

Dielectric Relaxation for a Three-Dimensional Rotator in a Crystalline Field: Theory for a General Six-Site Model

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A theory of dielectric relaxation is presented for a generalized six-site model where the transition probabilities for the turning of dipoles from one orientational site to another are arbitrary. The sites are arranged in three dimensions. The nature of the set of discrete relaxation times generated by this model is examined in a general manner. It is found that the relaxation times are all real and positive and the range of the relaxation times is established.

1. Introduction

Previous work [1]¹ with two simple models of a rather restricted nature has been sufficient to indicate that a set of discrete dielectric relaxation times can arise in a lattice consisting of dipoles that may occupy orientational sites arranged in three dimensions. As in studies on the single-axis rotator [2, 3], the source of the set of relaxation times was the anisotropy in the crystalline field, which hindered the turning of dipoles from one orientational site to another.

In the present paper the purpose is to extend the treatment of the three-dimensional rotator problem discussed in reference [1] by constructing the rate equations for a six-site model with *arbitrary* transition probabilities in order to examine the general nature of the set of relaxation times.

2. General Six-Site Model

2.1. Model

A model in which a dipole of moment μ on each lattice point can orient in any six directions is considered. These equilibrium orientations are along the Cartesian coordinate axes, x , y , and z (fig. 1 (a)). As in previous work [1, 2, 3], the following conditions are assumed:

(a) There is no correlation in the motion of dipoles on different lattice points.

(b) The barrier system is the same for all molecules in the lattice.

(c) The only elementary process is a reorientation to an adjacent site (single jump hypothesis, S - J). It should be noted that the general results obtained do not depend upon the orthogonal site orientations exhibited in figure 1 (a). This model was selected because it serves as well as any other for the general discussion and it was desirable to derive certain explicit expressions useful for polarizability calculations for this special case.

The transition probability for the turning of a dipole from a site i to an adjacent site j is given by

$$k_{ij} = B e^{-\frac{W_{ij}}{kT}} \quad (1)$$

where B is a frequency factor, k is Boltzmann's constant, and T is the absolute temperature. The quantity W_{ij} is the local free energy of activation barrier, which must be surmounted by a dipole in turning from site i to site j (fig. 1 (b)). The transition probability for the jump j to i , k_{ji} , is given by eq (1) with W_{ji} in place of W_{ij} . As transitions are permitted from a site i to four adjacent sites, there are 24 elementary process transition probabilities k_{ij} with $i, j=1, 2, \dots, 6$, and $i \neq j$ in the general model. From physical considerations it is shown in the appendix (section 3.1) that of these 24 constants only 17 are independent, and that relations exist for the k_{ij} corresponding to a closed circuit of transitions and the inverse circuit. Thus, if we consider the series of site-to-site transitions $1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 1$, and the inverse circuit $1 \rightarrow 3, 3 \rightarrow 2, 2 \rightarrow 1$, we find²

$$k_{12}k_{23}k_{31} = k_{13}k_{32}k_{21}. \quad (2a)$$

Other relations such as the above must apply, one for each site triplet for the remaining seven octants:

$$k_{13}k_{34}k_{41} = k_{14}k_{43}k_{31} \quad (2b)$$

$$k_{14}k_{45}k_{51} = k_{15}k_{54}k_{41} \quad (2c)$$

$$k_{15}k_{52}k_{21} = k_{12}k_{25}k_{51}; \quad (2d)$$

the four remaining equations, (2e) through (2h) are obtained from the equations above by substituting the subscript 6 for 1. Any one of the set of eight relations in eq (2) may be derived from the other seven.³ These are the basic equations which restrict the arbitrary choice of the k_{ij} for the six-site model. Equations (2) are also needed for a mathematical proof noted later.

²A single relation of this type was given in reference 3 for single-axis rotators (see eq (7) and (25)).

³For example, eq (2e), $k_{62}k_{23}k_{36} = k_{63}k_{32}k_{26}$, may be obtained as the quotient [eq (2a) × (2b) × (2c) × (2d)]/[eq (2f) × (2g) × (2h)].

¹Figures in brackets indicate the literature references at the end of this paper.

