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Polarization of Liquids[†]

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Abstract—Liquid media composed of structured particles may be polarized in a variety of ways. Such polarization is usually accompanied by changes in the electromagnetic and the transport properties of the media. In this work, we propose an informal theory of polarizable liquids, which covers the whole range of polarizations from very weak (many ordinary liquids) to very strong (liquid crystals).

For a system composed of rigid and transversely isotropic particles, we write an equation of change of the particle density, from which the equations of moments, called the polarization tensors, are derived. By allowing the macroscopic properties to depend on the polarization tensors, one can predict the behavior of a liquid under the polarizing influences such as an electromagnetic field, shearing or proximity to an interface. Some of these predictions, made for strong polarizations, are found to give a good description of a number of electromagnetic and transport phenomena in liquid crystals of nematic type.

1. Introduction

In classical continuum theory, a body of material is viewed as a set of points devoid of any structure. To remove this limitation of theory, one usually assigns some internal structure to each point. In this process, it seems natural to choose a model that is fairly close to known structures, such as molecules or atoms, of the material. A difficulty in this approach is that, since a point in a continuous body represents a great number of elementary particles in its neighborhood, the assigned structure as such corresponds only to some statistical average of the structures of the particles. For example, suppose that we idealize each molecule of a material as a

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director, called a microdirector, and assign a director field, called a macrodirector, to a body of the material. Then it is obvious that the spin of the macrodirector is not necessarily the same as the average of the spins of the microdirectors; this is best illustrated by the case of flow birefringence of liquids under a steady and simple shear. The notable success of Ericksen's⁽¹⁾ liquid crystal theory appears to be due to the fact that the macro and the microdirectors in liquid crystals coincide in most cases.

This work is aimed at obtaining a practical theory which is free of the foregoing difficulty. We proceed by assigning microstructures to elementary particles and obtaining the corresponding macrostructure as their statistical averages. Once this is done, dependence of material responses, such as the stress, on the assigned (macro) structure can be determined. The equation of change of macrostructure and the usual conservation laws of mass, momentum, angular momentum, and energy will then give a complete description of the material's behavior.

It is possible that a point of the body may be structureless and thus the classical continuum theory applies although its elementary particles are definitely structured. If such a point is subjected to various directing influences, such as a shear, an electromagnetic field, or proximity to an interface, then the particles may be aligned in a non-random fashion, resulting in some macrostructure. That is, the point may become polarized. The most obvious examples of polarizable or polarized media are provided by liquid crystals or mesophases. Also materials of polymeric constitution are certainly polarizable⁽²⁾ and certain phenomena exhibited by water and other low-molecular weight liquids⁽³⁾ may be the results of polarization.⁽⁴⁾

When a medium is composed of rigid and identical particles which are neither created nor destroyed, the macroscopic number density n of the particles is described by the usual equation of continuity:

$$\dot{n} + n(\nabla \cdot \mathbf{u}) = 0 \tag{1.1}$$

Here $\dot{n}$ denotes the material derivative of n and $\mathbf{u}$ is the so-called mass average velocity of the medium. Equation (1.1) follows from the principle of conservation of number of particles once n and $\mathbf{u}$ are defined and the usual smoothness assumptions made.

Equation (1.1) is not a sufficient expression of the principle of conservation of number of particles for media that are polarizable in the sense defined above, because the orientation of the particles is unaccounted for. A more general macroscopic number density and a correspondingly more general equation of continuity are needed. In the following, the requisite equation is given, constitutive equations for the fluxes that appear in it are suggested, and a set of quantities called the polarization tensors are introduced. The polarization tensors give a macroscopic description of the polarization of a medium.

2. The Equation of Continuity for Polarizable Media

We suppose that each particle of the medium is transversely isotropic about its major axis and we let the unit vector $\mathbf{d}$ specify the direction in which that axis is oriented at any time. If there is no means by which the " head " of a particle may be distinguished from its " tail ", then the sense of $\mathbf{d}$ (that is, $\mathbf{d}$ or $-\mathbf{d}$) may be chosen arbitrarily and subsequent equations in which $\mathbf{d}$ appears must reflect this arbitrariness of choice.

Consider the stationary five-dimensional domain shown in Fig. 1. All particles in this domain have their centers of mass contained in the sub-domain V and we let x denote the position vector of a particle's center of mass with respect to an arbitrarily chosen origin. In a similar fashion, the tips of particle orientation vectors lie in the sub-domain Ω on the surface of the unit sphere surrounding $\mathbf{x}$.

Define a number density function $n_{\mathbf{d}}(t, \mathbf{x}, \mathbf{d})$ such that $n_{\mathbf{d}}(t, \mathbf{x}, \mathbf{d})$ $dVd\Omega$ gives the number of particles with mass centers in the infinitesimal volume dV having the tips of their orientation vectors in the

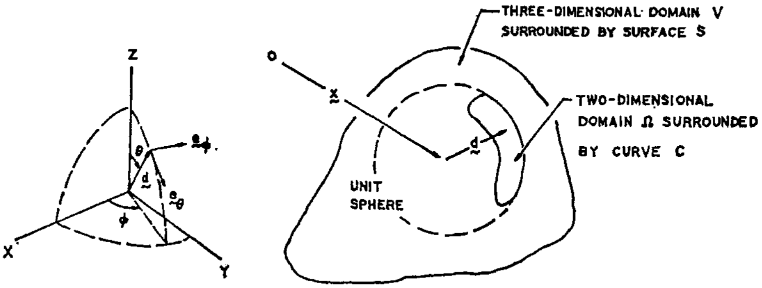

Figure 1

infinitesimal solid angle $d\Omega$. The ordinary density function, $n(t, \mathbf{x})$, is just

$$n(t, \mathbf{x}) = \oint_{4\pi} n_{\mathbf{d}}(t, \mathbf{x}, \mathbf{d})\, d\Omega \tag{2.1}$$

Hence, one can define a normalized density $f(t, \mathbf{x}, \mathbf{d})$ such that

$$f(t, \mathbf{x}, \mathbf{d}) = \frac{n_{\mathbf{d}}(t, \mathbf{x}, \mathbf{d})}{n(t, \mathbf{x})} \tag{2.2}$$

