# The Structure of Dielectric Fluids. III. Interaction between Impurities and Dielectric Saturation in Polar Fluids*

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The potential of mean force between two impurities in a sample of a fluid of rigid dipoles is studied. Each impurity may be a charge, an electric dipole or an electric quadrupole. It is found that the longest-range part of the potential of mean force obtained from a molecular theory is the same as the interaction energy obtained from macroscopic electrostatics, when the polar fluid is treated as a dielectric continuum, except that the impurity dipole and quadrupole have to be replaced by effective dipole moments. These effective dipole moments arise because of the local polarization of the polar molecules in the surrounding of the impurities, due to the local interactions. Next a pure polar fluid in the presence of an arbitrary external electric field is considered. The one-particle distribution function in the presence of the field is studied to all orders in the field. It is found that both this one-particle distribution function and the dielectric polarization are shape-independent functions of the local average macroscopic field.

## I. INTRODUCTION

This is the third in a series of papers dealing with the structure of equilibrium dielectric fluids. In the first paper, hereafter referred to as I, we obtained an explicit expression for the long-range part of the two-particle distribution function for a fluid composed of rigid dipoles. We calculated the polarization of the fluid to first order in the external field $\mathbf{E}_0(\mathbf{r})$, and demonstrated that the constitutive relation

$$\mathbf{P}_V(\mathbf{r}) = [(\epsilon-1)/4\pi]\mathbf{E}(\mathbf{r}) \qquad (1.1)$$

is valid with a dielectric constant $\epsilon$ independent of sample shape and surroundings.[1] In the second paper, hereafter referred to as II, we examined the statistical thermodynamics of a polar fluid, in the absence of any external field, on the basis of the two-particle distribution function determined in I. In addition, we obtained an explicit expression for the three-particle distribution function of the polar fluid and used this result to demonstrate the existence of a local Kerr constant, independent of sample shape and surroundings.[2]

In this paper we consider two further problems in the molecular theory of polar fluids. First we shall determine, using graphical techniques developed in I and II, the potential of mean force $w_2$ between two molecular impurities in the polar fluid at large separations. The potential of mean force, at large separations, is related to the two-particle distribution function $n_2$ for the two impurities by

$$n_2(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = [V^2\Omega_a\Omega_b]^{-1}[1-\beta w(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b)],$$
$$(1.2)$$

where $V$ is the volume of the sample, $\beta = (k_B T)^{-1}$, $\Omega_a$ and $\Omega_b$ are the integrals over the orientations of the rigid impurities $a$ and $b$, respectively. The coordinates $\mathbf{r}$ and $\boldsymbol{\omega}$ denote the position and orientation of the impurities. We compare the result obtained for $w_2$ with the interaction energy obtained from macroscopic electrostatics where the supporting polar fluid is as- sumed to be a continuous dielectric characterized by the dielectric constant $\epsilon$. We consider several molecular impurities: charges, dipoles, and quadrupoles and the potential of mean force between any two of these.

In general the potential of mean force will be a function of sample shape and surroundings. As in our previous work, we consider an arbitrary sample volume $V$ in a surrounding volume $W$, perhaps zero, which contains a dielectric continuum characterized by a dielectric constant $\epsilon_0$. Our results are that the potential of mean force obtained from the molecular theory is consistent with the interaction energy obtained from classical electrostatics, except that the impurity dipole moments or quadrupole moments are replaced by effective dipole moments. These effective dipole moments arise because of the short-range forces between the impurity and the molecules in the fluid.

For example, in the simple case of an infinite volume $V$, the potential of mean force between two impurity charges $q_a$ and $q_b$ is found to be

$$w_2^\infty = [q_a q_b/\epsilon \mid \mathbf{r}_a - \mathbf{r}_b \mid], \qquad (1.3)$$

which is consistent with linearized Debye–Hückel theory, while the potential of mean force between an impurity charge and an impurity dipole is

$$w_2^\infty = [q_a \boldsymbol{\mu}_{b,\mathrm{eff}}(\boldsymbol{\omega}_b) \cdot (\mathbf{r}_a - \mathbf{r}_b)/\epsilon \mid \mathbf{r}_a - \mathbf{r}_b \mid^3]. \quad (1.4)$$

We present a formal, unique molecular expression for the effective dipole moment $\boldsymbol{\mu}_{b,\mathrm{eff}}$. The dielectric constant $\epsilon$ which appears in these formulae is identical to the dielectric constant appearing in Eq. (1.1). The case of two impurity charges has been considered previously by Jepsen[3] and our work has been influenced by the interesting work of Mahan[4] and Mahan and Mazo[5] on impurities in simple ionic crystals.