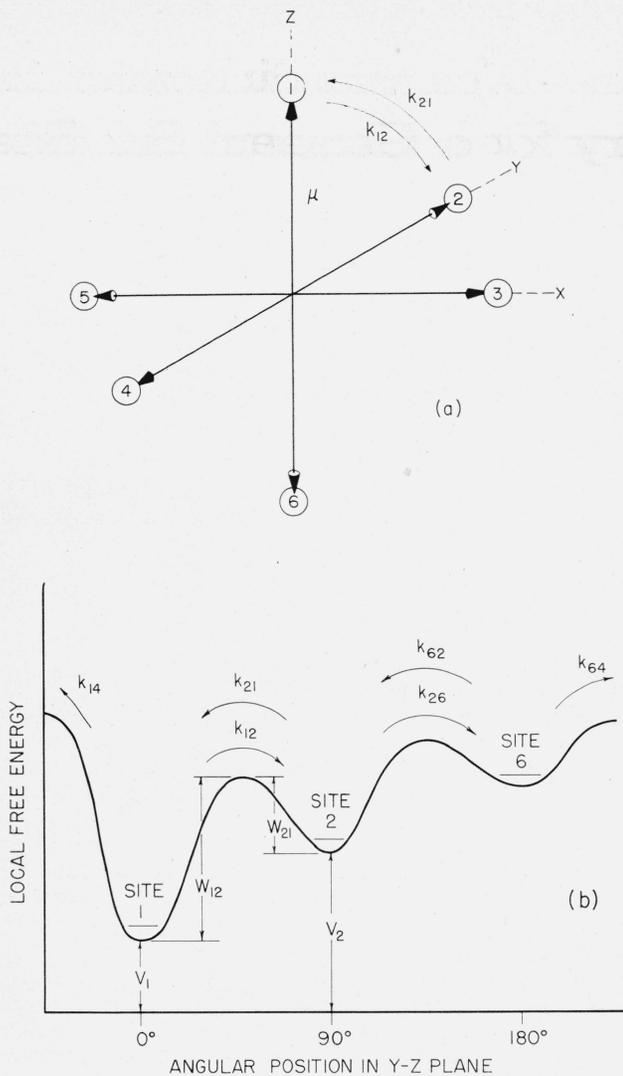


FIGURE 1. General six-site Cartesian axes model.

(a) The equilibrium orientations of the dipole moment μ . (b) Local free-energy barrier as a function of angular position in the y - z plane through sites 1, 2, and 6. W_{12} is the barrier for a transition from site 1 to site 2 and W_{21} is the barrier for the reverse transition. V_1 and V_2 are the free energies for sites 1 and 2, respectively, relative to an arbitrary zero.

2.2. Rate Equations

Assume a lattice with a total of N dipoles where the number of dipoles oriented in the i th site at any time t is given by N_i . The summation of the N_i is always N . The number of dipoles turning per unit time from a given site i to an adjacent site j is $k_{ij}N_i$, and the number entering site i from j is $k_{ji}N_j$; the total leaving site i to turn to adjacent sites is $\sum_{j,j \neq i} k_{ij}N_i$. Accordingly, the differential equations for

the change in population of each site are ⁴

$$\left. \begin{aligned} \frac{dN_1}{dt} &= -(k_{12} + k_{13} + k_{14} + k_{15})N_1 + k_{21}N_2 + k_{31}N_3 + k_{41}N_4 + k_{51}N_5 \\ \frac{dN_2}{dt} &= k_{12}N_1 - (k_{21} + k_{23} + k_{25} + k_{26})N_2 + k_{32}N_3 + k_{52}N_5 + k_{62}N_6 \\ \frac{dN_3}{dt} &= k_{13}N_1 + k_{23}N_2 - (k_{31} + k_{32} + k_{34} + k_{36})N_3 + k_{43}N_4 + k_{63}N_6 \\ \frac{dN_4}{dt} &= k_{14}N_1 + k_{34}N_3 - (k_{41} + k_{43} + k_{45} + k_{46})N_4 + k_{54}N_5 + k_{64}N_6 \\ \frac{dN_5}{dt} &= k_{15}N_1 + k_{25}N_2 + k_{45}N_4 - (k_{51} + k_{52} + k_{54} + k_{56})N_5 + k_{65}N_6 \\ \frac{dN_6}{dt} &= k_{26}N_2 + k_{36}N_3 + k_{46}N_4 + k_{56}N_5 - (k_{62} + k_{63} + k_{64} + k_{65})N_6 \end{aligned} \right\} \quad (3)$$

The molecular relaxation times, τ_β , will be included in the solutions of the above equations.