Let $\mathbf{v}(t, \mathbf{x}, \mathbf{d})$ and $\boldsymbol{\omega}(t, \mathbf{x}, \mathbf{d})$ be the velocity of the center of mass and the spin, respectively, of a particle with orientation vector $\mathbf{d}$ and position vector $\mathbf{x}$ at time t. Then the principle of conservation of number of particles applied to the five-dimensional domain shown in Fig. 1 yields

$$\frac{d}{dt}\int_V \int_\Omega n_{\mathbf{d}}\, d\Omega\, dV = -\int_\Omega \oint_S n_{\mathbf{d}} \mathbf{v} \cdot \boldsymbol{\nu}_s\, dS\, d\Omega - \int_V \oint_C n_{\mathbf{d}} (\boldsymbol{\omega} \times \mathbf{d}) \cdot \boldsymbol{\nu}_c\, dC\, dV \tag{2.3}$$

where $\boldsymbol{\nu}_s$ and $\boldsymbol{\nu}_c$ are the outer normal vectors to the bounding surface S of V and the bounding curve C of Ω, respectively. When the usual smoothness assumptions are made, this equation may be changed with the aid of the divergence theorem to the differential equation

$$\frac{\partial n_{\mathbf{d}}}{\partial t} + \nabla \cdot (n_{\mathbf{d}} \mathbf{v}) + \nabla_{\mathbf{d}} \cdot (n_{\mathbf{d}} \boldsymbol{\omega} \times \mathbf{d}) = 0 \tag{2.4}$$

where $\nabla_{\mathbf{d}}$ is the two-dimensional gradient operator (see the Appendix).

Equation (2.4) is the first form of the generalized equation of continuity; the usual equation of continuity (i.e., Eq. (1.1)) is obtained from it by integrating each term over all possible orientations of $\mathbf{d}$. Here, identity (A.17) of the Appendix must be used, and one defines the mass-average velocity by

$$\mathbf{u} = \langle \mathbf{v} \rangle = \oint_{4\pi} f \mathbf{v}\, d\Omega \tag{2.5}$$

Thus, the mass-average velocity is also the average of the particle velocities over the distribution of orientations.

3. Fluxes of Orientation

The velocity of the medium in the neighborhood of position vector $\mathbf{x}$

at time t is just the mass-average velocity, $\mathbf{u}$; the spin of the medium in the neighborhood of position vector $\mathbf{x}$ at time t is the vorticity:

$$\boldsymbol{\omega}_0 = \tfrac{1}{2}\nabla \times \mathbf{u} \tag{3.1}$$

In the presence of polarizing influences, the velocity of the particles ($\mathbf{v}$) will not necessarily correspond to the velocity of the medium ($\mathbf{u}$) nor will the spin of the particles ($\boldsymbol{\omega}$) necessarily be synchronized with the spin of the medium ($\boldsymbol{\omega}_0$). This will give rise to a flow or flux of orientation in the medium. We define the translational and rotational parts of this flux by

$$\mathbf{j}_T = (\mathbf{v} - \mathbf{u})f \tag{3.2}$$

$$\mathbf{j}_R = (\boldsymbol{\omega} - \boldsymbol{\omega}_0) \times \mathbf{d}f \tag{3.3}$$

Because of the definition of the flux $\mathbf{j}_T$, one finds that

$$\oint_{4\pi} \mathbf{j}_T d\Omega = \mathbf{0} \tag{3.4}$$

The equation of continuity (Eq. (2.4)) may be rewritten in terms of the fluxes; the result is

$$\dot{f} + \nabla_{\mathbf{d}} \cdot (f\boldsymbol{\omega}_0 \times \mathbf{d}) + \frac{1}{n}\nabla \cdot (n\mathbf{j}_T) + \nabla_{\mathbf{d}} \cdot \mathbf{j}_R = 0 \tag{3.5}$$

This form will be more useful in our subsequent considerations.

4. Constitutive Equations for the Fluxes of Orientation

In a rigorous formulation of the problem, the constitutive relations for the fluxes $\mathbf{j}_T$ and $\mathbf{j}_R$ should be found by solving the balance equations for momentum and angular momentum, somewhat as Condiff and Dahler⁽⁵⁾ have described. Here, however, we shall assume that such balance equations reduce to force and torque balances for each particle, presumably by neglecting acceleration terms, such that each flux can be expressed as the sum of a diffusion flux—that is, a flux due to random, thermal motions—and a linear superposition of fluxes due to polarizing influences. We shall also assume that any coupling between rotational and translational motions can be neglected. Then the assumed constitutive equations are

$$\mathbf{j}_T = -D_T \nabla f + \alpha_T(\mathbf{g} - \langle \mathbf{g} \rangle)f \tag{4.1}$$

$$\mathbf{j}_R = -D_R \nabla_{\mathbf{d}} f + \alpha_R \mathbf{l} \times \mathbf{d}f + \gamma f \mathbf{d} \cdot \mathbf{D} \cdot \nabla_{\mathbf{d}} \mathbf{d} \tag{4.2}$$

and these correspond to the constitutive equations calculated by Condiff and Dahler.(5) In these equations, **g** and **l** are the force and the torque, respectively, that an electromagnetic field **h** (electric or magnetic) exerts on a particle,

$$\mathbf{D} = \tfrac{1}{2}[\nabla\mathbf{u} + (\nabla\mathbf{u})^{\dagger}]$$

is the rate of strain dyadic, D_T, D_R, α_T, and α_R are phenomenological coefficients, the first pair being called diffusion coefficients and the second pair being called mobilities, and γ is a dimensionless constant that depends on the particle geometry. The rotational diffusion coefficient and mobility are related by Einstein's formula

$$D_R = \alpha_R kT \tag{4.3a}$$

where k is Boltzmann's constant. If the part $-D_T \nabla f$ of $\mathbf{j}_T$ is due to a diffusive motion alone, then the translational diffusion coefficient and mobility are also related by Einstein's formula

$$D_T = \alpha_T kT \tag{4.3b}$$

Equation (4.3b) may not be true in all cases, particularly in the case of mesophases. In mesophases, random motions undoubtedly contribute to the part $-D_T \nabla f$ of $\mathbf{j}_T$, but this effect is probably quite small in comparison with that of the long-range interactions between the particles which tend to align all particles. What we shall assume here is that this tendency for orientation to spread can be modelled as a diffusion process and characterized quantitatively by a diffusion coefficient. This motion was first introduced explicitly by Sullivan,(6) although it seems to be implicit in the work of Van Wyk.(7)

The last term on the right hand side of Eq. (4.2) represents the effect of a shear field on the rotational flux of orientation. In the absence of other polarizing influences, a spherical particle moving in a viscous medium will have a spin synchronized with the local spin of the fluid; i.e.,

$$\boldsymbol{\omega} - \boldsymbol{\omega}_0 = \mathbf{0} \quad \text{(spheres)}$$