The second problem we consider in this paper concerns dielectric saturation, i.e., the validity of the constitutive relation, Eq. (1.1), between the polarization $\mathbf{P}_V(\mathbf{r})$ and the macroscopic field $\mathbf{E}(\mathbf{r})$, beyond the linear term in $\mathbf{E}$. We investigate this problem by obtain-

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ing a formal expression for the one-particle distribution function *in the presence of the external field* $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$ to all orders in the external field for a pure polar fluid identical to that considered in I. Both the polarization $\mathbf{P}_V(\mathbf{r})$ and the macroscopic field $\mathbf{E}(\mathbf{r})$, to all orders in the external field, are simply related to this one-particle distribution function. We find that to all orders in the field the relation between $\mathbf{P}_V(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ may be expressed as

$$\mathbf{P}_V(\mathbf{r}) = (\{\epsilon[\mathbf{E}(\mathbf{r})] - 1\}/4\pi)\mathbf{E}(\mathbf{r}), \quad (1.5)$$

where the functional form of $\epsilon$ is a property of the fluid, independent of sample geometry and surroundings. Formal molecular expressions for the terms arising in the power series expansion of $\epsilon[\mathbf{E}(\mathbf{r})]$ are given in terms of local molecular distribution functions. To terms linear in the field $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$ has the form

$$n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0) = (\rho/\Omega)[1 + \beta\boldsymbol{\mu}_{\text{eff}}(\boldsymbol{\omega}) \cdot \mathbf{E}(\mathbf{r})], \quad (1.6)$$

which leads to results entirely consistent with those obtained in I. The free energy of the molecular sample in the external field is also discussed.

## II. GRAPHICAL EXPANSION OF THE IMPURITY CORRELATION FUNCTION

The graphical expansion technique that we employ to investigate the impurity problem is similar to the technique employed in I to treat the pure polar fluid. The major modification for the two-particle distribution function $n_2$ is that the root points refer to the two impurities which may or may not be of the same species. The system we consider consists of $N$ rigid dipoles and two impurities in a volume $V$ surrounded by a region $W$, perhaps zero, which is assumed to be a dielectric continuum with dielectric constant $\epsilon_0$. In the absence of external fields the potential energy of interaction of this $(N+2)$-particle system is

$$U = U_0 + u_{ab}(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) + \phi_a(\mathbf{r}_a, \boldsymbol{\omega}_a) + \phi_b(\mathbf{r}_b, \boldsymbol{\omega}_b)$$
$$+ \sum_{i=1}^{N} [u_{ai}(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_i, \boldsymbol{\omega}_i) + u_{bi}(\mathbf{r}_b, \boldsymbol{\omega}_b; \mathbf{r}_i, \boldsymbol{\omega}_i)]$$
$$- \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j), \quad (2.1)$$

where $U_0$ is the total potential energy contribution due to the short-range forces that act between the $(N+2)$ particles, the tensor $\mathbf{D}$ is given by

$$\mathbf{D}(\mathbf{r}_i, \mathbf{r}_j) = (1 - \delta_{ij})\mathbf{T}(\mathbf{r}_i, \mathbf{r}_j) + \mathbf{R}_W(\mathbf{r}_i, \mathbf{r}_j; \epsilon_0) \quad (2.2)$$

with $\mathbf{T}$ the direct dipole–dipole interaction tensor

$$\mathbf{T}(\mathbf{r}, \mathbf{r}') = [3(\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|^5] - [\mathbf{I}/|\mathbf{r} - \mathbf{r}'|^3]$$
$$(2.3)$$

and $\mathbf{R}_W(\mathbf{r}, \mathbf{r}'; \epsilon_0)$ the reaction field tensor. The quantity $\mathbf{R}_W(\mathbf{r}, \mathbf{r}'; \epsilon_0) \cdot \mathbf{p}$ is the field at point $\mathbf{r}$ from the polariza-

tion in $W$ induced by a dipole $\mathbf{p}$ at point $\mathbf{r}'$. The terms $u_{ai}(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_i, \boldsymbol{\omega}_i)$ and $u_{bi}(\mathbf{r}_b, \boldsymbol{\omega}_b; \mathbf{r}_i, \boldsymbol{\omega}_i)$ are the appropriate interaction energies between dipole $i$ at position $\mathbf{r}_i$ with orientation $\boldsymbol{\omega}_i$ and the impurity $a$ or $b$ respectively at position $\mathbf{r}_a(\mathbf{r}_b)$ with orientation $\boldsymbol{\omega}_a(\boldsymbol{\omega}_b)$. Both $u_{ai}$ and $u_{bi}$ are the direct interaction energies between the impurity and the dipole modified by the surrounding continuum $W$. Finally, the term $u_{ab}$ is the longest-range part of the interaction energy between the two impurities again modified by the surrounding continuum $W$. The shorter-range interaction energy is included in $U_0$. The terms $\phi_a$ and $\phi_b$ give the potential energy of impurity $a$ and $b$, respectively, with $W$. The short-range part of the potential energy will be assumed to consist of pair interactions only

$$U_0 = \frac{1}{2}\sum_{\substack{(i \neq j) \\ a,b,1}}^{N}\sum v_{ij}(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j) \quad (2.4)$$

with $v_{ij}$ identical for every dipole pair and identical for every pair involving one of the dipoles with each of the two impurities $a$, $b$. The complete potential energy may be summarized as

$$U = \frac{1}{2}\sum_{\substack{(i \neq j) \\ a,b,1}}^{N}\sum [v_{ij} + u_{ij}] - \frac{1}{2}\sum_{i=1}^{N} \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{R}_W(\mathbf{r}_i, \mathbf{r}_i; \epsilon_0)$$
$$\cdot \boldsymbol{\mu}(\boldsymbol{\omega}_i) + \phi_a + \phi_b, \quad (2.5)$$

where $u_{ij}$ is $[-\boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j)]$, $u_{ia} = u_{ai}$, $u_{ib} = u_{bi}$, $u_{ab} = u_{ba}$ according to whether the indices $i$ and $j$ refer to two dipoles, a dipole and impurity $a$, a dipole and impurity $b$, or the two impurities respectively.