2.3. Characteristic Determinant and Its Properties

Solutions of linear homogeneous differential equations of the type shown in eq (3) are of the form

$$N_i = \sum_{\beta} C_{i\beta} e^{f_{\beta}(k)t}, \quad (4)$$

where the symbol $f_{\beta}(k)$ represents a function of some or all of the k_{ij} . The functions $e^{f_{\beta}(k)t}$ are referred to as decay functions, since the $f_{\beta}(k)$ are always negative for $\beta \geq 2$ (see below). The index β refers to the mode of decay. Each decay function indicates the rate at which a particular mode of decay promotes the attainment of equilibrium after the abrupt removal of a disturbance. The $f_{\beta}(k)$ are obtained by forming the characteristic determinant of eq (3) and solving for its eigenvalues. This characteristic determinant is

$$\Delta(\mathbf{D}, k_{ij}) = \begin{vmatrix} A_1 & -k_{21} & -k_{31} & -k_{41} & -k_{51} & 0 \\ -k_{12} & A_2 & -k_{32} & 0 & -k_{52} & -k_{62} \\ -k_{13} & -k_{23} & A_3 & -k_{43} & 0 & -k_{63} \\ -k_{14} & 0 & -k_{34} & A_4 & -k_{54} & -k_{64} \\ -k_{15} & -k_{25} & 0 & -k_{45} & A_5 & -k_{65} \\ 0 & -k_{26} & -k_{36} & -k_{46} & -k_{56} & A_6 \end{vmatrix}, \quad (5a)$$

⁴ By the S-J hypothesis, $k_{16} = k_{61} = k_{24} = \dots = k_{53} = 0$.

where we let $\mathbf{D}=d/dt$ and define A_1, A_2, A_3, \dots as

$$\begin{aligned} A_1 &= \mathbf{D} + k_{12} + k_{13} + k_{14} + k_{15}, \\ A_2 &= \mathbf{D} + k_{21} + k_{23} + k_{25} + k_{26}, \\ A_3 &= \mathbf{D} + k_{31} + k_{32} + k_{34} + k_{36}, \\ &\vdots \\ A_6 &= \mathbf{D} + k_{62} + k_{63} + k_{64} + k_{65}. \end{aligned} \quad (5b)$$

The characteristic determinantal equation, obtained by setting Δ equal to zero in eq (5a), has six roots, or eigenvalues, f_β , for the operator \mathbf{D} . The nature of the elements in Δ permits one to answer some questions regarding the eigenvalues and, hence, about the relaxation times, τ_β .

The following questions may be raised: Are the eigenvalues real, what is their sign, what is their range, and are they distinct for the most general case, i.e., when the k_{ij} are distinct? The eigenvalues can be shown to be real by applying a theorem due to Goldberg.⁵ The line of reasoning is briefly thus: From the theory of matrices the characteristic determinant of a symmetric matrix has real roots. Hence, if a symmetric matrix, S , can be constructed that has the same characteristic determinantal equation as Δ , i.e., $\Delta=0$, then the eigenvalues of Δ will be real. Sufficient conditions for forming such a matrix S with the same roots as Δ are the set of relations given by eq (2) and the inequalities $k_{ij} \geq 0$. Since eq (2) and $k_{ij} \geq 0$ are imposed by physical considerations, it follows that the eigenvalues are always real.

The sign and range of the eigenvalues f_β are specified by applying a theorem derived by Gerschgorin [4] and rediscovered by Brauer [5] regarding the areas in the complex plane in which the roots of a matrix lie; it can be shown (see appendix, section 3.3) that for our particular case, eq (5a), the eigenvalues lie between zero and twice the most negative diagonal element in the matrix (a_{ij}) derived from Δ in eq (5a) by setting $\mathbf{D}=0$ and changing the sign. Since, by definition, $k_{ij} \geq 0$, the roots are all negative.

The proof that the eigenvalues are distinct if the k_{ij} are distinct has not been accomplished.

