzed in Sec. III. Based on this analysis the correlation function is decomposed into its irreducible tensorial set components in Sec. IV. The physical interpretation of the components is discussed in Sec. V.

II. ac KERR SUSCEPTIBILITY AS A CORRELATION FUNCTION

An expression is derived for the ac Kerr susceptibility. The molecular reorientation is produced by a strong optical field $\vec{F}$ at frequency ω_0, and is probed by a weak field $\vec{E}$ at a different frequency ω_p. The frequency difference $|\omega_0 - \omega_p|$ is assumed to be much greater than the inverse of the orientational relaxation time, so that these fields do not have cross terms contributing to the nonlinearity.[13] The medium is assumed to be transparent to both ω_0 and ω_p. The optical dielectric tensor will be calculated by taking averages of sums over bond polarizabilities[14] and proceeding to the appropriate local-field corrections. The averaging process is represented symbolically as a trace (tr) over a density matrix ρ.[15] In problems where only molecular reorientations are involved, ρ is an orientational distribution function that contains all angular coordinates of the moving molecular segments, and the tracing is in fact an integration over all these coordinates. In these problems the sum over bond polarizabilities can usually be made in two steps. First, one sums over each rigid molecular segment (these can be entire molecules in the absence of isomer formation); second, these segment polarizabilities are integrated over the distribution function, and a sum is taken over all segments. The total number of segments (which need not be all identical) in a sample of volume V is designated by $\mathfrak{N}$; the number per unit volume is $N = \mathfrak{N}/V$. The polarizability of segment a, for a probing field at frequency ω, and in the presence of $\vec{F}$, is designated by $\overleftrightarrow{\alpha}^a(\omega, \vec{F}^{\,\mathrm{loc}})$, where $\vec{F}^{\,\mathrm{loc}}$ is the local field corresponding to $\vec{F}$. The remainder of this section is organized as follows: (i) the reader is reminded of general statistical mechanical results for ρ, and an expansion of $\rho(\vec{F})$ is obtained; (ii) an expression is derived for $\overleftrightarrow{\chi}^{\mathrm{NL}}$ in terms of a sum over segments, taking into account local-field effects; (iii) these results are combined to yield an expression for $\overleftrightarrow{\chi}^{\mathrm{NL}}$ in terms of a correlation function of polarizabilities.

The free energy of a system whose Hamiltonian is $\mathcal{H}$ and whose temperature is T can be written

$$\mathfrak{F} = \mathrm{tr}(\rho\mathcal{H}) + k_B T\, \mathrm{tr}(\rho \ln \rho). \tag{2}$$

Minimization of $\mathfrak{F}$ with respect to variations $\delta\rho$ subject to the constraint $\mathrm{tr}\rho = 1$ leads to

$$\rho = e^{-\beta\mathcal{H}}/\mathrm{tr}\, e^{-\beta\mathcal{H}}, \tag{3}$$

where $\beta = 1/k_B T$. If $\mathcal{H}$ depends on a field $\vec{F}$, ρ can be expanded as

$$\rho(\vec{F}) = \rho_0 + \left(\frac{\partial\rho}{\partial F_i}\right)_{\vec{F}=0} F_i + \frac{1}{2}\left(\frac{\partial^2\rho}{\partial F_i \partial F_j}\right)_{\vec{F}=0} F_i F_j + \cdots. \tag{4}$$

The expressions for the derivatives of ρ are easily obtained from Eq. (3), and are given in Appendix A. In the present case

$$\mathcal{H} = \mathcal{H}_0 - \int dV \int \vec{F} \cdot d\vec{P}, \tag{5}$$

where $\mathcal{H}_0$ is the Hamiltonian in the absence of field, $\vec{P}$ is the polarization produced by $\vec{F}$, and the first integral is over the sample volume. Again, in such expressions, the use of peak amplitude divided by $\sqrt{2}$ is implied for $\vec{F}$ and $d\vec{P}$. The polarization increment is written in terms of the polarizabilities and of the local field

$$d\vec{P} = \sum_N \vec{\alpha}^a(\omega_0, \vec{F}^{\rm loc}) \cdot d\vec{F}^{\rm loc}, \tag{6}$$

where the sum is over all segments a in the unit volume. Strictly, one should also allow for a stress dependence of $\vec{\alpha}^a$, and the strain-stress dependence of $\mathcal{H}_0$ should be exhibited. This would allow the calculation of electrostriction.[16] This problem will not be tackled here, and the results will be restricted to the orientational plus nonlinear polarizability contributions to the ac Kerr effect. As the nonlinearities are additive in first order, the electrostrictive contribution could simply be added later to the present result. The local field $\vec{F}^{\rm loc}$ is calculated as for an isotropic solid; this is appropriate for a cubic material. Corrections to $\vec{F}^{\rm loc}$ due to the dielectric tensor anisotropy induced by $\vec{F}$ contribute to fourth-order $\vec{F}$ terms in $\mathcal{H}$ which need not be considered here. Hence[17]

$$\vec{F}^{\rm loc} = \vec{F} + \tfrac{4}{3}\pi\kappa_0 \vec{F}^{\rm loc} = \tfrac{1}{3}(\epsilon_0 + 2)\vec{F}, \tag{7a}$$

with

$$\kappa_0 \delta_{ij} = {\rm tr}\Big(\rho_0 \sum_N \alpha^a_{ij}(\omega_0, 0)\Big), \tag{7b}$$

where ϵ_0 is the linear dielectric constant at ω_0; in (7b) use has been made of the cubic symmetry of the solid. One notes that (7a) leads to the usual Clausius-Mossotti result[18]

$$\epsilon_0 = \frac{1 + \frac{8}{3}\pi\kappa_0}{1 - \frac{4}{3}\pi\kappa_0}\,. \tag{7c}$$

Using the last equality in Eq. (7a), Eq. (5) is rewritten

$$\mathcal{H} = \mathcal{H}_0 - L_0 \int \vec{F} \cdot \sum_a \vec{\alpha}^a(\omega_0, \vec{F}^{\rm loc}) \cdot d\vec{P}, \tag{8}$$

where L_0 is the Lorentz-Lorenz factor $\frac{1}{3}(\epsilon_0 + 2)$, and the summation is over all segments in the entire sample. This expression allows calculation of the derivatives entering in Eq. (4) (Appendix A), leading to the result

$$\rho(\vec{F}) = \rho_0 + \tfrac{1}{2}\beta\rho_0 L_0 \sum_a \{\alpha^a_{ij}(\omega_0, 0) - {\rm tr}[\rho_0 \alpha^a_{ij}(\omega_0, 0)]\} F_i F_j + \cdots. \tag{9}$$

The macroscopic polarization produced by the probing field is

$$P_i(\omega_p) = \sum_N {\rm tr}[\rho(\vec{F})\, \alpha^a_{ij}(\omega_p, \vec{F}^{\rm loc})]\, E^{\rm loc}_j, \tag{10}$$

where $\vec{E}^{\rm loc}$ is the local field corresponding to $\vec{E}$. One defines

$$\kappa_p \delta_{ij} + \kappa^{\rm NL}_{ij} \equiv \sum_N {\rm tr}[\rho(\vec{F})\, \alpha^a_{ij}(\omega_p, \vec{F}^{\rm loc})]. \tag{11}$$