The reduced two-particle distribution function for the two impurities is defined by

$$n_2(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = \int_V d\mathbf{r}^N d\boldsymbol{\omega}^N f(\mathbf{r}^{N+2}, \boldsymbol{\omega}^{N+2}), \quad (2.6)$$

where

$$f(\mathbf{r}^{N+2}, \boldsymbol{\omega}^{N+2}) = \exp[-\beta U(\mathbf{r}^{N+2}, \boldsymbol{\omega}^{N+2})]$$
$$\times \left(\int_V \exp[-\beta U(\mathbf{r}^{N+2}, \boldsymbol{\omega}^{N+2})]d\mathbf{r}^{N+2}d\boldsymbol{\omega}^{N+2}\right)^{-1} \quad (2.7)$$

with $U$ given by Eq. (2.1) or alternatively Eq. (2.5). The distribution function $n_2$ is related to the correlation function $G_2$ by the definition

$$n_2(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = [V^2\Omega_a\Omega_b]^{-1} + G_2(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) \quad (2.8)$$

with $\Omega_j = \int d\boldsymbol{\omega}_j$, $j = a, b$. The graphical expansion we shall use for $G_2$ is based on the linear graph theory of Uhlenbeck and Ford[6] and is closely related to the formalism of Lebowitz, Stell, and Baer.[7] The terminology and the procedures we shall use are extensively discussed in I and II, to which the interested reader should refer for details. According to the well-known graphical expansion theory,[6,8,1] the virial expansion of the correlation

function $G_2$ may be represented by

$$G_2(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b)$$

$$= \sum_{M=0}^{\infty} C_M(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b)[V^2\Omega_a\Omega_b]^{-1}\left(\frac{\rho}{\Omega}\right)^M, \quad (2.9)$$

where as in I we made the simplifying assumption that the single particle distribution functions are constant, independent of position and orientation, and

$$C_M(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = (M!)^{-1} \sum_{(R_M)} \int_V d\mathbf{r}^M d\boldsymbol{\omega}^M \prod_{R_M} f_{ij}. \quad (2.10)$$

The sum is over all different 2-irreducible connected graphs $R_M$ with $(M+2)$ points labeled $a, b, 1, 2, \cdots, M$, where the points $a$ and $b$ are the root points.

In the expression for $C_M$ any two points with a bond $f_{ij}$ present contribute a factor to the integrand in Eq. (2.10) given by

$$f_{ij} = \exp[-\beta(v_{ij}+u_{ij})] - 1. \quad (2.11)$$

The factor $f_{ij}$ is expanded in the standard way (Refs. 9 and 10 of II)

$$f_{ij} = a_{ij} + \sum_{\alpha=1}^{\infty} (\alpha!)^{-1}(b_{ij})^{\alpha}, \quad (2.12)$$

where

$$a_{ij} = [\exp(-\beta v_{ij}) - 1] \exp(-\beta u_{ij}) \quad (2.13)$$

and

$$b_{ij} = -\beta u_{ij}. \quad (2.14)$$

The factor $a_{ij}$ is of short range and it will be represented by a dotted line (a short-range bond) between the points $i$ and $j$. A factor $(1/\alpha!)(b_{ij})^{\alpha}$ in the expansion of $f_{ij}$ is represented by $\alpha$ solid lines between the points $i$ and $j$. The factors $a_{ij}$ and $b_{ij}$ depend upon whether the particles $i$ and $j$ are dipoles or impurities. This is indicated in the graphs by denoting the impurity $a$ by an open circle, the impurity $b$ by an open square and the dipoles by a black point. Thus the $f$ bond between impurity $a$ and a representative dipole is represented by

$$f_{ai} = \text{o---•} + \text{o——•} + \text{⊂⊃•} + \text{⊂⊃•} + \cdots \quad (2.15)$$

If every $f$ bond in Eq. (2.10) is replaced by this expansion we obtain a set of *composite* graphs, which have between each pair of points one dotted bond (an $a$ bond) or any number of solid bonds ($b$ bonds) or no bonds at all. The expansion of $C_M$, Eq. (2.10), may be expressed as

$$C_M(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = (M!)^{-1} \sum_{(T_M)} \int_V d\mathbf{r}^M d\boldsymbol{\omega}^M$$

$$\times \prod_{T_M} a_{ij} \prod_{T_M} [(\alpha!)^{-1}(b_{pq})^{\alpha}]. \quad (2.16)$$

The sum is over all different connected 2-irreducible composite graphs $T_M$ with $(M+2)$ points labeled

$a, b, 1, 2, \cdots, M$. The indices $(i, j)$ and $(p, q)$ refer to points of the graph $T_M$. The contribution of a graph clearly does not depend on the labeling of the points other than the points $a$ and $b$. This property enables us to express $C_M$ in terms of 2-irreducible graphs in which only the points $a$ and $b$ are labeled (root points) and the other points are unlabeled (field points). Hence we may write $C_M$ as

$$C_M(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = \sum_{(S_M)} \sigma^{-1} \int_V d\mathbf{r}^M d\boldsymbol{\omega}^M$$

$$\times \prod_{T_M} a_{ij} \prod_{T_M} [(\alpha!)^{-1}(b_{pq})^{\alpha}], \quad (2.17)$$

where $\sigma$ is the symmetry number of the graph and the sum is over all different connected 2-irreducible composite graphs $S_M$ with $(M+2)$ points in which only the points $a$ and $b$ are labeled.