From the theory of matrices we obtain two other properties of the characteristic determinant Δ . In the matrix (a_{ij}) , defined above, it is evident (see eq (5b)) that each column sum vanishes. This indicates that one eigenvalue of Δ corresponds to the root $\mathbf{D}=0$. Next, the trace or diagonal sum of a matrix (b_{ij}) is equal to the sum of the eigenvalues, $\sum_s \lambda_s$, of the characteristic determinant $|b_{ij} - \lambda \delta_{ij}|$, where δ_{ij} is the Kronecker delta. From eq (5) it is seen that for the matrix $(-a_{ij})$ the diagonal sum is $\sum_{i,j} k_{ij}$, where the prime means $i \neq j$. Since the eigenvalues of the characteristic determinant are un-

⁵ See appendix, section 3.2.

changed if each element is replaced by its negative, the sum of the eigenvalues of Δ is $-\sum_{i,j} k_{ij}$. The latter property is useful as a check when the eigenvalues are determined in a particular problem.

2.4. Relaxation Times

With the general results obtained in section 2.3, we may write the solutions of the rate equations, noting that f_1 is zero, in the form

$$\begin{aligned} N_i &= C_{i1} + C_{i2} e^{f_2(k)t} + \dots \\ &= C_{i1} + C_{i2} e^{-t/\tau_2} + \dots \end{aligned} \quad (4')$$

where the τ_β are defined as the molecular relaxation times [1,2,3]

$$\tau_\beta = -1/f_\beta(k). \quad (6)$$

Since we have shown that the f_β are all real and negative, it follows that the τ_β for the general six-site Cartesian axes model are all real and positive. As implied earlier, eq (4') show how and at what rate a system tends to return to equilibrium after the abrupt removal of a disturbance such as a static electric field. Thus, for any arbitrary choice of the k_{ij} , consistent with eq (2), the return of the system to equilibrium is described by an exponential decay and cannot include any oscillatory modes.

Also, from the application of Gerschgorin's Theorem to the range of the eigenvalues, we find that the shortest relaxation time τ_{\min} is⁶

$$\tau_{\min} \geq \frac{1}{2|a_{mm}|}, \quad (7)$$

where a_{mm} is the most negative diagonal element in the matrix (a_{ij}) defined in section 2.3. If k_{pq} is the largest of the k_{ij} , eq (5) and (7) lead to

$$\tau_{\min} \geq \frac{1}{8k_{pq}}. \quad (8)$$

The above results cover the inferences that may be readily drawn regarding the molecular relaxation times for the general six-site model.

2.5. Dielectric Relaxation Spectrum

If we assume the molecular and macroscopic relaxation times are equal, an approximation used previously [1,2,3,5], the molecular relaxation times τ_β describe the approach to equilibrium of the polarization. The coefficients $C_{i\beta}$ (for $\beta \geq 2$) in general measure the "strength" of each mode contributing to the relaxation process. In the case where we consider the restoration of equilibrium following the removal of a static electric field, the polarization

⁶ In eq (7) the symbol $|a_{mm}|$ represents the absolute value of the a_{mm} .

$P(t)$ decays with time as

$$P(t) = \sum_{\beta} P_{\beta} e^{f_{\beta}(k) i} = \sum_{\beta} P_{\beta} e^{-t/\tau_{\beta}}. \quad (9)$$

The coefficients P_{β} , and hence the orientational polarizabilities α_{β} associated with each mode, may be obtained from the quantities $C_{i\beta}$ ($\beta \geq 2$) for a particular model by standard methods [1]. The α_{β} are calculated assuming a polycrystalline substance.

We note that for sinusoidal fields eq (9) leads to the approximate expression [1,6]

$$\epsilon''(\omega) \cong K \sum_{\beta} \alpha_{\beta} \omega \tau_{\beta} / (1 + \omega^2 \tau_{\beta}^2), \quad (10)$$

where $\epsilon''(\omega)$ is the dielectric-loss factor as a function of angular frequency ω , K is a constant, and α_{β} is the orientational polarizability associated with the β th mode. Although the expression is not exact, it is sufficient for an approximate analysis of the general characteristics of the dielectric relaxation spectrum. For the case of a single relaxation time, eq (10) reduces to the form of the Debye equation [7] for $\epsilon''(\omega)$.