The linear part $\kappa_p \delta_{ij}$ is defined in a similar manner to Eq. (7b). The relation between $\vec{\chi}^{\rm NL}$ in Eq. (1) and $\vec{\kappa}^{\rm NL}$ in Eq. (11) will now be derived. To this effect, one notes that

$$E^{\rm loc}_i = E_i + \tfrac{4}{3}\pi P_i(\omega_p) = E_i + \tfrac{4}{3}\pi(\kappa_p \delta_{ij} + \kappa^{\rm NL}_{ij}) E^{\rm loc}_j. \tag{12}$$

Using the fact that $\kappa^{\rm NL}_{ij}$ is small compared to $(1 - \frac{4}{3}\pi\kappa_p)\delta_{ij}$, this relation can be inverted, giving

$$E^{\rm loc}_j = [(1 - \tfrac{4}{3}\pi\kappa_p)^{-1}\delta_{ij} + (1 - \tfrac{4}{3}\pi\kappa_p)^{-2}\tfrac{4}{3}\pi\kappa^{\rm NL}_{ij} + \cdots] E_i\,. \tag{13}$$

This is introduced in Eq. (10), and the result is replaced in $\epsilon_{ij} E_j = E_i + 4\pi P_i(\omega_p)$, where ϵ_{ij} is given by Eq. (1). The field-independent terms lead to the Clausius-Mossotti relation between ϵ_p and κ_p. The nonlinear terms give

$$\chi^{\rm NL}_{ijkl} F_k F_l + \cdots = L_p^2 \kappa^{\rm NL}_{ij} + \cdots, \tag{14}$$

where $L_p = \frac{1}{3}(\epsilon_p + 2)$.

It now remains to introduce Eq. (9) in Eq. (11), and Eq. (11) in Eq. (14), to obtain the desired result. Before doing this, it is useful to expand $\vec{\alpha}^a(\omega_p, \vec{F}^{\rm loc})$,

$$\alpha^a_{ij}(\omega_p, \vec{F}^{\rm loc}) = \alpha^a_{ij}(\omega_p, 0) + L_0 \alpha^a_{ijk}(\omega_p, \omega_0) F_k + \tfrac{1}{2} L_0^2 \alpha^a_{ijkl}(\omega_p, \omega_0, -\omega_0) F_k F_l + \cdots, \tag{15a}$$

where

$$\alpha^a_{ijk}(\omega_p, \omega_0) = \left(\frac{\partial \alpha^a_{ij}(\omega_p, \vec{F}^{\rm loc})}{\partial F^{\rm loc}_k}\right)_{\vec{F}=0}, \tag{15b}$$

and

$$\alpha^a_{ijkl}(\omega_p, \omega_0, -\omega_0) = \left(\frac{\partial^2 \alpha^a_{ij}(\omega_p, \vec{F}^{\rm loc})}{\partial F^{\rm loc}_k \partial F^{\rm loc}_l}\right)_{\vec{F}=0}. \tag{15c}$$

The tensor (15b) is allowed for noncentrosymmetric molecules as their response to an ac field can be fast and need not be symmetric. However, the averaging over ρ and N involved in Eq. (11) cancels the linear terms in $\vec{F}$ that appear in (15a). This results from the over-all cubic symmetry. To express the final result of the calculation it is convenient to define

$$A^a_{ij}(\omega) \equiv \alpha^a_{ij}(\omega, 0) - {\rm tr}[\rho_0 \alpha^a_{ij}(\omega, 0)]. \tag{16}$$

$\vec{A}^a$ is a traceless second-order tensor which represents the anisotropic part of the molecular (or segment) polarizability. Proceeding to the required substitutions, and taking note of $\sum_N = (N/\mathfrak{N})\sum_a$, one finally obtains

$$\chi^{\mathrm{NL}}_{ijkl} = (\chi^{\mathrm{NL}}_{ijkl})_O + (\chi^{\mathrm{NL}}_{ijkl})_{\mathrm{NL}P}, \tag{17a}$$

with

$$(\chi^{\mathrm{NL}}_{ijkl})_O = \mathrm{N}\mathrm{L}_p^2 L_0 \beta G_{ijkl}, \tag{17b}$$

where

$$G_{ijkl} = \frac{1}{2\mathfrak{N}} \sum_{a,b} \mathrm{tr}[\rho_0 A^a_{ij}(\omega_p) A^b_{kl}(\omega_0)], \tag{17c}$$

and

$$(\chi^{\mathrm{NL}}_{ijkl})_{\mathrm{NL}P} = \tfrac{1}{2} L_p^2 L_0^2 \sum_N \mathrm{tr}[\rho_0 \alpha^a_{ijkl}(\omega_p, \omega_0, -\omega_0)]. \tag{17d}$$

Equation (17a) reflects the fact that the nonlinearities are additive in first order; the subscript O refers to nonlinearities of orientational origin, and the subscript NLP to those arising from the nonlinear polarizability of the molecules. The tensor $\overleftrightarrow{\mathrm{G}}$ is a correlation function of the anisotropic part of the segment polarizabilities; the summation over a and b in (17c) is a summation over all $\mathfrak{N}^2$ segment pairs in the entire sample volume. In spite of this, the magnitude of $\overleftrightarrow{\mathrm{G}}$ is not of order $\mathfrak{N}$ but of order 1, the reason being that the contribution of distant uncorrelated segment pairs is zero, as shown in the following sections. The result (17d) is well known.[19] One should observe that the Lorentz-Lorenz factor L_0 occurs with first power in (17b), and is squared in (17d). Some nonlinear mechanisms have been neglected in the derivation. The main ones are electrostriction and the local-field variation from site to site. The latest is known to contribute to about 50% of the nonlinearity in CCl_4.[20] However, the nonlinearity in CCl_4 is about an order of magnitude smaller than that in a typical plastic crystal succinonitrile.[10]

The remainder of the paper is devoted to a study of the orientational contribution $(\overleftrightarrow{\chi}^{\mathrm{NL}})_O$ and, in particular, of the transformation properties of the distribution function $\overleftrightarrow{\mathrm{G}}$. For a crystal belonging to any cubic group with fourfold symmetry one finds only three types on nonzero components in $\overleftrightarrow{\mathrm{G}}$. These are G_{1111}, G_{1122}, and G_{1212}, where the subscripts refer now to the cubic axes. Moreover, A^a_{ij} being a traceless tensor, the 12 trace of $\overleftrightarrow{\mathrm{G}}$ is zero, which immediately leads to $G_{1111} + 2G_{1122} = 0$. Therefore there are only two independent components in $\overleftrightarrow{\mathrm{G}}$. For a crystal belonging to the tetrahedral point group T,[21] the absence of fourfold symmetry leads in general to $G_{1122} \neq G_{2211}$. This difference only exists in the presence of dispersion of the polarizabilities, as evident from Eq. (17c). There are then three independent components G_{1111}, G_{1122}, and G_{1212}; the fourth component G_{2211} is related to those by $G_{1111} + G_{1122} + G_{2211} = 0$. The analysis of $\overleftrightarrow{\mathrm{G}}$ is based on the symmetries of ρ_0 which are described in Sec. III.