On the other hand, a long, thin, rod-like particle will move such that its tips move with the fluid;(8) this implies that

$$\boldsymbol{\omega} - \boldsymbol{\omega}_0 = \mathbf{d} \times (\mathbf{d} \cdot \mathbf{D}) \quad \text{(rods)}$$

For particles of intermediate shape, we postulate that

$$\boldsymbol{\omega} - \boldsymbol{\omega}_0 = \gamma \mathbf{d} \times (\mathbf{d} \cdot \mathbf{D})$$

where γ is a dimensionless geometric factor, being 0 for a sphere or 1 for a rod. For a prolate spheroid, Jeffery's calculation would give

$$\gamma = \frac{a^2 - 1}{a^2 + 1} \tag{4.5}$$

where a is the ratio of the length of the major axis to the length of the minor axis. Thus, the contribution of the polarizing influence of a shear field to the rotational orientation flux is

$$f\gamma[\mathbf{d} \times (\mathbf{d} \cdot \mathbf{D})] \times \mathbf{d} = \gamma f \mathbf{d} \cdot \mathbf{D} \cdot \nabla_{\mathbf{d}} \mathbf{d}$$

where the identities (A.5) and (A.6) of the Appendix have been used.

The constitutive equations given above are not useful unless further hypotheses to relate the force, $\mathbf{g}$, and the torque, $\mathbf{l}$, to the field, $\mathbf{h}$ are advanced. Here, we shall assume that the force is independent of particle orientation so that

$$\mathbf{g} - \langle \mathbf{g} \rangle = \mathbf{0} \tag{4.6}$$

Next we assume that the material is linear and that the field is essentially uniform, so that

$$\mathbf{l} = [\boldsymbol{\chi} \cdot \mathbf{h} + \mathbf{p}] \times \mathbf{h} \tag{4.7}$$

where $\boldsymbol{\chi}$ is the polarizability dyadic of the material and $\mathbf{p}$ is its permanent dipole moment. Finally, with the hypotheses that particles are transversely isotropic, it must be true that

$$\boldsymbol{\chi} = \chi_t \boldsymbol{\delta} + (\chi_a - \chi_t)\mathbf{dd} \tag{4.8}$$

$$\mathbf{p} = p\mathbf{d} \tag{4.9}$$

where χ_t and χ_a are the polarizabilities of the particle in the transverse and axial directions, respectively, and $\boldsymbol{\delta}$ is the unit dyadic. Notice that if the particle has a permanent dipole moment, then the sense of the orientation vector can be chosen uniquely (cf. Sec. 2).

If we put

$$\mathbf{F} = \frac{(\chi_a - \chi_t)}{kT}\mathbf{h} \tag{4.10}$$

and

$$\mathbf{h}_p = \frac{p}{kT}\mathbf{h} \tag{4.11}$$

then the orientation fluxes become for the material just described:

$$\mathbf{j}_T = -D_T\nabla f \tag{4.12}$$

$$\mathbf{j}_R = -D_R\nabla_{\mathbf{d}}f + f\mathbf{d}\cdot(D_R\mathbf{F}+\gamma\mathbf{D})\cdot\nabla_{\mathbf{d}}\,\mathbf{d} + D_R f\mathbf{h}_p\cdot\nabla_{\mathbf{d}}\,\mathbf{d} \tag{4.13}$$

where Eq. (A.6) of the Appendix has been used.

5. Moments: Polarization Tensors

In principle, one could solve subject to appropriate initial and boundary conditions the equation of continuity (3.5), with the fluxes written in terms of the distributions of orientation and its gradients by means of the constitutive Eqs. (4.12) and (4.13). In most cases, however, this goes beyond what is needed, and knowledge of the moments of the distribution of orientation is sufficient. In this section, we obtain the equations of change for the so-called polarization tensors, which are just the moments of the distribution of orientation.

Let $z(\mathbf{d})$ be a function of $\mathbf{d}$ which can be differentiated with respect to $\mathbf{d}$ as many times as desired. The average of z will be a function of t and $\mathbf{x}$, and is defined by

$$Z(t, \mathbf{x}) \equiv \langle z(\mathbf{d})\rangle \tag{5.1}$$

The equation of change for Z is obtained by multiplying both sides of Eq. (3.5) by z and integrating all terms over all possible orientations of $\mathbf{d}$. The result can be written as

$$Z = -\nabla\cdot\mathbf{J}_z + \sigma_z \tag{5.2}$$

Where the co-rotational time derivative, $\overset{*}{\dot{Z}}$, the flux, $\mathbf{J}_z$, and the source term, σ_z, are defined by

$$\overset{*}{\dot{Z}} = \dot{Z} - \langle(\boldsymbol{\omega}_0\times\mathbf{d})\cdot\nabla_{\mathbf{d}}\,z\rangle \tag{5.3}$$

$$\mathbf{J}_z = \oint_{4\pi}\mathbf{j}_T\,z\,d\Omega \tag{5.4}$$

and

$$\sigma_z = \oint_{4\pi}\mathbf{j}_R\cdot\nabla_{\mathbf{d}}\,z\,d\Omega \tag{5.5}$$

In order to obtain these results, the identity (A.18) of the Appendix must be used. It has also been assumed that the medium is incompressible.

We define a set k-adics $\mathbf{P}^{(k)}$ that we call the polarization tensors:

$$\mathbf{P}^{(k)} = \langle \mathbf{d}^k \rangle, \quad k = 1, 2, 3, \ldots \tag{5.6}$$

The equations of change for the polarization tensors are obtained by putting $z = \mathbf{d}^k$ in Eqs. (5.2)–(5.5). The manipulations involved in reducing the formulas to the results given below are quite lengthy, and so are relegated to the Appendix. The results can be expressed most compactly if we define two tensor-valued functions $\mathbf{G}^{(k)}$ and $\mathbf{H}^{(k)}$ by

$$\mathbf{G}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{X}) = k(\mathbf{X}\cdot\mathbf{P}^{(k)})_s - k\mathbf{X}_s\!:\ \mathbf{P}^{(k+2)} \tag{5.7}$$

$$\mathbf{H}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{a}) = k(\mathbf{a}\mathbf{P}^{(k-1)})_s - k\mathbf{a}\cdot\mathbf{P}^{(k+1)} \tag{5.8}$$

Here, $\mathbf{X}$ and $\mathbf{a}$ are a second order tensor and a vector, respectively. The subscript s denotes the completely symmetric part of a tensor as defined in the Appendix.