The analysis of the order of magnitude of the graphs contributing to $G_2$, Eq. (2.9), proceeds in a manner closely analogous to the analysis employed in I. The 2-irreducible, connected composite graphs contributing to $G_2$ are either stars, or composed of stars hung together at the articulation points of the graphs. At large separations of the impurities $a$ and $b$ the major contribution will come from those graphs that contain a single $b$ bond, which is a star, between two points at least once. A single $b$ bond between two points which is a star shall be referred to as the star $S_0$. For small separations of the impurities $a$ and $b$ all graphs contribute in the same order of magnitude.

The set of composite connected 2-irreducible graphs which do not have the star $S_0$ as one of its building stars is called $Z$. The 2-irreducible graphs which are completely free of $b$ bonds or which are stars other than $S_0$ are included in $Z$. The contribution to $G_2$ of the graphs in $Z$ at large impurity separation is smaller than the contribution of the graphs not in $Z$. The leading contribution of the graphs in $Z$ is called $G_2^{(0)}(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b)$. It must be emphasized that $G_2^{(0)}$ has a unique definition in terms of the graphical expansion.

The contribution to $G_2$ from the graphs not in $Z$ are star chains which have the star $S_0$ as at least one of its building stars. The leading contribution of these graphs to $G_2$ is denoted $G_2^{(1)}(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b)$. Thus

$$G_2(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = G_2^{(0)}(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b)$$

$$+ G_2^{(1)}(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b). \quad (2.18)$$

Note that while $G_2^{(1)}$ is the leading contribution to $G_2$ at large impurity separation, both $G_2^{(0)}$ and $G_2^{(1)}$ have comparable contributions at small impurity separations.

We can construct an equation for $G_2^{(1)}$ by recognizing that all the graphs contributing to $G_2^{(1)}$, i.e., those not in $Z$, may be constructed from the star $S_0$ and all the graphs in $Z$. The graphs contributing to $G_2^{(1)}$ are found by taking one or more stars $S_v$ and hanging them together directly or via other graphs, which do not

contain $S_0$ as a building star, in such a way that the resulting graph is 2 irreducible. The endpoints of the stars $S_0$ must be articulation points of the resulting graphs so that closed loops of stars $S_0$ are precluded. According to Eq. (2.17) the field points are integrated over the volume $V$. In the case of the pure polar fluid considered in I and II the graphical expansion for $G_2^{(1)}$ is illustrated in Fig. 1 where a wavy line together with its endpoints denotes the graphs not in $Z$, i.e., those contributing to $G_2^{(1)}$, and a large open circle with two vertices attached to it represents the graphs in $Z$, i.e., those contributing to $G_2^{(0)}$. The graphical expansion is obtained by resumming the graphical expansion of Eq. (2.9) where $C_M$ is given by Eq. (2.17). The result, displayed in Fig. 1, may easily be constructed by adding all graphs with exactly one building star $S_0$ (the first four graphs) to all possible graphs that have more than one building star $S_0$. For the pure polar fluid the integral equation for $G_2^{(1)}$, found by writing down the contributions of the graphs in Fig. 1, is exactly Eq. (3.28) of Ref. 1.

For the impurity problem the graphical expansion of $G_2^{(1)}$ takes a different form than Fig. 1. The reason is that the impurities at the root points of the graphs interact with the polar molecules at the field points differently than the polar molecules interact among themselves. Thus $b$ bonds or large circles which have an impurity as an end point differ from $b$ bonds or large circles which have fluid molecules at both end points. However, we may construct an expansion for $G_2^{(1)}$ in the impurity case by making use of the long-range part

of $G_2$ determined for the pure polar fluid, which we denote $G_{2,p}^{(1)}$. The integral equation for $G_{2,p}^{(1)}$ and its solution for several geometries has been presented in I. For the impurity case we consider the resummed graphical expansion for $G_2^{(1)}$ as the sum of all graphs that contain exactly one star $S_0$, exactly two stars $S_0$, or more than two stars $S_0$. All the graphs that contain more than two stars $S_0$ have at least one star $S_0$ between two field points. Thus the graphical expansion of $G_2^{(1)}$ may be expressed in terms of the graphs arising in the expansion of $G_{2,p}^{(1)}$, as is indicated in Fig. 2. There are 16 graphs in the expansion that have been numbered for reference in the following development.

The large circles in the expansion of $G_2^{(1)}$, Fig. 2, depend, of course, on the character of the two end points. Formally, these large circle diagrams may be obtained from the graphs in the set $Z$, defined as described above, with the end points appropriately interpreted as impurities or polar molecules. Except in low density it is not possible to obtain an explicit expression for these contributions. For our purposes, however, it is sufficient to note that the contributions of these graphs have a unique definition and that the effective range of this contribution may be determined from examination of the graphs in $Z$. We denote the contribution of the large circle with the impurity $a$ as one end point by $G_{2,a}^{(0)}$, the large circle with impurity $b$ as one end point $G_{2,b}^{(0)}$, and the large circle with two polar molecule end points by $G_{2,p}^{(0)}$.