The coefficients $C_{i\beta}$ (and hence the P_{β} and α_{β}) cannot be obtained explicitly in the general case as they depend (eq (3) and (4)) on the eigenvalues, and the latter cannot be expressed explicitly in terms of the k_{ij} . As a consequence, we have not been able to prove in the general case, where the k_{ij} are distinct, that all relaxation modes are active in the dielectric spectrum. However, the latter situation seems quite possible, since in earlier calculations inactive modes (compensatory reorientation of dipoles to maintain a net dipole moment of zero) were formed only for very simple models, such as those containing two pairs of equivalent sites.

To obtain further information about the dielectric behavior of dipolar systems represented by the general six-site model, it is necessary to examine special models. This is planned for a subsequent paper.

A few useful formulas to apply to special models are given in the appendix, section 3.4.

The author is indebted to John D. Hoffman for numerous helpful discussions regarding the general subject and to Karl Goldberg and Martin Greenspan for assistance with mathematical aspects.

3. Appendix

3.1. Relations Between k_{ij}

Let the free energies relative to an arbitrary zero of energy for two adjacent sites i and j be designated as V_i and V_j , and the free-energy barriers for i to j and j to i transitions be defined as W_{ij} and W_{ji} , respectively. The height of the free-energy barrier between sites i and j , referred to the zero of energy, is then

$$W(i,j) = V_i + W_{ij} = V_j + W_{ji}. \quad (11a)$$

Consider a series of transitions i to j , j to l , l to i for

a closed circuit of three adjacent sites and write the equations corresponding to eq (11a) for the barrier heights referred to the zero of energy

$$j \rightarrow l \quad W(j,l) = V_j + W_{jl} = V_l + W_{lj} \quad (11b)$$

$$l \rightarrow i \quad W(l,i) = V_l + W_{li} = V_i + W_{il}. \quad (11c)$$

The sum of the eq (11) is

$$W_{ij} + W_{jl} + W_{li} = W_{ji} + W_{lj} + W_{il}. \quad (12)$$

If we recall the definition of k_{ij} , eq (1), inspection shows that eq (12) corresponds to $\log(k_{ij}k_{jl}k_{li}) = \log(k_{ji}k_{lj}k_{il})$, and hence

$$k_{ij}k_{jl}k_{li} = k_{ji}k_{lj}k_{il}. \quad (13)$$

The same type of relations, eq (12) and (13), can be obtained for any closed circuit of transitions between adjacent sites with three or more jumps to the circuit.⁷ For the six-site model there are seven independent relations, such as eq (13), namely, any seven of the eight eq (2). All others and those involving more sites are derivable from eq (13). Accordingly, of the 24 transition probabilities only 17 are independent. This is plausible on physical grounds. The local free-energy system of the general model is fixed when six minus one site energies and 12 barriers $W(i, j)$ are specified; the "minus one" arises because the zero of energy is arbitrary.

The following geometrical argument illustrates how all product relations of the type in eq (13), but involving more sites, can be constructed from suitable products of the product relations given in eq (2) for three adjacent sites.

The six orientational sites (fig. 1) are located at the corners of an octahedron. Associated with the product relations on the k_{ij} , eq (13), for a closed circuit of transitions between the adjacent sites i, j, l , is the circuit of the perimeter of the face with vertices i, j, l , and the inverse circuit. Consider a closed circuit along the edges of the octahedron connecting the successively adjacent sites i, j, l, \dots, m, i , for example, where there are 4, 5, or 6 sites. This closed circuit divides the octahedron, a simply connected surface, into two parts, each of which is constituted of triangular faces; for convenience, choose the surface with the fewer faces, labeled T_1, \dots, T_p . If we traverse in succession in the same sense⁸ as that on the whole perimeter (i, j, l, \dots, m, i), the perimeters of each of the triangular faces T_1, \dots, T_p this is the same as traversing the bounding path i, j, l, \dots, m, i .

⁷ An alternate method of arriving at product relations of the type in eq (13) or eq (2) is to invoke "detailed balancing" for each pair of adjacent sites. This means that at equilibrium the number of dipoles turning in unit time from site i to site j is equal to the number turning from site j to site i , or $k_{ij}C_{i1} = k_{ji}C_{j1}$; C_{i1} is the equilibrium number of dipoles in the i th site. For a particular case, sites 1, 2, 3, we may then write $k_{12}C_{11} = k_{21}C_{21}$, $k_{23}C_{21} = k_{32}C_{31}$, and $k_{31}C_{31} = k_{13}C_{11}$. The product of the last three equations yields eq (2a), $k_{12}k_{23}k_{31} = k_{21}k_{32}k_{13}$.