The co-rotational derivative, the flux, and the source term for the case $z = \mathbf{d}^k$ can then be written as

$$\overset{*}{\dot{Z}} = \dot{\mathbf{P}}^{(k)} + \mathbf{G}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{W}) = \mathbf{P}^{(k)} + k(\mathbf{W}\cdot\mathbf{P}^{(k)})_s \tag{5.9}$$

$$\mathbf{J}_z = -D_T\nabla\mathbf{P}^{(k)} \tag{5.10}$$

$$\sigma_z = \mathbf{G}^{(k)}(\mathbf{P}^{(k)};\ \gamma\mathbf{D} + D_R\mathbf{F}) + \mathbf{H}^{(k)}(\mathbf{P}^{(k)};\ D_R\mathbf{h}_p) - 6D_R\mathbf{A}^{(k)} \tag{5.11}$$

in which

$$\mathbf{W} = \tfrac{1}{2}[\nabla\mathbf{u} - (\nabla\mathbf{u})^\dagger] \tag{5.12}$$

is the vorticity tensor, and the $\mathbf{A}^{(k)}$, defined by

$$\mathbf{A}^{(k)} = \frac{k}{6}[(k+1)\mathbf{P}^{(k)} - (k-1)(\boldsymbol{\delta}\mathbf{P}^{(k-2)})_s] \tag{5.13}$$

are called the anisotropy tensors.

The equation of change for the kth polarization tensor is thus

$$\begin{aligned}\dot{\mathbf{P}}^{(k)} = D_T\nabla^2\mathbf{P}^{(k)} + \mathbf{G}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{W}^\dagger + \gamma\mathbf{D} + D_R\mathbf{F}) +\\ \mathbf{H}^{(k)}(\mathbf{P}^{(k)};\ D_R\mathbf{h}_p) - 6D_R\mathbf{A}^{(k)}\end{aligned} \tag{5.14}$$

From the definitions of $\mathbf{G}^{(k)}$ and $\mathbf{H}^{(k)}$, it will be seen that in general this equation for $\mathbf{P}^{(k)}$ will also contain terms involving $\mathbf{P}^{(k-1)}$, $\mathbf{P}^{(k+1)}$, and $\mathbf{P}^{(k+2)}$. Thus, in general we cannot find the polarization tensors by solving *successively* for $\mathbf{P}^{(1)}$, then for $\mathbf{P}^{(2)}$, etc.

6. Some Special Cases

We consider here a number of cases in which the medium is static; that is $\mathbf{u} = \mathbf{0}$, so that $\mathbf{D}$ and $\mathbf{W}$ also vanish and the co-rotational time derivative becomes the partial time derivative.

1) When the system considered is in a steady state with no applied electromagnetic field and its surface-to-volume ratio is very small so that polarization is uniform, Eq. (5.14) reduces to

$$\mathbf{A}^{(k)} = \mathbf{0} \tag{6.1}$$

This may be called the disoriented state; it implies a purely random distribution of particle orientations.

2) When polarization is spatially uniform and steady under the influence of an electromagnetic field, Eq. (5.14) reduces to

$$\mathbf{A}^{(k)} = \tfrac{1}{6}[\mathbf{G}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{F}) + \mathbf{H}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{h}_p)] \tag{6.2}$$

One can show that this equation in fact represents a Boltzmann distribution of the energy of particles in the field. The equation is also a recurrence formula for the polarization tensors, and from it we can show that all $\mathbf{P}^{(k)}$ with $k \geqslant 3$ can be expressed in terms of $\mathbf{P}^{(1)}$ and $\mathbf{P}^{(2)}$. Thus, in this case only the first two polarization tensors need be considered.

3) When the electromagnetic field is changing in time but the polarization is uniform in space, Eq. (5.14) reduces to

$$\frac{1}{D_R}\frac{d\mathbf{P}^{(k)}}{dt} = \mathbf{G}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{F}) + \mathbf{H}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{h}_p) - 6\mathbf{A}^{(k)} \tag{6.3}$$

This is the equation used by Debye(9) in his dielectric theory.

4) When no electromagnetic field is applied, Eq. (5.14) for the case $k = 2$ reduces to

$$\frac{\partial \mathbf{A}^{(2)}}{\partial t} = D_T \nabla^2 \mathbf{A}^{(2)} - 6D_R\,\mathbf{A}^{(2)} \tag{6.4}$$

This is a diffusion equation with a sink term and was proposed by Sullivan(6) for the description of the orientation in a nematic liquid crystal near an interface. In Eq. (6.4), a characteristic length,

$$L = \sqrt{D_T/6D_R} \tag{6.5}$$

appears; this is a measure of the distance to which an interfacial polarization will propagate into the bulk of the medium.

5) If no electromagnetic field is applied and if the polarization is spatially uniform, then Eq. (5.14) for the case $k = 2$ reduces to

$$\frac{d\mathbf{A}^{(2)}}{dt} = -6D_R\mathbf{A}^{(2)} \tag{6.6}$$

This was proposed by Frenkel⁽¹⁰⁾ for the decay of orientation of a system of rod-like particles suspended in a liquid.

7. Two Limiting Cases

We have noted that in general one cannot solve the equations of change of the polarization tensors successively because of the presence of the tensors $\mathbf{P}^{(k+1)}$ and $\mathbf{P}^{(k+2)}$ in the equation of change for $\mathbf{P}^{(k)}$. However, when the polarization is either very weak or very strong, certain approximations can be made and the difficulty of the problem is reduced.

1) Let us assume first that the polarization is very weak. This might be the case, for instance, in most ordinary liquids, for which D_R is very large.