III. SYMMETRIES OF DISTRIBUTION FUNCTION IN CUBIC CRYSTALS

The density matrix ρ_0 that appears in Eqs. (16) and (17c) is an orientational distribution function for all molecular segments in the sample. The orientation of a given segment a can be expressed by the rotation R_a away from a reference position. Thus if the value of $\overleftrightarrow{\alpha}^a$ in the reference position is $\underline{\overleftrightarrow{\alpha}}^a$, one has

$$\overleftrightarrow{\alpha}^a = \mathrm{P}_{R_a} \underline{\overleftrightarrow{\alpha}}^a, \tag{18}$$

where P_{R_a} is the unitary rotation operator corresponding to the physical rotation R_a.[22] These rotations span the full rotation group $\{R\}$. The tracing in Eq. (16), or in (17c), can first be made on all segments which do not explicitly appear as superscripts in these expressions. This leads to single-segment distribution functions ρ_a, and to pair distribution functions ρ_{ab}, defined by

$$\mathrm{tr}_{(a)}(\rho_0) \equiv \rho_a(R_a), \tag{19a}$$

$$\mathrm{tr}_{(a,b)}(\rho_0) \equiv \rho_{ab}(R_a, R_b), \tag{19b}$$

where the segments in parentheses on the left-hand side are excluded from the tracing operation. Section III discusses the relevant symmetries of ρ_a and ρ_{ab} in a cubic plastic crystal.

For the purpose of the present calculation the single-segment distribution ρ_a that occurs in Eq. (16) can be thought to have cubic symmetry. Here, and in what follows, the cubic-symmetry axes coincide with the crystal axes; the point group need not yet be specified. The cubic symmetry of ρ_a changes (16) into

$$A^a_{ij}(\omega) = \alpha^a_{ij}(\omega, 0) - \tfrac{1}{3}\underline{\alpha}^a_{kk}(\omega, 0)\delta_{ij} \tag{20}$$

with summation over the repeated subscript k. If there are many segments of the same type within the unit cell there can be a situation where the over-all cubic symmetry does not imply cubic symmetry of ρ_a. Grouping segments a of the same type in Eq. (17c) it becomes obvious however that the over-all symmetry guarantees that identical results for $\overleftrightarrow{\mathrm{G}}$ are obtained whether $\overleftrightarrow{\mathrm{A}}^a$ is given by (16) or by (20). The simpler form (20) will thus be preferred. In the spirit of Eq. (18) one writes

$$A^a_{ij} = \mathrm{P}_{R_a} \underline{A}^a_{ij} \tag{21}$$

and, from (17c),

$$\overleftrightarrow{G}=\frac{1}{2\mathfrak{N}}\sum_{a,b}\int\int\rho_{ab}(R_a,R_b)\,\mathsf{P}_{R_a}\underline{\overleftrightarrow{A}}^a\;\mathsf{P}_{R_b}\underline{\overleftrightarrow{A}}^b\,dR_a\,dR_b\,. \tag{22}$$

The integrals are Hurwitz integrals[23] over $\{R\}$, and it is assumed that ρ_{ab} is properly normalized. The explicit indication of dispersion is not made, and can always be restored in the final result if required.

There are three types of pair distributions which are of interest: (i) Uncorrelated:

$$\rho_{ab}(R_a,R_b)=\rho_a(R_a)\rho_b(R_b), \tag{23}$$

where ρ_a and ρ_b have at least cubic symmetry; (ii) correlated spherical:

$$\rho_{ab}(R_a,R_b)=f(R_{ab}), \tag{24}$$

meaning that ρ_{ab} depends only on the relative orientation of segments a and b. This is indicated by the functional dependence f on the rotation R_{ab} defined by

$$R_b=R_aR_{ab}\,; \tag{25}$$

(iii) correlated cubic: ρ_{ab} depends on R_a and R_{ab}. However, when expressed as a function of R_a and R_{ab} only, the R_a dependence has cubic symmetry:

$$\rho_{ab}(R_a,R_aR_{ab})=\rho_{ab}(SR_a,SR_aR_{ab}), \tag{26}$$

where S is any operation of the appropriate point group.

The cubic symmetry of ρ_{ab} is not necessary to the cubic symmetry of ρ_0. However, if ρ_0 has cubic symmetry the three types of pair distributions (23), (24), and (26) are all that need to be considered for the calculation of $\overleftrightarrow{G}$. Indeed, for any given pair a-b one can consider the set $\{a\text{-}b\}$ of all pairs obtained by applying the operation of the cubic point group to a-b. The sum $\sum_{\{a-b\}}\rho_{ab}$ does have cubic symmetry when ρ_0 does, and Eq. (22) can be broken down into such sums.

IV. DECOMPOSITION OF $\overleftrightarrow{G}$ INTO IRREDUCIBLE TENSORIAL SETS

The contributions to $\overleftrightarrow{G}$ of the three types of ρ_{ab}'s that have just been discussed are now analyzed using group theory. The technique will be to extract from the Hurwitz integrals in Eq. (23) an integral (for spherical symmetry), or a sum (for cubic symmetry), running over all group elements, the integrand (or summand) being the coefficients of a group representation. This representation is then reduced to its irreducible components, and the integral (or sum) vanishes for all irreducible representations which are not the identity. This well-known property is an immediate result of the orthogonality of the coefficients of any two inequivalent irreducible unitary representations, the coefficients being summed or integrated over all group elements[24]; indeed, if one of these representations is taken to be the identity, the above property results. By this reduction process one obtains the independent contributions to $\overleftrightarrow{G}$.

Referring to Eqs. (22)–(24) and (26), one sees easily how the Hurwitz integrals should be decomposed for the various ρ_{ab} symmetries. If ρ_{ab} is uncorrelated, Eq. (22) becomes

$$\overleftrightarrow{G}=\frac{1}{2\mathfrak{N}}\sum_{a,b}\int\rho_a(R_a)\,\mathsf{P}_{R_a}\underline{\overleftrightarrow{A}}^a\,dR_a\times\int\rho_b(R_b)\,\mathsf{P}_{R_b}\underline{\overleftrightarrow{A}}^b\,dR_b\,. \tag{27}$$

Furthermore, if ρ_a is spherical, that is constant, the first of these integrals is immediately zero since the components of a symmetric traceless tensor transform as $\mathfrak{D}^{(2)}$ [see below, Eq. (31)].[25] If ρ_a and ρ_b have cubic symmetry, the first integral is decomposed as

$$\int_{\{R\}}\rho(R)\,\mathsf{P}_R\underline{\overleftrightarrow{A}}\,dR=\int_{\{R_1\}}\rho(R)\,dR\;\mathsf{P}_R\Big(\sum_{\{s\}}\mathsf{P}_S\underline{\overleftrightarrow{A}}\Big)=\int_{\{R\}}\rho(R)\,dR\;\mathsf{P}_R\Big(\frac{1}{h_S}\sum_{\{s\}}\mathsf{P}_S\underline{\overleftrightarrow{A}}\Big)\,. \tag{28}$$

In Eq. (28) the first integral is over the full rotation group $\{R\}$, whereas the second is over a subset $\{R_1\}$ of $\{R\}$. The volume of this subset is h_S^{-1} times the volume of $\{R\}$, where h_S is the number of elements of the point group $\{S\}$ which is the symmetry group of $\rho(R)$, and is of course a subgroup of $\{R\}$. The elements in $\{R_1\}$ are selected in such a way that the set $\{R_1\}\times\{S\}$, which is the set of all possible products R_1S, is identical to $\{R\}$. The fact that this can be done is shown in Appendix B; it justifies the equalities in (28). In simple words, this equation simply states that $\rho(R)$ having a given symmetry $\underline{\overleftrightarrow{A}}$ can be symmetrized in the same manner before being integrated with the weight function $\rho(R)$. Since $\underline{\overleftrightarrow{A}}$ transforms as $\mathfrak{D}^{(2)}$, and since $\mathfrak{D}^{(2)}$ does not contain the identity representation A_1 for any of the cubic point groups,[26] the sum over $\{S\}$ in Eq. (28) vanishes. Therefore, there is no contribution to $\overleftrightarrow{G}$ coming from uncorrelated pairs a-b.