⁸ That is, if the perimeter of the portion of the surface bounded by the sites (i, j, \dots, m, i) is traversed in a clockwise sense by the above sequence, then each of the constituent triangles is traversed in the same sense.

m, i . Hence if we multiply the product equations such as (13) for the triangles T_1, \dots, T_p , traversing their edges in the correct sense, we obtain the corresponding product relation for the circuit (i, j, l, \dots, m, i) and the inverse circuit (i, m, \dots, l, j, i) . In this way the k_{ij} product relation for any sequence of connected sites can be formed by multiplying the product relations for the enclosed triangular circuits.

3.2. Application of Goldberg's Theorem⁹ to the Matrix for the Six-Site Model

Theorem: If a real matrix $A=(a_{ij})$ of order n has the properties $a_{ij} \geq 0$ for $i, j=1, \dots, n$ with $i \neq j$ and

$$a_{i_1 i_2} a_{i_2 i_3} \dots a_{i_m i_1} = a_{i_2 i_1} a_{i_3 i_2} \dots a_{i_1 i_m} \quad (14)$$

for all (i_1, \dots, i_m) belonging to $(1, \dots, n), m \geq 3$, then all the characteristic roots of A are real.

We wish to apply the theorem to the matrix $-\Delta_0$ derived from Δ in eq (5a) by letting \mathbf{D} be zero and changing the signs of the elements. If we let a_{ij} be the element of $-\Delta_0$ in the i th row and the j th column, the usual order of index notation, we note that for $i \neq j$

$$a_{ij} = k_{ji}, \quad (15)$$

i. e., the order of indices is reversed on the k 's. Hence with eq (15), eq (14) can be written as follows, after interchanging the left and right sides and then reversing the factor order on the right side:

$$\begin{aligned} k_{i_1 i_2} k_{i_2 i_3} \dots k_{i_m i_1} &= k_{i_2 i_1} k_{i_3 i_2} \dots k_{i_1 i_m} \\ &= k_{i_1 i_m} \dots k_{i_3 i_2} k_{i_2 i_1}. \end{aligned} \quad (14')$$

Equation (14') now evidently equates the product of k_{ij} 's for the closed circuit of m sites ($3 \leq m \leq 6$) $i_1 \rightarrow i_2, i_2 \rightarrow i_3, \dots, i_m \rightarrow i_1$ to the corresponding product for the inverse circuit $i_1 \rightarrow i_m, \dots, i_2 \rightarrow i_1$. There are two types of circuits: (a) circuits in which at least one successive pair i_p, i_q are nonadjacent sites, and (b) circuits in which all successive site pairs are adjacent. Since by the S - J hypothesis $k_{i_p i_q} \equiv k_{i_q i_p} \equiv 0$ for all nonadjacent site pairs, eq (14'), and hence eq (14), is valid for case (a). Next we have indicated in section 3.1 that closed-circuit product relations of the type eq (14') are valid for a sequence of three or more adjacent sites. Hence our matrix $-\Delta_0$ for the general six-site model satisfies the above theorem.

3.3. Range of Eigenvalues

Brauer [5] has derived the following theorem regarding the characteristic roots (eigenvalues) of a matrix.

⁹ K. Goldberg of the Applied Mathematics Division of the Bureau. His proof is published in RP2652 in this Journal. The theorem as stated above is in a slightly different form from that as stated by Goldberg; his condition (2) has been replaced by the condition $a_{ij} \geq 0$ which still permits the construction of an equivalent symmetric matrix, namely, $b_{ij} = (a_{ij} a_{ji})^{1/2}$.

Theorem: Let $A=(a_{ij})$ be an arbitrary matrix and

$$\sum_{\substack{j=1 \\ j \neq i}}^n |a_{ij}| = P_i, \quad \sum_{\substack{i=1 \\ i \neq j}}^n |a_{ij}| = Q_j.$$

Each characteristic root λ lies in at least one of the circles

$$|z - a_{ii}| \leq P_i$$

and in at least one of the circles

$$|z - a_{jj}| \leq Q_j.$$

A is a square matrix of order n over the complex field; z is the complex variable $x + iy$. P_i is the sum of the absolute values of the off-diagonal elements in the i th row; Q_j is a similar sum for the j th column.