In the case of weak polarization $\mathbf{A}^{(k)} \doteq \mathbf{0}$ so that from Eq. (5.13), we have

$$(k+1)\mathbf{P}^{(k)} \doteq (k-1)(\boldsymbol{\delta}\mathbf{P}^{(k-2)})_s \tag{7.1}$$

This again is a recurrence formula for the polarization tensors, and from it we obtain formulas for $\mathbf{P}^{(k+1)}$ and $\mathbf{P}^{(k+2)}$ in terms of $\mathbf{P}^{(k-1)}$ and $\mathbf{P}^{(k)}$, respectively. Thus Eq. (5.14) for $\mathbf{P}^{(k)}$ will contain no polarization tensors of order greater than k, and successive solution of the equations becomes possible. However, it often turns out to be easier in these cases to solve Eq. (3.5)—for the density function f—directly. Examples are given by Debye.⁽⁹⁾

2) Consider now the case where one or more polarizing influences are very strong, so that thermal rotations of particles will be suppressed, and the medium becomes completely polarized. Under these conditions, we can write

$$f(t, \mathbf{x}, \mathbf{d}) \doteq \delta(\mathbf{n}(t, \mathbf{x}) - \mathbf{d}) \tag{7.2}$$

where δ denotes Dirac's delta function and $\mathbf{n}(t, \mathbf{x})$ is a field of unit vectors. Under these conditions

$$\mathbf{P}^{(k)} \doteq \mathbf{n}^k \tag{7.3}$$

and Eq. (5.14) becomes

$$\begin{aligned}\dot{\mathbf{n}}^k = {} & D_T \nabla^2 \mathbf{n}^k + \mathbf{G}^{(k)}(\mathbf{n}^k;\ \mathbf{W}^{\dagger} + \gamma \mathbf{D} + D_R \mathbf{F}) \\ & + \mathbf{H}^{(k)}(\mathbf{n}^k;\ D_R \mathbf{h}_p) - D_R k(k+1)\mathbf{n}^k + D_R k(k-1)(\boldsymbol{\delta}\mathbf{n}^{k-2})_s\end{aligned} \tag{7.4}$$

which is not difficult to solve.

Suppression of thermal rotations requires very strong polarizing influences and this requirement may be expressed as

$$\lim_{f \to \delta(\mathbf{n}-\mathbf{d})} \mathbf{P}^{(k)} \underset{(k\ \text{dots})}{\vdots} \mathbf{P}^{(k)} = 1 \tag{7.5}$$

Use of Eq. (7.4) when Eq. (7.5) is not satisfied will lead to some inconsistencies in the results.

8. The First Two Polarization Tensors

We have seen (cf. Sec. 6) that in certain cases, the higher polarization tensors $\mathbf{P}^{(k)}$, $k \geqslant 3$, can be written in terms of $\mathbf{P}^{(1)}$ and $\mathbf{P}^{(2)}$. On the other hand, $\mathbf{P}^{(1)}$ and $\mathbf{P}^{(2)}$ are irreducible. Hence, these two are the most important polarization tensors.

The polarization tensor $\mathbf{P}^{(2)}$, a dyadic, can be written as

$$\mathbf{P}^{(2)} = \sum_{i=1} \lambda_i \mathbf{n}_i \mathbf{n}_i \tag{8.1}$$

where the λ_i are the eigenvalues (real) of $\mathbf{P}^{(2)}$, and the $\mathbf{n}_i$ are the corresponding normalized eigenvectors. As polarization becomes very strong so that $f \to \delta(\mathbf{n}_1 - \mathbf{d})$, we will have $\lambda_1 \to 1$, λ_2, $\lambda_3 \to 0$ so that

$$\mathbf{P}^{(2)} = \mathbf{n}_1 \mathbf{n}_1 \tag{8.2}$$

It is to be noted that the *sense* of $\mathbf{n}_1$ is unimportant here.

In the literature on liquid crystals, the term " the preferred direction of particle orientation " is often encountered. When particles have permanent polarity along their major axis (i.e., when p in Eq. (4.9) is non-zero), then $\mathbf{P}^{(1)} = \mathbf{d}$ may be considered to represent this direction. In particular, for the case of very strong polarization in the direction of $\mathbf{n}_1$, we have $\mathbf{P}^{(1)} = \mathbf{n}_1$. However, when permanent polarity of the particles is absent, the orientations $\mathbf{d}$ and $-\mathbf{d}$ will be equally probable (that is, $f(t, \mathbf{x}, \mathbf{d}) = f(t, \mathbf{x}, -\mathbf{d})$)

and all the polarization tensors of odd order will vanish:

$$\mathbf{P}^{(k)} = \mathbf{0}, \quad k \text{ odd.} \tag{8.3}$$

In particular, $\mathbf{P}^{(1)} = \mathbf{0}$ even for strong polarization. Hence, when permanent polarity of the particles is absent, one of the eigenvectors of $\mathbf{P}^{(2)}$ may be considered to be the direction of preferred particle orientation. For the case of very strong polarization, this direction is then either $\mathbf{n}_1$ or $-\mathbf{n}_1$.

A special case arises when $\mathbf{P}^{(2)}$ is transversely isotropic so that (8.1) becomes

$$\mathbf{P}^{(2)} = \lambda_1 \mathbf{n}_1 \mathbf{n}_1 + \tfrac{1}{2}(1 - \lambda_1)(\boldsymbol{\delta} - \mathbf{n}_1 \mathbf{n}_1). \tag{8.4}$$

The unit vector field $\mathbf{n}$ appearing in the liquid crystal theories of Ericksen,(1,13) Leslie,(18) Lubensky(19) and others is identifiable with the eigenvector $\mathbf{n}_1$ in the above. Since the equation of change of $\mathbf{P}^{(2)}$ (Eq. (5.14) with $k = 2$) contains $\mathbf{P}^{(4)}$, it is not possible to derive the equation of change of $\mathbf{n}_1$ from Eq. (5.14) unless $\mathbf{P}^{(4)}$ is representable in terms of $\mathbf{P}^{(2)}$. This difficulty seems to be common in statistical theories of rod-like particles e.g. Prager(16). Hand(17) proposed an evaluation of $\mathbf{P}^{(4)}$ in terms of $\mathbf{P}^{(2)}$ when the polarization is very weak. For an illustrative purpose, let us consider the case where the polarization is relatively strong

$$\mathbf{P}^{(4)} \doteq \mathbf{P}^{(2)}\mathbf{P}^{(2)} \tag{8.5}$$

and uniform in space, where no electromagnetic field is applied and where $\lambda_1 \geqslant 1/3$. We introduce a vector field of variable magnitude

$$\mathbf{m} = m\mathbf{n}_1, \quad m = \sqrt{(3\lambda_1 - 1)/2}. \tag{8.6}$$

Then $\mathbf{P}^{(2)}$ and $\mathbf{A}^{(2)}$ can be written as

$$\mathbf{P}^{(2)} = \mathbf{m}\mathbf{m} + \tfrac{1}{3}(1 - m^2)\boldsymbol{\delta}, \quad \mathbf{A}^{(2)} = \mathbf{m}\mathbf{m} - \tfrac{1}{3}m^2\boldsymbol{\delta}, \tag{8.7}$$

substitution of which into Eq. (5.14) with $k = 2$ and multiplication of both sides of the equation by $\mathbf{m}$ give