If ρ_{ab} is correlated spherical, Eqs. (22) and (24) give

$$\overleftrightarrow{G}=\frac{1}{2\mathfrak{N}}\sum_{a,b}\int f(R_{ab})\,dR_{ab}\int dR\;\mathsf{P}_R(\underline{\overleftrightarrow{A}}^a\,\mathsf{P}_{R_{ab}}\underline{\overleftrightarrow{A}}^b). \tag{29}$$

Here P_R applies to both $\underline{\overleftrightarrow{A}}^a$ and $\mathsf{P}_{R_{ab}}\underline{\overleftrightarrow{A}}^b$, and they both transform as $\mathfrak{D}^{(2)}$. The product which transforms as $\mathfrak{D}^{(2)}\times\mathfrak{D}^{(2)}$ contains all $\mathfrak{D}^{(L)}$ with $L=0-4$.[27] Only the $L=0$ (identity) representation contributes to the integral over R. This is a contribution to the *tensor strength* that will be derived in detail below.

If ρ_{ab} is correlated cubic, Eqs. (22) and (26) give

$$\overleftrightarrow{G}=\frac{1}{2\mathfrak{N}}\sum_{a,b}\int dR_{ab}\int dR\,\rho_{ab}(R,RR_{ab})\times \mathsf{P}_R\left(\frac{1}{h_S}\sum_{\{s\}}\mathsf{P}_S(\overleftrightarrow{\underline{A}}^a\,\mathsf{P}_{R_{ab}}\overleftrightarrow{\underline{A}}^b)\right). \tag{30}$$

The sum within large parentheses is obtained in the same manner as in Eq. (28), and P_R applies to all terms. Each irreducible representation $\mathfrak{D}^{(L)}$ ($L=0-4$) is also a representation of the appropriate point group. For all cubic point groups except T (the tetrahedral group), only $\mathfrak{D}^{(0)}$ and $\mathfrak{D}^{(4)}$ contain the identity representation A_1.[26] Again, $\mathfrak{D}^{(0)}$ contributes to the tensor strength, whereas $\mathfrak{D}^{(4)}$ reflects the *tensor anisotropy*. For the point group T, $\mathfrak{D}^{(3)}$ also contains the identity representation; this is a consequence of the absence of any fourfold symmetry, and in fact does lead to the *tensor asymmetry* $G_{1122}\neq G_{2211}$. These various contributions will now be calculated in detail.

A traceless second-order symmetric tensor $\overleftrightarrow{\underline{A}}$ transforms under $\{R\}$ as $\mathfrak{D}^{(2)}$.[28] If ψ_μ ($\mu=2,1,0,-1,-2$) is a basis vector for $\mathfrak{D}^{(2)}$, one can write

$$\psi_\mu=\sum_{ij}d_{\mu;ij}\underline{A}_{ij}, \tag{31a}$$

$$\underline{A}_{ij}=\sum_{\mu}c_{ij;\mu}\psi_\mu. \tag{31b}$$

The matrices d and c can be selected such that

$$\mathsf{P}_R\psi_\mu=\sum_\nu \mathfrak{D}^{(2)}_{\nu\mu}(R)\psi_\nu, \tag{32}$$

where $\mathfrak{D}^{(2)}$ is *identical* to its usual definition, and this independently of the starting tensor $\overleftrightarrow{\underline{A}}$. The particular values of d and c are listed in Appendix C. The basis vector corresponding to $\overleftrightarrow{\underline{A}}^a$ in Eqs. (29) and (30) is written ψ^a_μ, and that corresponding to $\mathsf{P}_{R_{ab}}\overleftrightarrow{\underline{A}}^b$ is ψ^b_ν. The product of these vectors transforms as $\mathfrak{D}^{(2)}\times\mathfrak{D}^{(2)}$, which is reduced using the vector coupling coefficients $S_{Lm;\mu\nu}$, in Wigner's notation,[27]

$$\psi^a_\mu\psi^b_\nu=\sum_{Lm}S_{Lm;\mu\nu}\Psi^{L,ab}_m, \tag{33a}$$

$$\Psi^{L,ab}_m=\sum_{\mu\nu}S_{Lm;\mu\nu}\psi^a_\mu\psi^b_\nu. \tag{33b}$$

These coefficients form a 25×25 orthogonal transformation matrix, the sum over L running from 0 to 4, and that over m from $-L$ to $+L$. The Ψ^L_m's are basis vectors for the representations $\mathfrak{D}^{(L)}$,

$$\mathsf{P}_R\Psi^{L,ab}_m=\sum_{m'}\mathfrak{D}^{(L)}_{m'm}(R)\Psi^{L,ab}_{m'}. \tag{34}$$

Introducing this notation in Eq. (22) one obtains

$$G_{ijkl}=\sum_{Lm}\left(\sum_{\mu\nu}c_{ij;\mu}c_{kl;\nu}S_{Lm;\mu\nu}\right)Q^{(L)}_m, \tag{35a}$$

where

$$Q^{(L)}_m=\frac{1}{2\mathfrak{N}}\sum_{a,b}\mathrm{tr}(\rho_{ab})\Psi^{L,ab}_m, \tag{35b}$$

with

$$\Psi^{L,ab}_m=\sum_{\mu\nu}\sum_{ij}\sum_{kl}S_{Lm;\mu\nu}d_{\mu;ij}d_{\nu;kl}\underline{A}^a_{ij}(\mathsf{P}_{R_{ab}}\overleftrightarrow{\underline{A}}^b)_{kl}. \tag{35c}$$

The trace in Eq. (35b) will be taken as shown in Eq. (29) for the correlated spherical case, or as shown in Eq. (30) for the correlated cubic case. The $Q^{(L)}_m$'s are the components of the irreducible tensors $\vec{Q}^{(L)}$ on which $\overleftrightarrow{G}$ depends. It will be shown that the m dependence in the $Q^{(L)}_m$'s is trivial when $\overleftrightarrow{G}$ is referred to the cubic-symmetry axes.