The equation for $G_2^{(1)}$ may be written down from the graphical expansion in Fig. 2,

$$G_2^{(1)}(ab) = [V^2\Omega_a\Omega_b]^{-1}b_{ab} + [V\Omega_b]^{-1}\int_V d(i)G_{2,a}^{(0)}(ai)b_{ib} + [V\Omega_a]^{-1}\int_V d(i)b_{ai}G_{2,b}^{(0)}(ib)$$

$$+ \int_V d(i)d(j)G_{2,a}^{(0)}(ai)b_{ij}G_{2,b}^{(0)}(jb) + [V^2\Omega_a\Omega_b]^{-1}\int_V d(i)d(j)b_{ai}[H_{2,p}^{(0)}(ij)+G_{2,p}^{(1)}(ij)]b_{jb}$$

$$+ [V\Omega_b]^{-1}\int_V d(i)d(j)d(k)G_{2,a}^{(0)}(ai)b_{ij}[H_{2,p}^{(0)}(jk)+G_{2,p}^{(1)}(jk)]b_{kb}$$

$$+ [V\Omega_a]^{-1}\int_V d(i)d(j)d(k)b_{ai}[H_{2,p}^{(0)}(ij)+G_{2,p}^{(1)}(ij)]b_{jk}G_{2,b}^{(0)}(kb)$$

$$+ \int_V d(i)d(j)d(k)d(l)G_{2,a}^{(0)}(ai)b_{ij}[H_{2,p}^{(0)}(jk)+G_{2,p}^{(1)}(jk)]b_{kl}G_{2,b}^{(0)}(lb), \quad (2.19)$$

where for convenience we have introduced

$$H_{2,p}^{(0)}(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j) = (\rho/\Omega)\delta(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)$$
$$+ G_{2,p}^{(0)}(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j), \quad (2.20)$$

and we denote the coordinates $(\mathbf{r}_i, \boldsymbol{\omega}_i)$ of particle $i$ by $(i)$, and the integration element $d\mathbf{r}_i \cdot d\boldsymbol{\omega}_i$ by $d(i)$.

Not all of the 16 graphs in the expansion for $G_2^{(1)}$ are of the same order of magnitude at large impurity separation. The dominant graphs, i.e., those that decrease least rapidly as the end points separate, depend

on the character of the impurities $a$ and $b$. In order to identify, for a particular choice of impurities, which of the sixteen graphs are dominant, it is necessary to determine the effective ranges of the constituent large circles and $b$ bonds. We shall consider a number of different impurities, charges, dipoles, and quadrupoles. Before proceeding to the discussion of special cases we collect for reference the leading behavior of the $b$ bonds and large circles that occur with various impurities.

If impurity $a$ is a charge $q_a$, a dipole $\boldsymbol{\mu}_a$ or a quad-

rupole $Q_a$, then the $b$ bond between the impurity $a$ and a field point $b_{ai}$ is of order $(q_a\mu/r^2)$, $(\mu_a\mu/r^3)$, and $(Q_a\mu/r^4)$, respectively. The large circles between the impurity and a field dipole, which represents $G_{2,a}{}^{(0)}$, is of the order of the square of $b_{ai}$ if the impurity is a charge or a dipole. For a quadrupole impurity $G_{2,a}{}^{(0)}$ is of order $(\mu_{\rm eff}\mu/r^3)^2$ which is a longer-range interaction than $b_{ai}{}^2$. This is the leading contribution to $G_{2,a}{}^{(0)}$ for the quadrupole because the formalism allows for short-range forces to align dipoles locally around the impurity, which in turn can interact with the field dipole. The effective range goes as the square of the effective dipole–dipole interaction since the first order interaction is not included in $Z$.

The leading contributions of single $b$ bonds between the two impurities is of order $(q_aq_b/r)$, $(q_a\mu_b/r^2)$, $(q_aQ_b/r^3)$ for the case of a charge impurity $q_a$ interacting with a charge impurity $q_b$, dipole impurity $\mu_b$, and quadrupole impurity $Q_b$ respectively. The large circle between the two impurities, which represents $G_2{}^{(0)}$, is of order $(q_aq_b/r)^2$ and $(q_a\mu_b/r^2)^2$ for the charge–charge and charge–dipole cases, respectively. For the charge–quadrupole case $G_2{}^{(0)}$ is of order $(q_a\mu_{\rm eff}/r^2)^2$ again because the short-range forces may cause an alignment of dipoles around the quadrupole impurity.

The leading contribution of a single $b$ bond between an impurity dipole $\mu_a$ and an impurity dipole $\mu_b$ or impurity quadrupole $Q_b$ is of order $(\mu_a\mu_b/r^3)$ and $(\mu_aQ_b/r^4)$, respectively. For the dipole–dipole impurity case $G_2{}^{(0)}$ is of order $(\mu_a\mu_b/r^3)^2$ while for the dipole–quadrupole impurity case $G_2{}^{(0)}$ is of order $(\mu_a\mu_{\rm eff}/r^3)^2$. Finally, for two quadrupole impurities the $b$ bond is of order $(Q_aQ_b/r^5)$ and the corresponding $G_2{}^{(0)}$ is of order $(\mu_{\rm eff}{}^2/r^3)^2$.