$$\begin{aligned} \mathbf{m} = \gamma\left(\frac{2}{3m^2} + \frac{1}{3}\right)\mathbf{D}\cdot\mathbf{m} + \gamma\left(\frac{1}{3m^2} - \frac{4}{3}\right)\mathbf{D} : \mathbf{m}\mathbf{m}\mathbf{m} \\ - \left\{\frac{1}{3}\frac{\dot{m}}{m} + \frac{2}{9}\gamma(1 - m^2)\left(2 + \frac{1}{m^2}\right)\mathbf{D} : \boldsymbol{\delta} + 4D_R\right\}\mathbf{m}, \end{aligned} \tag{8.8}$$

where $\dot{m}$ may be eliminated if so desired. As the polarization becomes stronger, that is, as $m \rightarrow 1$, Eq. (8.8) reduces to

$$\overset{*}{\mathbf{m}} = \gamma \mathbf{D} \cdot \mathbf{m} - \gamma \mathbf{D} : \mathbf{mmm} - 4 D_R \mathbf{m}, \tag{8.9}$$

which can also be obtained directly by setting $k = 2$ in (7.4) and which is identical in form to the equation proposed by Ericksen(1)

$$\overset{*}{\mathbf{n}} = \mu_1 \mathbf{n} + \mu_2 \mathbf{D} : \mathbf{nnn} + \mu_3 \mathbf{D} \cdot \mathbf{n} \tag{8.10}$$

for describing the change of direction of preferred orientation in a flowing nematic liquid crystal. If the magnitude of the vector field $\mathbf{n}$ in Eq. (8.10) is variable, the coefficients μ_1, μ_2, and μ_3 may be interpreted according to Eq. (8.8).

9. Discussion

In the present paper, we have concentrated on the problems of describing polarization macroscopically by the set of polarization tensors and developing the equations of change for the polarization tensors. No attention has been given to application of the polarization tensors for macroscopic problems, but that is of course the principal purpose for attacking the two problems mentioned. To conclude this paper, it seems worthwhile to mention some of the uses to which the theory can be put.

The moment of inertia dyadic of a transversely isotropic particle will be $I_0 \boldsymbol{\delta} + I_1 \mathbf{dd}$. Hence, one finds that the macroscopic volume density of moment of inertia, $\bar{\mathbf{I}}$, is given by

$$\bar{\mathbf{I}} = n(I_0 \boldsymbol{\delta} + I_1 \mathbf{P}^{(2)}) \tag{9.1}$$

In a similar fashion, the torque on a transversely isotropic particle in an electromagnetic field is $[\chi_t \boldsymbol{\delta} + (\chi_a - \chi_t)\mathbf{dd}] \dot{\times} \mathbf{hh} + p\mathbf{d} \times \mathbf{h}$ so that the body couple exerted by the field is

$$\bar{\mathbf{l}} = nkT(\mathbf{P}^{(2)} \dot{\times} \mathbf{F} + \mathbf{P}^{(1)} \times \mathbf{h}_p) \tag{9.2}$$

For example, consider the balance equations for structured continua, proposed by Dahler and Scriven:(15)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$

$$\frac{\partial \mathbf{m}}{\partial t} + \nabla \cdot (\mathbf{um}) = \nabla \cdot \mathbf{T} + \mathbf{f}$$

$$\frac{\partial}{\partial t}(\mathbf{r}\times\mathbf{m}+\bar{\mathbf{I}}\cdot\boldsymbol{\omega})+\nabla\cdot\{\mathbf{u}(\mathbf{r}\times\mathbf{m}+\bar{\mathbf{I}}\cdot\bar{\boldsymbol{\omega}})\}=\nabla\cdot(-\mathbf{T}\times\mathbf{r}+\mathbf{C})$$
$$+(\mathbf{r}\times\mathbf{f}+\bar{\mathbf{l}}) \tag{9.3}$$

$$\frac{\partial\bar{\mathbf{I}}}{\partial t}+\nabla\cdot(\mathbf{u}\bar{\mathbf{I}})+\bar{\mathbf{I}}\times\bar{\boldsymbol{\omega}}-\bar{\boldsymbol{\omega}}\times\bar{\mathbf{I}}=\nabla\cdot\mathbf{J}+\boldsymbol{\Pi}+\mathbf{Q} \tag{9.4}$$

where ρ, $\mathbf{m}$, $\bar{\mathbf{I}}$, f and $\bar{\mathrm{l}}$ are densities of mass, momentum, moment of inertia, body force and body couple per unit volume, respectively, where $\mathbf{T}$ is the stress, $\mathbf{C}$ the couple stress, $\mathbf{r}$ the position vector and $\bar{\boldsymbol{\omega}}$ the macroscopic spin, and where $\mathbf{J}$ is the flux, $\boldsymbol{\Pi}$ the external supply density and $\mathbf{Q}$ the internal supply density of $\bar{\mathbf{I}}$ per unit volume. Then one can identify ρ with n times the particle mass, $\bar{\mathbf{I}}$ with (9.1) and $\bar{\mathrm{l}}$ with (9.2). Furthermore, in an incompressible case, (5.14) provides

$$\mathbf{J}=nI_1 D_T\nabla\mathbf{P}^{(2)}$$
$$\boldsymbol{\Pi}=nI_1\ \{\mathbf{G}^{(2)}(\mathbf{P}^{(2)};\ \gamma\mathbf{D}+D_R\mathbf{F})+\mathbf{H}^{(2)}(\mathbf{P}^{(2)};\ D_R\mathbf{h}_p)\}$$
$$\mathbf{Q}=nI_1\mathbf{G}^{(2)}(\mathbf{P}^{(2)};\ \boldsymbol{\epsilon}\cdot(\bar{\boldsymbol{\omega}}-\boldsymbol{\omega}_0))-6nI_1 D_R\mathbf{A}^{(2)}$$

where $\boldsymbol{\epsilon}$ is the alternator so that $\boldsymbol{\epsilon}\cdot\boldsymbol{\omega}_0=\mathbf{W}$. It is not difficult to see that $\mathbf{Q}=\mathbf{0}$ when $\mathbf{P}^{(2)}\propto\boldsymbol{\delta}$. This list could be extended, but this example should suffice to illustrate how polarization can appear at the macroscopic level and its equation of change complement a theory of transport phenomena. More interested readers are referred to a discussion of Prager's(16) theory of suspended dumbbells by Hand.(17)

One may note that we have not attempted to relate the macroscopic spin $\bar{\boldsymbol{\omega}}$ to the microscopic spin $\boldsymbol{\omega}$, appearing in (2.4) and (3.3). As discussed in § 4, such is possible only when one introduces an equation, which is more general than (2.4), but which is very difficult to integrate.(5) Hence we leave $\bar{\boldsymbol{\omega}}$ to be described by the macroscopic equation (9.3). In the liquid crystal theory of Ericksen(1,13) and Leslie,(18) the internal angular momentum $\bar{\mathbf{I}}\cdot\bar{\boldsymbol{\omega}}$ is replaced by

$$\rho_1\mathbf{n}\times\dot{\mathbf{n}}$$

which we prefer to interpret as a limiting case of very strong polarization, although we realize that their theory may also apply to weaker polarizations (cf. (8.8) and 8.10)).