In the correlated spherical case the last integral in Eq. (29) leads to

$$\int dR\,\mathfrak{D}^{(L)}_{m'm}(R)\Psi^{L,ab}_{m'}=\delta_{L0}\delta_{m0}\Psi^{L,ab}_m. \tag{36}$$

Therefore the only nonvanishing $\vec{Q}^{(L)}$ is $Q^{(0)}$. The $S_{Lm;\mu\nu}$ coefficients that are needed to evaluate $Q^{(0)}$ using Eqs. (35b) and (35c) are given in Eq. (C3). One finds, taking into account the tracelessness of the $\overleftrightarrow{\underline{A}}$'s,

$$Q^{(0)}_0=\frac{1}{2\mathfrak{N}}\sum_{a,b}\int dR_{ab}f(R_{ab})\times\frac{4}{\sqrt{5}}\left(\sum_i\underline{A}^a_{ii}(\mathsf{P}_{R_{ab}}\overleftrightarrow{\underline{A}}^b)_{ii}+2\sum_{i<j}\underline{A}^a_{ij}(\mathsf{P}_{R_{ab}}\overleftrightarrow{\underline{A}}^b)_{ij}\right). \tag{37}$$

In order to express such results in an abbreviated manner it will be convenient to define the quantities

$$U\equiv\frac{1}{6\mathfrak{N}}\sum_{a,b}\mathrm{tr}\left(\rho_{ab}\sum_i A^a_{ii}A^b_{ii}\right), \tag{38a}$$

$$V\equiv\frac{1}{6\mathfrak{N}}\sum_{a,b}\mathrm{tr}\left(\rho_{ab}\sum_{i<j}A^a_{ij}A^b_{ij}\right). \tag{38b}$$

With these definitions, Eq. (37) can be written

$$Q^{(0)}_0=(12/\sqrt{5})(U+2V). \tag{39}$$

The $Q^{(0)}$ contribution to $\overleftrightarrow{G}$, which is noted $\overleftrightarrow{G}^{(0)}$, is obtained from Eq. (35a), using Eq. (39) and the numerical values given in Appendix C. The two components of interest are

$$G^{(0)}_{1111}=\tfrac{2}{5}(U+2V), \qquad (40a)$$

$$G^{(0)}_{1212}=\tfrac{3}{10}(U+2V), \qquad (40b)$$

and one finds $G^{(0)}_{1122}=-\frac{1}{2}G^{(0)}_{1111}$. The Cauchy relation, which characterizes isotropy,[29] $G^{(0)}_{1111}-G^{(0)}_{1122}-2G^{(0)}_{1212}=0$ is satisfied. In the correlated spherical case the tracing in Eq. (38) can, of course, be done as shown in Eq. (37); that is, there is no need to integrate over R as was originally done in Eq. (29). In this case, the two quantities U and V are also not independent, but are related by $3U=4V$. This can be shown most easily by calculating $\vec{Q}^{(4)}$ in terms of U and V, using (35b) and (35c) together with the numerical values in Appendix C. One notes then that $\vec{Q}^{(4)}$ vanishes in view of Eq. (36), and the relation results. This will become clear in the following analysis.

In the correlated cubic case, the trace in Eq. (35b) is made in the manner indicated in (30). The last summation in (30) leads now to

$$\frac{1}{h_S}\sum_{\{s\}}\mathsf{P}_S\Psi^{L,ab}_{m}=\frac{1}{h_S}\sum_{\{s\}}\sum_{m'}\mathfrak{D}^{(L)}_{m'm}(S)\Psi^{L,ab}_{m'}. \qquad (41)$$

The $\mathfrak{D}^{(L)}_{m'm}(S)$ are representations of the cubic point groups, irreducible for $L=0$ and 1, and reducible for $L>1$. For all cubic groups except T, only $\mathfrak{D}^{(0)}$ and $\mathfrak{D}^{(4)}$ contain A_1, the identity representation.[26] For T, A_1 is also contained in $\mathfrak{D}^{(3)}$. An orthogonal transformation which transforms $\mathfrak{D}^{(L)}$ to a block-diagonal form $\mathfrak{D}$ formed of the irreducible representations $\mathfrak{D}^{(\Gamma)}$ is written $\mathfrak{U}^{(L)}$. One has

$$\mathfrak{D}=\tilde{\mathfrak{U}}^{(L)}\mathfrak{D}^{(L)}\mathfrak{U}^{(L)}, \qquad (42a)$$

$$\phi^{(L)}_{\Gamma i}=\sum_{m}\mathfrak{U}^{(L)}_{m,\Gamma i}\Psi^{L}_{m}, \qquad (42b)$$

$$\Psi^{L}_{m}=\sum_{\Gamma i}\mathfrak{U}^{(L)}_{m,\Gamma i}\,\phi^{(L)}_{\Gamma i}. \qquad (42c)$$

The Γ's are the labels for the irreducible representations into which $\mathfrak{D}^{(L)}$ reduces, and the subscript i labels the elements of the representation Γ whose basis vector is $\phi^{(L)}_{\Gamma i}$ ($i=1$ to h_Γ); the tilde in Eq. (42a) indicates the transposed matrix. With this notation (41) becomes

$$\frac{1}{h_S}\sum_{\{s\}}\mathsf{P}_S\Psi^{L,ab}_{m}=\sum_{\Gamma i}\mathfrak{U}^{(L)}_{m,\Gamma i}\sum_{j}\frac{1}{h_S}\sum_{\{s\}}\mathfrak{D}^{(\Gamma)}_{ji}(S)\phi^{(L),ab}_{\Gamma j}. \qquad (43)$$

The sum over $\{S\}$ vanishes unless $\Gamma\equiv A_1$. For $L=0$, $\mathfrak{U}^{(0)}_{0,A_1}=1$, and the results (40) carry through. However, in taking the traces in Eq. (38), there remains now an integral over R as in (30). The result of this integration is just to average ρ_{ab}, as Ψ^0_0 is invariant under P_R. The transformation $\mathfrak{U}^{(4)}$ is well known,[30] and the vector $\mathfrak{U}^{(4)}_{m,A_1}$ is given in Appendix C [Eq. (C6)]. The particular form of this vector depends on the fact that all transformations leading to the $\vec{\Psi}^{L}$'s have been carefully selected so that the z axis coincides with the third cubic axis. Using Eq. (43) in Eq. (35b) one obtains

$$Q^{(4)}_{m}=\mathfrak{U}^{(4)}_{m,A_1}\frac{1}{2\mathfrak{N}}\sum_{a,b}\mathrm{tr}(\rho_{ab}\phi^{(4),ab}_{A_1}), \qquad (44a)$$

with

$$\phi^{(4),ab}_{A_1}=\sum_{m}\sum_{\mu\nu}\sum_{ij}\sum_{kl}\mathfrak{U}^{(4)}_{m,A_1}\times S_{4m;\mu\nu}\,d_{\mu;ij}\,d_{\nu;kl}\,\underline{A}^{a}_{ij}(\mathsf{P}_{R_{ab}}\underline{\overleftrightarrow{A}}^{b})_{kl}. \qquad (44b)$$