In the matrix $-\Delta_0$ derived from the characteristic determinant, eq (5a), by letting \mathbf{D} be zero and changing the signs, we know that the off-diagonal elements are all real and positive, and so an off-diagonal column sum is Q_j . Also from eq (5a) we see that the j th diagonal element a_{jj} is $-Q_j$. Hence, for the j th circle ($j=1, \dots, 6$) the radius is Q_j , and the center is on the real axis at $-Q_j$. Let $Q_m \geq Q_j$ ($j=1, \dots, 6$). Q_m defines the largest circle. Previously all roots were shown to be real. Hence all roots lie on or within the m th circle on the axis of reals, that is between zero and $2a_{mm}$ (a_{mm} being the most negative of the diagonal elements in $-\Delta_0$).

3.4. Useful Formulas

Relation between the equilibrium number of dipoles in each site with and without a static electric field. We refer to the method of solving the rate equations in reference 1. After a "mode analysis" in which for each given mode β the coefficients $C_{i\beta}$ are determined relative to one another, the boundary condition at $t=0$ is introduced. This condition corresponds to the sudden removal of a static electric field. This results in the equations

$$C_{i1}^F = \sum_{\beta} C_{i\beta},$$

where C_{i1}^F is the equilibrium number of dipoles in the i th site in the presence of the field. A general expression for these coefficients in terms of the equilibrium coefficients for zero field is helpful in solving any particular model.

The equations below for the C_{i1}^F are derived in a manner similar to that indicated in section 2.4 of reference 1.

We assume a static electric field \vec{F} defined by the magnitude F and the polar angles ξ and θ , with ξ being the azimuth angle measured from the z -axis. For convenience, let

$$\gamma = \mu F / kT \quad \text{and} \quad \gamma_x = \gamma \sin \xi \cos \theta$$

$$\gamma_y = \gamma \sin \xi \sin \theta$$

$$\gamma_z = \gamma \cos \xi.$$

Then

$$\left. \begin{aligned}
 C_{11}^F &= C_{11} \left[1 - \gamma_x(C_{31} - C_{51})/N - \gamma_y(C_{21} - C_{41})/N - \gamma_z \left(\frac{C_{11} - C_{61}}{N} - 1 \right) \right] \\
 C_{21}^F &= C_{21} \left[1 - \gamma_x(C_{31} - C_{51})/N - \gamma_y \left(\frac{C_{21} - C_{41}}{N} - 1 \right) - \gamma_z(C_{11} - C_{61})/N \right] \\
 C_{31}^F &= C_{31} \left[1 - \gamma_x \left(\frac{C_{31} - C_{51}}{N} - 1 \right) - \gamma_y(C_{21} - C_{41})/N - \gamma_z(C_{11} - C_{61})/N \right] \\
 C_{41}^F &= C_{41} \left[1 - \gamma_x(C_{31} - C_{51})/N - \gamma_y \left(\frac{C_{21} - C_{41}}{N} + 1 \right) - \gamma_z(C_{11} - C_{61})/N \right] \\
 C_{51}^F &= C_{51} \left[1 - \gamma_x \left(\frac{C_{31} - C_{51}}{N} + 1 \right) - \gamma_y(C_{21} - C_{41})/N - \gamma_z(C_{11} - C_{61})/N \right] \\
 C_{61}^F &= C_{61} \left[1 - \gamma_x(C_{31} - C_{51})/N - \gamma_y(C_{21} - C_{41})/N - \gamma_z \left(\frac{C_{11} - C_{61}}{N} + 1 \right) \right]
 \end{aligned} \right\} \quad (16)$$

The total polarizability, α_{tot} . We assume a polycrystalline substance and follow the procedure outlined in section 2.4, reference 1, for obtaining the polarizability associated with each mode. Here, however, we introduce for each site i the value of N_i at $t=0$, namely, C_{i1}^F . With the use of the expressions for the C_{i1}^F given in the preceding paragraph, one can obtain

$$\alpha_{\text{tot}} = \left[1 - \frac{(C_{31} - C_{51})^2 + (C_{21} - C_{41})^2 + (C_{11} - C_{61})^2}{N^2} \right] \frac{\mu^2}{3kT} \quad (17)$$

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