In discussing the order of magnitude of these various terms we have neglected the angular factors in the interactions altogether. Consequently, some of the leading terms we have quoted for the large circles $G_2{}^{(0)}$ or $G_{2,a}{}^{(0)}$ might vanish if the short-range intermolecular forces have some particular symmetry. The cases of special symmetry in the short-range intermolecular potentials must be examined separately. Furthermore, in discussing the order of magnitude of the various terms, we have not explicitly referred to the additional terms in the effective interaction potentials that will
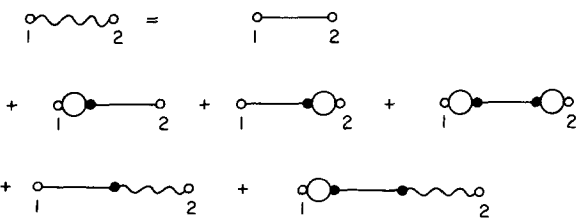


FIG. 1. Graphical expansion of $G_{2,p}{}^{(1)}$ for the pure polar fluid. A wavy line with its endpoints represents $G_{2,p}{}^{(1)}$, a large circle with two points attached to it represents $G_{2,p}{}^{(0)}$, and a solid bond represents a factor $b$. Black points are integrated over the volume $V$ and over all orientations.
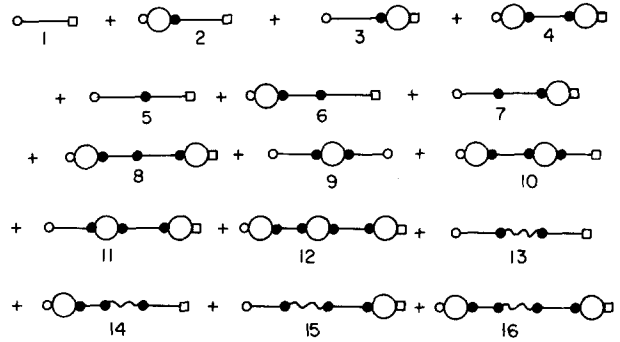


FIG. 2. Graphical expansion of the long-range part $G_2{}^{(1)}$ of the impurity–impurity correlation function. Open small circles represent the impurity $a$, open squares represent the impurity $b$. Solid lines are $b$ bonds, wavy lines with its endpoints represent $G_{2,p}{}^{(1)}$. Large circles refer to all graphs in $Z$ in the impurity problem defined by its endpoints and the large open circles give rise to a short-range factor $G_2{}^{(0)}$.

arise when the external dielectric continuum $W$ is present. These terms are smaller than the direct interaction terms by a factor which is some power of $(r/V^{1/3})$ depending on the multipole nature of the interacting pair of particles. Careful examination shows that the effects of the medium $W$ on $b$ bonds for large separation of its end points is of equal importance as the other term. In $G_2{}^{(0)}$ contributions which decrease as $r^{-4}$ or faster the effects of the medium $W$ are negligible because these interactions are effectively short-ranged. Hence in each $b$ bond the entire $u_{ij}$, including terms of order $V^{-1/3}$ will be included, but the order of magnitude of the term may be estimated by use of the direct interaction alone.

## III. POTENTIAL OF MEAN FORCE FOR IMPURITIES

In this section we obtain expressions for $G_2{}^{(1)}$ and the resulting potential of mean force $w_2{}^{(1)}$ for different impurity pairs. For each case the procedure we follow is to use the estimates of the constituent large circles and $b$ bonds developed in the previous section to select the dominant graphs in the expression for $G_2{}^{(1)}$ given in Fig. 2. The effective range of each of the sixteen graphs is obtained by writing down the integral corresponding to the graph, substituting the effective range dependence of the constituent large circles and $b$ bonds, and performing the integration over field points treating all factors which decrease as $r^{-4}$ or faster as spatial delta functions. For example, in the case of two impurity charges the contribution of graph (9) in Fig. 2 is

$$(9) = [V^2\Omega_a\Omega_b]^{-1}\int_V d\mathbf{r}_i d\boldsymbol{\omega}_i d\mathbf{r}_j d\boldsymbol{\omega}_j b_{ai} G_{2,p}{}^{(0)}(ij) b_{jb}, \quad (3.1)$$

$$(9) \approx \int d\mathbf{r}_i d\mathbf{r}_j \frac{q_a\mu}{|\mathbf{r}_a - \mathbf{r}_i|^2} \frac{\mu^4}{|\mathbf{r}_i - \mathbf{r}_j|^6} \frac{\mu q_b}{|\mathbf{r}_j - \mathbf{r}_b|^2}$$

$$\approx \text{constant}/|\mathbf{r}_a - \mathbf{r}_b|. \quad (3.2)$$

Other graphs are estimated in a similar manner; the wavy line which denotes $G_{2,p}{}^{(1)}$ has a range $r^{-3}$ as

determined in I. In estimating the contributions of the various graphs the angular factors and the effects of the medium in $W$ need not be explicitly considered.

We now turn to an examination of several impurity cases of interest.