These expressions are evaluated using the numerical values given in Appendix C; the required $S_{4m;\mu\nu}$'s are given in Eq. (C4). Using Eq. (38), one finds

$$Q^{(4)}_{m}=(3U-4V)(1,0,0,0,\sqrt{\tfrac{14}{5}},0,0,0,1). \qquad (45)$$

The second factor is a constant vector and only the first factor contains physically relevant information. In taking the traces in (38), it is now necessary to account for the fact that Ψ^4_m transforms as $\mathfrak{D}^{(4)}$ under P_R [see Eq. (30)]. The fact that $\vec{Q}^{(4)}$ vanishes in the correlated spherical case demonstrates that $3U=4V$ in that case. Using Eq. (45), together with the numerical values of Appendix C, one finds from Eq. (35a) the contribution $\overleftrightarrow{G}^{(4)}$ of $\vec{Q}^{(4)}$ to $\overleftrightarrow{G}$

$$G^{(4)}_{1111}=\tfrac{1}{5}(3U-4V), \qquad (46a)$$

$$G^{(4)}_{1212}=-\tfrac{1}{10}(3U-4V). \qquad (46b)$$

For all cubic point groups except T, $\overleftrightarrow{G}^{(0)}$ and $\overleftrightarrow{G}^{(4)}$ are the only two contributions to $\overleftrightarrow{G}$. From Eqs. (40) and (46) their sum is

$$G_{1111}=U, \qquad (47a)$$

$$G_{1212}=V \qquad (47b)$$

with $G_{1122}=-\frac{1}{2}U$. The anisotropy can be characterized by

$$G_{1111}-G_{1122}-2G_{1212}=\tfrac{1}{2}(3U-4V). \qquad (48)$$

If the crystal belongs to the tetrahedral point group T, there is also a contribution from $L=3$. This is listed here for completeness as this case does not seem to have occurred among the plastic crystals whose structure is known to date. The vector $\mathfrak{U}^{(3)}_{m,A_1}$ is given in Eq. (C7). Equations (44a) and (44b) carry through with "4" simply replaced everywhere by "3"; Eq. (45) is now replaced by

$$\phi^{(3),ab}_{A_1}=\sqrt{\tfrac{8}{3}}\sum_{i<j}(-1)^{i+j}[\underline{A}^{a}_{jj}(\mathsf{P}_{R_{ab}}\underline{\overleftrightarrow{A}}^{b})_{ii}-\underline{A}^{a}_{ii}(\mathsf{P}_{R_{ab}}\underline{\overleftrightarrow{A}}^{b})_{jj}], \qquad (49a)$$

with

$$Q_m^{(3)} = \frac{1}{2\mathfrak{N}} \sum_{a,b} \mathrm{tr}(\rho_{ab}\phi_{A_1}^{(3),ab}) \times (0, 1/\sqrt{2}, 0, 0, 0, -1/\sqrt{2}, 0). \tag{49b}$$

Using Eq. (35a) and the numerical values in Appendix C, one finds the contribution $\overleftrightarrow{G}^{(3)}$ to $\overleftrightarrow{G}$

$$G_{1111}^{(3)} = G_{1212}^{(3)} = 0, \tag{50a}$$

$$G_{1122}^{(3)} = -G_{2211}^{(3)} = \frac{1}{2\mathfrak{N}} \sum_{a,b} \mathrm{tr}\Big(\rho_{ab}\ \tfrac{1}{6}\sum_{i<j} (-1)^{i+j} \times [A_{jj}^{a}(\omega_p)A_{ii}^{b}(\omega_0) - A_{ii}^{a}(\omega_p)A_{jj}^{b}(\omega_0)]\Big). \tag{50b}$$

The polarizability dispersion has been shown explicitly in (50b). In its absence the expression vanishes as the summation over all pairs includes the pair b-a as well as a-b.

V. INTERPRETATION OF RESULTS

Having reduced $\overleftrightarrow{G}$ to its irreducible components one is in a position (i) to express rather simply $\overleftrightarrow{G}$ in other coordinate frames; (ii) to give a physical interpretation to each component.

The first advantage, which is only mathematical, will be dealt with very briefly. To rotate the object $\overleftrightarrow{G}$ given by Eq. (35a) amounts to rotating the sets $\vec{Q}^{(L)}$ of which it is built. One has

$$\mathrm{P}_R Q_m^{(L)} = \mathcal{D}_{m'm}^{(L)}(R) Q_{m'}^{(L)}. \tag{51}$$

Introducing this in (35a) one obtains G'_{ijkl}, where $\mathrm{P}_R\overleftrightarrow{G} \equiv \overleftrightarrow{G}'$. The $Q^{(0)}$ contribution to $\overleftrightarrow{G}'$ is R independent. The $\vec{Q}^{(4)}$ contribution involves, in general, all nine components of $\mathrm{P}_R\vec{Q}^{(4)}$. The fact that only three components occurred in Eq. (45) was due to the fact that $\vec{\Psi}^{(4)}$ transforms as $\mathcal{D}^{(4)}$, with the z axis parallel to a cubic axis and to the third axis of the reference frame. In other words, the ψ_μ's transform *identically* to the spherical harmonics $Y_m^{(2)}$ due to the particular choice of $d_{\mu;ij}$ in Eq. (C1), and the $\Psi_m^{(L)}$'s transform *identically* to the $Y_m^{(L)}$'s due to the particular form of the ψ_μ's and the $S_{Lm;\mu\nu}$'s. Once $\vec{\Psi}^{(L)}$ is rotated, the z axis is no longer parallel to the third reference axis, and all components of $\vec{Q}^{(L)}$ occur.

Let us now turn to the physical interpretation of the components. The $\vec{Q}^{(3)}$ component, which reflects polarizability dispersion and occurs only in the absence of fourfold axes, is rather peculiar, and will not need much discussion. One should simply note that $\vec{Q}^{(3)}$ has no contribution to either the *tensor strength* or to the *tensor anisotropy*, about to be defined. This results from Eq. (50a); $\vec{Q}^{(3)}$ only contributes to the asymmetry, as seen in (50b).

The *tensor strength* is defined as

$$Q \equiv U + 2V = G_{1111} + 2G_{1212}. \tag{52}$$

It is proportional to $Q^{(0)}$ in Eq. (39). The *tensor anisotropy* is defined as

$$\zeta \equiv \frac{G_{1111} - \frac{1}{2}G_{1122} - \frac{1}{2}G_{2211} - 2G_{1212}}{2G_{1111} - G_{1122} - G_{2211}}. \tag{53}$$

This quantity is related to

$$C \equiv U - \tfrac{4}{3}V, \tag{54}$$

which characterizes the cubic order and is proportional to $\vec{Q}^{(4)}$ in Eq. (45); both C and ζ are zero in isotropic media. From Eq. (53) one finds

$$\zeta = C/2U = \tfrac{1}{2} - \tfrac{2}{3}(V/U) \tag{55a}$$

or, in terms of C and Q,

$$\zeta = 5C/(6C + 4Q). \tag{55b}$$

As shown in Sec. IV (i) uncorrelated segment pairs a-b do not contribute to either Q or C [Eqs. (27) and (28)]; (ii) correlated segment pairs contribute to Q irrespective of whether the symmetry of the correlation function is spherical or cubic. In fact, as discussed below Eq. (43), in the correlated cubic case it is the spherical average of ρ_{ab} over R which is relevant to the calculation of Q. This average can be written $f(R_{ab})$ as in Eq. (24); (iii) correlated segment pairs contribute to C only to the extent that ρ has cubic rather than spherical symmetry.