Polarization also affects the constitutive relations for the medium. Hence, the polarization tensors, particularly $\mathbf{P}^{(1)}$ and $\mathbf{P}^{(2)}$, should be included in the list of independent variables when such relations are to be considered. More generally, one can even include the $\overset{*}{\mathbf{P}}^{(k)}$—which are objective entities—as in Ericksen's(1,13) works. Hand(17) assumes that the stress tensor is a linear function of **D** and a symmetric tensor, which is identifiable with our $\mathbf{P}^{(2)}$, and shows that the predictions thus obtained for a simple shear flow are in good agreement with the experimental measurements of normal stress and apparent viscosity of certain high polymer solutions. Yun and Fredrickson(14,20,21) apply this notion to the transport phenomena in polarizable liquids by assuming that the transport coefficients are linear functions of $\mathbf{P}^{(2)}$. They obtain the following asymptotic formulas for the apparent viscosity(20) η in a viscometric flow and the apparent conductivity(21) K:

1) When the rate of shear at the boundary is S and the characteristic dimension of the viscometer is L, the " adsorption layer " thickness can be expressed as a simple function $f(\eta)$. Then $f(\eta) = c_1(SL^2)^{-1/2}$.

2) When an electromagnetic field **h** is applied in the direction of the velocity gradient, $\eta = c_2 + c_3(h^2/S)^2$.

3) In a gap of width L, $K = c_4 + c_5 L^{-1}$.

4) When a large volume is subjected to **h**, $K = c_6 + c_7 h^{-2}$.

Here, $c_1, \ldots, c_7$ are constants. These predictions are in good agreement with the experimental measurements in nematic liquid crystals: Viscosities in microcapillaries,(20a) in an electric field,(20b) and in a magnetic field;(20c) thermal conductivity in a gap;(21a) and dielectric constant,(21b) mass diffusion coefficient,(21c) and thermal conductivity(21d) in magnetic fields. The prediction (3) is confirmed also for thermal conductivity of water in narrow gaps.(21e) Our attempt to obtain similar predictions from other liquid crystal theories has been unsuccessful.

We do not claim that this theory contains the established continuum or molecular theories of liquid crystals. Nor does it give *all* predictions others have proposed for liquid crystals, although some predictions for major special cases are identical as discussed by Yun.(14) However, it is equipped with a complete equation of change of the distribution of particle orientations ((3.5), (4.12)and (4.13)) so that one may consider the averages of any entities associated with the particles. And, because of this flexibility, we believe that this informal theory will be useful in relating our understanding of liquid crystals to that of ordinary liquids.

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Appendix

DEFINITIONS, IDENTITIES, AND THE EQUATIONS OF CHANGE FOR THE POLARIZATION TENSORS

In terms of the coordinates shown in Fig. 1, operations involving the two-dimensional del operator ∇_d may be written as

$$\nabla_d B = \mathbf{e}_\theta \frac{\partial B}{\partial \theta} + \mathbf{e}_\phi \frac{1}{\sin\theta}\frac{\partial B}{\partial \phi} \tag{A.1}$$

$$\nabla_d \cdot \mathbf{b} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta b_\theta) + \frac{1}{\sin\theta}\frac{\partial b\phi}{\partial\phi} \tag{A.2}$$

$$\nabla_d{}^2 B = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial B}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 B}{\partial\phi^2} \tag{A.3}$$

Herein, B is any sufficiently differentiable scalar, vector, or tensor, $\mathbf{b} = b_\theta \mathbf{e}_\theta + b_\phi \mathbf{e}_\phi$ is a " surface " (two-dimensional) vector, and $\mathbf{e}_\theta$, $\mathbf{e}_\phi$ are the unit vectors shown in Fig. 1.

Application of Eq. (A.1) to the unit orientation vector **d** gives

$$\begin{aligned}\nabla_d \mathbf{d} &= \mathbf{e}_\theta \mathbf{e}_\theta + \mathbf{e}_\phi \mathbf{e}_\phi \\ &= \boldsymbol{\delta} - \mathbf{dd}\end{aligned} \tag{A.4}$$

where $\boldsymbol{\delta}$ is the unit dyadic. One can call $\nabla_d \mathbf{d}$ the unit two-dimensional dyadic, since for any surface vector **b** (i.e., any vector for which $\mathbf{b}\cdot\mathbf{d} = 0$), one finds

$$\nabla_d \mathbf{d}\cdot\mathbf{b} = \mathbf{b} \tag{A.5}$$

Another useful result follows from Eq. (A.4) and the decomposition of the vector triple product; for any vector **a**, it is

$$(\nabla_d \mathbf{d})\cdot\mathbf{a} = \mathbf{d}\times(\mathbf{a}\times\mathbf{d}) \tag{A.6}$$

Application of Eq. (A.3) to the unit orientation vector **d** yields

$$\nabla_{\mathbf{d}}{}^2\mathbf{d} = -2\mathbf{d} \tag{A.7}$$

and it is useful to generalize this result to find the two-dimensional Laplacian of $\mathbf{d}^k$. In order to do so, it is convenient to resort to Cartesian tensor notation; the $pqr\ldots$ Cartesian component of $\nabla_{\mathbf{d}}{}^2\mathbf{d}^k$ is found to be

$$[\nabla_{\mathbf{d}}{}^2\mathbf{d}^k]_{pqr\ldots} = -2k\,d_p d_q d_r \ldots + 2\sum_{j>i}^{k}\sum_{i=p}^{k}\frac{\delta_{ij}-d_i d_j}{d_i d_j}\,d_p d_q d_r \ldots \tag{A.8}$$

where δ_{ij} is the Kronecker delta, and $\sum_{i=p}^{k}(\ldots)_{ipq\ldots}$ means $(\ldots)_{ppq\ldots}$ $+(\ldots)_{qpq\ldots}+(\ldots)_{rpq\ldots}+\ldots$.