## A. Charge–Charge

In the case of two charge impurities one finds that the major contribution to $G_2^{(1)}$ comes from four graphs

$$G_2^{(1)} = (1) + (5) + (9) + (13), \qquad (3.3)$$

which have an effective range of $|\mathbf{r}_a - \mathbf{r}_b|^{-1}$. All other graphs in Fig. 2 have a shorter range. We denote the charge–charge potential by $q_a q_b \gamma(\mathbf{r}_a, \mathbf{r}_b)$, where $\gamma$ includes the direct Coulomb interaction $|\mathbf{r}_a - \mathbf{r}_b|^{-1}$ plus the effects of the polarization in $W$. The charge–dipole interaction is denoted $-q_a \boldsymbol{\mu}(\omega) \cdot \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a)$, where again the effects of the external medium in $W$ is present in $\boldsymbol{\Gamma}$ and $\boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}') = -\nabla_r \gamma(\mathbf{r}, \mathbf{r}')$. Hence the expression for the charge–charge correlation function in the asymptotic limit of large separation is given by

$$G_2^{(1)}(\mathbf{r}_a, \omega_a; \mathbf{r}_b, \omega_b) = [V^2 \Omega_a \Omega_b]^{-1} \left\{ -\beta q_a q_b \gamma(\mathbf{r}_a, \mathbf{r}_b) + \int_V d\mathbf{r} d\omega [\beta q_a \boldsymbol{\mu}(\omega) \cdot \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a)] \frac{\rho}{\Omega} [\beta q_b \boldsymbol{\mu}(\omega) \cdot \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_b)] \right.$$

$$\left. + \int_V d\mathbf{r} d\omega d\mathbf{r}' d\omega' [\beta q_a \boldsymbol{\mu}(\omega) \cdot \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a)] [G_{2,p}^{(0)}(\mathbf{r}, \omega; \mathbf{r}', \omega') + G_{2,p}^{(1)}(\mathbf{r}, \omega; \mathbf{r}', \omega')] [\beta q_b \boldsymbol{\mu}(\omega') \cdot \boldsymbol{\Gamma}(\mathbf{r}', \mathbf{r}_b)] \right\}. \quad (3.4)$$

To reduce this expression further we use results for $G_{2,p}^{(0)}$ and $G_{2,p}^{(1)}$ obtained in I. For the case of a pure polar fluid $G_{2,p}^{(0)}$ is of microscopic range and $G_{2,p}^{(1)}$ is given by

$$G_{2,p}^{(1)}(\mathbf{r}, \omega; \mathbf{r}', \omega') = (\beta \rho^2 / \Omega^2) \boldsymbol{\mu}_{\text{eff}}(\omega) \cdot \mathsf{F}(\mathbf{r}, \mathbf{r}') \cdot \boldsymbol{\mu}_{\text{eff}}(\omega'), \qquad (3.5)$$

where $\boldsymbol{\mu}_{\text{eff}}$ is an effective dipole moment defined by

$$\boldsymbol{\mu}_{\text{eff}}(\omega) = \boldsymbol{\mu}(\omega) + \boldsymbol{\kappa}(\omega) \qquad (3.6)$$

with $\boldsymbol{\kappa}$ determined in terms of $G_{2,p}^{(0)}$

$$\rho / \Omega \boldsymbol{\kappa}(\omega) = \int_V d\mathbf{r}' d\omega' G_{2,p}^{(0)}(\mathbf{r}, \omega; \mathbf{r}', \omega') \boldsymbol{\mu}(\omega'). \qquad (3.7)$$

The dielectric constant of the pure polar fluid is found to be

$$(\epsilon - 1)/4\pi = \tfrac{1}{3}\beta \rho \boldsymbol{\mu} \cdot \boldsymbol{\mu}_{\text{eff}}. \qquad (3.8)$$

The interaction tensor $\mathsf{F}(\mathbf{r}, \mathbf{r}')$ in Eq. (3.5) is given by the solution of an integral equation [Eq. (4.8) of I]

$$\mathsf{F}(\mathbf{r}, \mathbf{r}') = \mathsf{D}(\mathbf{r}, \mathbf{r}') + \tfrac{1}{3}\beta \rho \boldsymbol{\mu} \cdot \boldsymbol{\mu}_{\text{eff}} \int_V d\mathbf{r}'' \mathsf{D}(\mathbf{r}, \mathbf{r}'') \cdot \mathsf{F}(\mathbf{r}'', \mathbf{r}'), \qquad (3.9)$$

where $\mathsf{D}(\mathbf{r}, \mathbf{r}') = \mathsf{T}(\mathbf{r}, \mathbf{r}') + \mathsf{R}_W(\mathbf{r}, \mathbf{r}'; \epsilon_0)$. In the particular case where the surrounding medium $W$ has a dielectric constant given by Eq. (3.8) the function $\mathsf{F}(\mathbf{r}, \mathbf{r}')$ is[1]

$$\mathsf{F}(\mathbf{r}, \mathbf{r}') = \epsilon^{-1}[\mathsf{T}(\mathbf{r}, \mathbf{r}') + \mathsf{R}_{(V+W)}^*(\mathbf{r}, \mathbf{r}'; \epsilon^{-1})]. \qquad (3.10)$$

The term $\mathsf{R}_{(V+W)}^* \cdot \mathbf{p}$ has the interpretation of the reaction field established at the point $\mathbf{r}$ in $V$ by a dipole $\mathbf{p}$ at $\mathbf{r}'$, when $(V+W)$ is empty and the surroundings are filled with a dielectric continuum with dielectric constant $\epsilon^{-1}$.