The correlation of segment pairs is a short-range property in the plastic phase. For any given pair a-b, the degree of correlation depends on the departure of

$$f(R_{ab}) \equiv \int dR\, \rho(R, RR_{ab}) \tag{56}$$

from isotropy. The strength Q depends on the degree of correlation of given pairs a-b, and on the number of pairs contributing to the sum in Eq. (37), which is the correlation range. Therefore Q is a generalized susceptibility which measures the short-range molecular ordering. It can be compared to the paramagnetic susceptibility of a magnet above the Curie point, which measures the short-range spin ordering. As the temperature is lowered toward the plastic-solid phase transition, segments become correlated over longer distances. They are correlated over the entire sample in the solid. Consequently, Q is expected to increase on the approach of the solid phase. Such a remarkable increase has been observed recently in succinonitrile.[10]

The quantity C results from the over-all cubic symmetry of ρ_{ab}, which is a long-range property, but also from the short-range correlation of molecular pairs, which is required to obtain a nonvanishing contribution to $\overleftrightarrow{G}$. This is clear from points (i) and (iii) above. By defining the dimensionless anisotropy parameter ζ, which depends only on C/Q, it appears that the short-range aspect is eliminated and only the long-range aspect remains. This cannot strictly be demonstrated in all generality, but can be intuitively understood from consideration of the second equality in Eq. (55a); if one assumes that the correlation range affects in the same way the off-diagonal and the diagonal components of $\overleftrightarrow{A}^a$ and $\overleftrightarrow{A}^b$ in Eq. (38), the quotient V/U is independent of the range. Therefore ζ measures the over-all cubic anisotropy of the average molecular orientations, and, as such, can be considered as an orientational order parameter of the plastic phase. It turns out that ζ is related to the average over the angular distribution function of fourth-order spherical harmonics. Within a mean-field theory, and for symmetric top molecules, ζ is found to be directly related to the average of $(\cos^4\theta - \frac{1}{5})$, where θ is the angle between the molecular axis and a cube fourfold axis. Such an order parameter is a direct extension to higher-order harmonics of angular order parameters proposed by Kobayashi for liquid crystals.[31] As opposed to liquid crystals, the average of $(\cos^2\theta - \frac{1}{3})$ is always zero in the present case in view of the cubic symmetry. Recent measurements on succinonitrile have shown that ζ decreases markedly on the approach of the plastic-liquid transition.[10] This result indicates that the melting of the lattice requires a high degree of rotational isotropy. Roughly speaking, the anisotropy parameter below the melting point can be compared to the magnetization of a magnet below the Curie point; however, the melting phenomenon is considerably more subtle in that more than one order parameter is involved.

VI. SUMMARY AND CONCLUSIONS

On the basis of very general thermodynamical arguments an expression has been derived for the ac orientational Kerr-effect susceptibility of cubic plastic crystals. The susceptibility has been related to a tensorial correlation function $\overleftrightarrow{G}$. This function expresses the correlation between the anisotropic part of the optical susceptibility tensor of pairs of molecules (or molecular segments, in case of dynamical isomerization). The analysis is facilitated by the fact that local-field corrections can be treated rather simply in cubic molecular crystals.

By simple consideration of the cubic symmetry, one finds only two independent components to $\overleftrightarrow{G}$ whenever the crystal point group has fourfold axes (there is one more component in the case of the proper tetrahedral group T). Using more elaborate group-theoretical considerations, $\overleftrightarrow{G}$ is then decomposed into two irreducible tensorial sets related to two independe [illegible] stants. One of these, which was labeled Q, [illegible] en named the tensor strength. Its magnitude depends on the amount and range of short-range molecular ordering. For the plastic-solid transition this quantity plays a role similar to that of the paramagnetic susceptibility above the Curie point. The second quantity ζ has been called the tensor anisotropy. Its magnitude depends on the long-range anisotropy of the average molecular ordering. For the plastic-liquid transition ζ plays a role somewhat similar to that of the magnetization of a magnet below the Curie point.

The measurement of Q and ζ on one substance (succinonitrile) has already indicated that these quantities show a remarkable pretransitional behavior on the approach of the respective transition points.[10] One experimental task will be to determine whether this behavior is peculiar to succinonitrile or is a rather general behavior of all plastic crystals. In the latter case, microscopic theories will have to be developed to account for these effects. Our results are also relevant to light-scattering investigations of these compounds. The depolarized Rayleigh wing is described by a correlation function somewhat similar to $\overleftrightarrow{G}$.[32] In view of our analysis, several components are expected in the depolarized Rayleigh-wing spectrum. There is little doubt that a better understanding of the plastic-solid and of the plastic-liquid transition will improve the general understanding we have of melting phenomena.

APPENDIX A

Using Eq. (3) one obtains

$$\frac{\partial \rho}{\partial F_i} = -\beta\rho\left[\frac{\partial \mathcal{H}}{\partial F_i} - \mathrm{tr}\left(\rho\frac{\partial \mathcal{H}}{\partial F_i}\right)\right], \tag{A1}$$

and

$$\begin{aligned}\frac{\partial^2 \rho}{\partial F_i \partial F_j} = &-\beta\rho\left[\frac{\partial^2 \mathcal{H}}{\partial F_i \partial F_j} - \mathrm{tr}\left(\rho\frac{\partial^2 \mathcal{H}}{\partial F_i \partial F_j}\right)\right]\\ &+\beta^2\rho\left[\frac{\partial \mathcal{H}}{\partial F_i}\frac{\partial \mathcal{H}}{\partial F_j} + 2\,\mathrm{tr}\left(\rho\frac{\partial \mathcal{H}}{\partial F_i}\right)\mathrm{tr}\left(\rho\frac{\partial \mathcal{H}}{\partial F_j}\right)\right.\\ &-\frac{\partial \mathcal{H}}{\partial F_i}\,\mathrm{tr}\left(\rho\frac{\partial \mathcal{H}}{\partial F_j}\right)\\ &\left.-\frac{\partial \mathcal{H}}{\partial F_j}\,\mathrm{tr}\left(\rho\frac{\partial \mathcal{H}}{\partial F_i}\right) - \mathrm{tr}\left(\rho\frac{\partial \mathcal{H}}{\partial F_i}\frac{\partial \mathcal{H}}{\partial F_j}\right)\right].\end{aligned} \tag{A2}$$

For the problem treated in Sec. II,

$$\left(\frac{\partial \mathcal{H}}{\partial F_i}\right)_{\vec{F}=0}=0,$$

and

$$\left(\frac{\partial^2 \mathcal{H}}{\partial F_i \partial F_j}\right)_{\vec{F}=0}=-\tfrac{1}{3}(\epsilon_0+2)\sum_{\mathfrak{N}} \alpha^a_{ij}(\omega_0,0).$$

This leads to

$$\left(\frac{\partial \rho}{\partial F_i}\right)_{\vec{F}=0}=0, \tag{A3}$$

$$\left(\frac{\partial^2 \rho}{\partial F_i \partial F_j}\right)_{\vec{F}=0}=\beta\rho_0\tfrac{1}{3}(\epsilon_0+2) \times \sum_{\mathfrak{N}}\{\alpha^a_{ij}(\omega_0,0)-\mathrm{tr}[\rho\,\alpha^a_{ij}(\omega_0,0)]\}. \tag{A4}$$

APPENDIX B

This appendix shows that the full rotation group $\{R\}$ can be decomposed into h_S nonoverlapping subsets $\{R_i\}$ ($i=1$ to h_S), where h_S is the number of elements of a point group $\{S\}$, the subsets being such that $\{R_i\}\times\{S\}\equiv\{R\}$. This theorem justifies the decomposition of the integrals in Eqs. (28) and (30). It is demonstrated in the following simple steps:

(i) The set $\{R\}\times S_j\equiv\{R\}$ when S_j is an element of $\{S\}$; this is evident since S_j is also an operation of $\{R\}$.