If we put

$$[U^{(k)}]_{pqr\ldots} = \sum_{i,j=}^{k}\sum_{p}^{k}\frac{\delta_{ij}}{d_i d_j}\,d_p d_q d_r \ldots \tag{A.9}$$

then Eq. (A.8) can be written in coordinate-free form as

$$\nabla_{\mathbf{d}}{}^2\mathbf{d}^k = -k(k+1)\mathbf{d}^k + 2\mathbf{U}^{(k)} \tag{A.10}$$

It can be shown that the k-adic $\mathbf{U}^{(k)}$ obeys the recursion relation

$$\mathbf{d}\cdot\mathbf{U}^{(k)} = (k-1)\mathbf{d}^{k-1} + \mathbf{U}^{(k-1)} \tag{A.11}$$

The k-adic $\mathbf{U}^{(k)}$ is completely symmetric in the sense that its Cartesian components are unchanged when any pair of indices in them is interchanged. If we denote the completely symmetric part of a k-adic by a subscript s, then we could write

$$\mathbf{U}^{(k)} = \tfrac{1}{2}k(k-1)(\boldsymbol{\delta}\mathbf{d}^{k-2})_s \tag{A.12}$$

Although the symmetric part of any polyadic may be defined, definitions for only two special cases will suffice for this paper. In particular, if **a** is a vector and **Y** is a *symmetric dyadic*, then for the k-adics $\mathbf{a}\mathbf{d}^{k-1}$ and $\mathbf{Y}\mathbf{d}^{k-2}$ we have

$$[(\mathbf{a}\mathbf{d}^{k-1})_s]_{pqr\ldots} = \frac{(k-1)!1!}{k!}\sum_{i=p}^{k}\frac{a_i}{d_i}\,d_p d_q d_r \ldots \tag{A.13}$$

and

$$[(\mathbf{Y}\mathbf{d}^{k-2})_s]_{pqr\ldots} = \frac{(k-2)!2!}{k!}\sum_{j>i}^{k}\sum_{i=p}^{k}\frac{Y_{ij}}{d_i d_j}\,d_p d_q d_r \ldots \tag{A.14}$$

A useful formula that results from Eq. (A.13) is

$$\mathbf{a}\cdot\nabla_{\mathbf{d}}\mathbf{d}^k = k(\mathbf{a}\mathbf{d}^{k-1})_s - k\mathbf{a}\cdot\mathbf{d}^{k+1} \tag{A.15}$$

Also, by putting $\mathbf{a} = \mathbf{X} \cdot \mathbf{d}$, where $\mathbf{X}$ is *any* dyadic, we find

$$(\mathbf{X} \cdot \mathbf{d}) \cdot \nabla_{\mathbf{d}} \mathbf{d}^k = k(\mathbf{X} \cdot \mathbf{d}^k)_s - k\mathbf{X}_s : \mathbf{d}^{k+2} \tag{A.16}$$

For a continuously differentiable surface vector $\mathbf{b}$, we have

$$\oint_{4\pi} \nabla_{\mathbf{d}} \cdot \mathbf{b}\, d\Omega = 0 \tag{A.17}$$

Hence, since for an entity $z = z(\mathbf{d})$ it is true that

$$z\nabla_{\mathbf{d}} \cdot \mathbf{b} = \nabla_{\mathbf{d}} \cdot (\mathbf{b}z) - \mathbf{b} \cdot \nabla_{\mathbf{d}} z$$

we find that

$$\oint_{4\pi} z\nabla_{\mathbf{d}} \cdot \mathbf{b}\, d\Omega = -\oint_{4\pi} \mathbf{b} \cdot \nabla_{\mathbf{d}} z\, d\Omega \tag{A.18}$$

The average over the distribution of orientations is defined in the text. The polarization tensor $\mathbf{P}^{(k)}$ is $\langle \mathbf{d}^k \rangle$. Let $\mathbf{a}$ and $\mathbf{X}$ appearing in the formulas (A.15) and (A.16) be independent of $\mathbf{d}$. Then from the formulas (A.15) and (A.16), there results

$$\begin{aligned} \langle \mathbf{a} \cdot \nabla_{\mathbf{d}} \mathbf{d}^k \rangle &= k(\mathbf{a}\mathbf{P}^{(k-1)})_s - k\mathbf{a} \cdot \mathbf{P}^{(k+1)} \\ &= \mathbf{H}^{(k)}(\mathbf{P}^{(k)};\ \mathbf{a}) \end{aligned} \tag{A.19}$$

and

$$\begin{aligned} \langle (\mathbf{X} \cdot \mathbf{d}) \cdot \nabla_{\mathbf{d}} \mathbf{d}^k \rangle &= k(\mathbf{X} \cdot \mathbf{P}^{(k)})_s - k\mathbf{X}_s : \mathbf{P}^{(k+2)} \\ &= \mathbf{G}^{(k)}(\mathbf{P}^{(k)}; \mathbf{X}) \end{aligned} \tag{A.20}$$

where $\mathbf{H}^{(k)}$ and $\mathbf{G}^{(k)}$ are defined in the text, Eqs. (5.7) and (5.8).

Still another useful identity is the following:

$$(\nabla_{\mathbf{d}} f) \cdot (\nabla_{\mathbf{d}} z) = \nabla_{\mathbf{d}} \cdot (f\nabla_{\mathbf{d}} z) - f\nabla_{\mathbf{d}}^2 z$$

Hence, when (A.17) is used, we obtain

$$\oint_{4\pi} (\nabla_{\mathbf{d}} f) \cdot (\nabla_{\mathbf{d}} z)\, d\Omega = -\langle \nabla_{\mathbf{d}}^2 z \rangle \tag{A.21}$$

so that if $z = \mathbf{d}^k$, we get with the help of Eqs. (A.10) and (A.12) the result

$$\begin{aligned} \oint_{4\pi} (\nabla_{\mathbf{d}} f) \cdot (\nabla_{\mathbf{d}} \mathbf{d}^k)\, d\Omega &= -\langle \nabla_{\mathbf{d}}^2 \mathbf{d}^k \rangle \\ &= k(k+1)\mathbf{P}^{(k)} - k(k-1)(\boldsymbol{\delta}\mathbf{P}^{(k-2)})_s \\ &= 6\mathbf{A}^{(k)} \end{aligned} \tag{A.22}$$

The foregoing identities are sufficient to establish the equations of change of the polarization tensors from the equation of change of the density function, Eq. (3.5).

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