(ii) The condition $S_i\neq S_j$ leads to $RS_i\neq RS_j$ for all R belonging to $\{R\}$. Let us assume that $RS_i=RS_j$ for a particular R; this gives $RS_iS_j^{-1}=R$. The product of two rotations being a third (different) rotation unless at least one of them is the identity, this leads to $S_iS_j^{-1}=I$, or $S_i=S_j$ in contradiction to the initial assumption.

(iii) $\{R\}$ can be decomposed into h_S subsets $\{R_i\}$ ($i=1$ to h_S) which have identical volume and are such that

$$\{R_1\}\times S_1\equiv\{R_2\}\times S_2\equiv\cdots\equiv\{R_{h_S}\}\times S_{h_S}.$$

This is shown by building up such a decomposition. One starts with any element R, builds all h_S products RS_i^{-1}, and distributes them in the corresponding sets R_i. All these products are different, by (ii). Then one picks a new element R' not among any of the previously distributed rotations $R'\neq RS_i^{-1}$ (for all i), and forms all products $R'S_j^{-1}$. The demonstration hinges on the fact that $R'S_j^{-1}\neq RS_i^{-1}$ for all i and j. Indeed, if one had $R'S_j^{-1}=RS_i^{-1}$, one would also have $R'=RS_i^{-1}S_j$, and since $S_i^{-1}S_j$ is equal to some S_k^{-1} of $\{S\}$ this result is in contradiction to our selection procedure for R'. Proceeding in this manner, all elements of $\{R\}$ can be distributed in the $\{R_i\}$'s, and the above relation between the sets follows immediately.

(iv) $\{R_i\}$ being any one of these subsets, $\{R_i\}\times\{S\}\equiv\{R\}$. This is evident from the fact that the junction of all $\{R_i\}$'s is $\{R\}$, and from using the equality demonstrated in (iii) above.

APPENDIX C

This appendix contains the detailed numerical information that is required for the decompositions of $\overleftrightarrow{G}$ into irreducible tensorial sets. The basis vector ψ_μ transforming as $\mathfrak{D}^{(2)}$, which is obtained from a traceless second-order symmetric tensor $\underline{A}$, is[28]

$$\begin{aligned}
\psi_2&=\underline{A}_{11}-\underline{A}_{22}+2i\underline{A}_{12},\\
\psi_1&=-2\underline{A}_{13}-2i\underline{A}_{23},\\
\psi_0&=\sqrt{6}\,\underline{A}_{33},\\
\psi_{-1}&=2\underline{A}_{13}-2i\underline{A}_{23},\\
\psi_{-2}&=\underline{A}_{11}-\underline{A}_{22}-2i\underline{A}_{12}.
\end{aligned} \tag{C1}$$

It is written in such a way that the z axis of ψ_μ coincides with the third axis of $\underline{A}_{ij}$. Equations (C1) give the coefficients $d_{\mu;ij}$ defined in Eq. (31a). This set is inverted taking account of $\sum_i \underline{A}_{ii}=0$. One obtains

$$\begin{aligned}
\underline{A}_{11}&=\tfrac{1}{4}(\psi_2+\psi_{-2})-(1/2\sqrt{6})(\psi_0),\\
\underline{A}_{22}&=-\tfrac{1}{4}(\psi_2+\psi_{-2})-(1/2\sqrt{6})(\psi_0),\\
\underline{A}_{33}&=(1/\sqrt{6})(\psi_0),\\
\underline{A}_{12}&=(1/4i)(\psi_2-\psi_{-2}),\\
\underline{A}_{13}&=\tfrac{1}{4}(\psi_{-1}-\psi_1),\\
\underline{A}_{23}&=-(1/4i)(\psi_{-1}+\psi_1),
\end{aligned} \tag{C2}$$

which gives the coefficients $c_{ij;\mu}$ of (31b).

The $S_{Lm;\mu\nu}$ coefficients in Eq. (33) can also be labeled $S^{(2,2)}_{Lm;\mu\nu}$ to indicate that they originate from $\mathfrak{D}^{(2)}\times\mathfrak{D}^{(2)}$. These coefficients can further be written $s^{(2,2)}_{L,\mu,\nu}$, as they vanish unless $m=\mu+\nu$. A formula for these coefficients has been derived by Wigner.[27] The numerical values relevant to the calculation of $Q^{(0)}$ are

$$s^{(2,2)}_{0,\mu,-\mu}=(-1)^\mu/\sqrt{5}\,. \tag{C3}$$

For the calculation of $\vec{Q}^{(4)}$ they are

$$\begin{aligned}
&s^{(2,2)}_{4,2,2}=s^{(2,2)}_{4,-2,-2}=1,\\
&s^{(2,2)}_{4,2,-2}=s^{(2,2)}_{4,-2,2}=1/(70)^{1/2},\\
&s^{(2,2)}_{4,1,-1}=s^{(2,2)}_{4,-1,1}=4/(70)^{1/2},\\
&s^{(2,2)}_{4,0,0}=6/(70)^{1/2}.
\end{aligned} \tag{C4}$$

For the calculation of $\vec{Q}^{(3)}$ they are

$$S^{(2,2)}_{3,2,0} = S^{(2,2)}_{3,0,-2} = -S^{(2,2)}_{3,0,2} = -S^{(2,2)}_{3,-2,0} = 1/\sqrt{2}\,,$$
$$S^{(2,2)}_{3,1,1} = S^{(2,2)}_{3,-1,-1} = 0. \tag{C5}$$

The vector $\mathfrak{U}^{(4)}_{m,A_1}$, which is one column of the unitary transformation matrix that reduces $\mathfrak{D}^{(4)}$ is, for all cubic point groups,[30]

$$\mathfrak{U}^{(4)}_{m,A_1} = [(\tfrac{5}{24})^{1/2}, 0, 0, 0, (\tfrac{7}{12})^{1/2}, 0, 0, 0, (\tfrac{5}{24})^{1/2}]. \tag{C6}$$

The vector $\mathfrak{U}^{(3)}_{m,A_1}$, which is one column of the unitary transformation matrix that reduces $\mathfrak{D}^{(3)}$ into irreducible representations of the tetrahedral group T, is[25]

$$\mathfrak{U}^{(3)}_{m,A_1} = (0, 1/\sqrt{2}\,, 0, 0, 0, -1/\sqrt{2}\,, 0). \tag{C7}$$

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