With the results of Eqs. (3.5)–(3.7) we find that $G_2^{(1)}$, Eq. (3.4) becomes

$$G_2^{(1)} = \beta q_a q_b / V^2 \Omega_a \Omega_b \left[ -\gamma(\mathbf{r}_a, \mathbf{r}_b) + (\tfrac{1}{3}\beta \rho \boldsymbol{\mu} \cdot \boldsymbol{\mu}_{\text{eff}}) \int_V d\mathbf{r} \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a) \cdot \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_b) \right.$$

$$\left. + (\tfrac{1}{3}\beta \rho \boldsymbol{\mu} \cdot \boldsymbol{\mu}_{\text{eff}})^2 \int_V d\mathbf{r} d\mathbf{r}' \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a) \cdot \mathsf{F}(\mathbf{r}, \mathbf{r}') \cdot \boldsymbol{\Gamma}(\mathbf{r}', \mathbf{r}_b) \right]. \quad (3.11)$$

From Eq. (1.2) the potential of mean force $w_2^{(1)}$ which gives the total potential of mean force $w_2$ in the asymptotic limit of large separation is determined to be

$$w_2^{(1)} = q_a q_b \left[ \gamma(\mathbf{r}_a, \mathbf{r}_b) - (\tfrac{1}{3}\beta \rho \boldsymbol{\mu} \cdot \boldsymbol{\mu}_{\text{eff}}) \int_V d\mathbf{r} \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a) \cdot \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_b) - (\tfrac{1}{3}\beta \rho \boldsymbol{\mu} \cdot \boldsymbol{\mu}_{\text{eff}})^2 \int_V d\mathbf{r} d\mathbf{r}' \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a) \cdot \mathsf{F}(\mathbf{r}, \mathbf{r}') \cdot \boldsymbol{\Gamma}(\mathbf{r}', \mathbf{r}_b) \right].$$

$$(3.12)$$

For smaller separation Eq. (3.12) does not give the total potential of mean force, and the other $G_2$ graphs should

be taken into account. Using the integral equation for F, Eq. (3.9) and the fact that

$$D(\mathbf{r}, \mathbf{r}') = \nabla_r \Gamma(\mathbf{r}', \mathbf{r}) = -\nabla_r \nabla_{r'} \gamma(\mathbf{r}, \mathbf{r}') \tag{3.13}$$

one may obtain an integral equation for $w_2^{(1)}(\mathbf{r}_a, \mathbf{r}_b)$

$$w_2^{(1)}(\mathbf{r}_a, \mathbf{r}_b) = q_a q_b \gamma(\mathbf{r}_a, \mathbf{r}_b) + (\epsilon - 1)/4\pi \int_V d\mathbf{r}' \Gamma(\mathbf{r}', \mathbf{r}_a) \cdot \nabla_r \cdot w_2^{(1)}(\mathbf{r}', \mathbf{r}_b). \tag{3.14}$$

It is easy to show that this integral equation is equivalent to Eq. (3.12) by substitution of Eq. (3.12) for $w_2$ in the right-hand side of Eq. (3.14) and use of Eqs. (3.8), (3.9), and (3.13).

The solution of this integral equation for $w_2$ gives an expression for the potential of mean force between two impurity ions at large separation in a dipolar fluid. An explicit solution may be obtained either from Eq. (3.14) or from Eq. (3.12) if $F(\mathbf{r}, \mathbf{r}')$ is determined from Eq. (3.9). For arbitrary geometries of the regions $V$ and $W$ it may be difficult to obtain these solutions. However, it is easy to establish the important point that the potential of mean force obtained from these equations is identical to the potential energy of the two charges $w_m(\mathbf{r}_a, \mathbf{r}_b)$ obtained from the macroscopic Maxwell equations and the constitutive relation $\mathbf{P}_V(\mathbf{r}) = [(\epsilon - 1)/4\pi]\mathbf{E}(\mathbf{r})$. The identity follows by noting that $w_m(\mathbf{r}_a, \mathbf{r}_b) = q_a \psi(\mathbf{r}_a, \mathbf{r}_b)$ where $\psi(\mathbf{r}, \mathbf{r}_b)$ is the potential at $\mathbf{r}$ due to a charge $q_b$ at $\mathbf{r}_b$. From Maxwell's equations we obtain an integral equation for $\psi$

$$\psi(\mathbf{r}, \mathbf{r}_b) = q_b \gamma(\mathbf{r}, \mathbf{r}_b) + \frac{\epsilon - 1}{4\pi} \int_V d\mathbf{r}' \Gamma(\mathbf{r}', \mathbf{r}) \cdot \nabla_{r'} \psi(\mathbf{r}', \mathbf{r}_b), \tag{3.15}$$

which follows by noting that $\psi(\mathbf{r}, \mathbf{r}_b)$ is the sum of the potential due to the charge $q_b$ in the presence of the medium in $W$, and the potential due to the polarization $\mathbf{P}_V(\mathbf{r}) = [(\epsilon - 1)/4\pi]\mathbf{E}(\mathbf{r})$ in $V$ in the presence of the medium in $W$. Equation (3.15) for $\psi$ is identical to the molecular equation for $w_2$, Eq. (3.14).

A particularly important special geometry is the case of an infinite volume $V$. The solution of Eq. (3.14) for the potential of mean force in this case is

$$w_2^\infty(\mathbf{r}_a, \mathbf{r}_b) = (1/\epsilon)(q_a q_b / |\mathbf{r}_a - \mathbf{r}_b|). \tag{3.16}$$

This is the expected result for the effective potential energy of interaction between two impurity charges at large separation in an infinite dielectric solvent.

## B. Charge–Dipole

We next consider the case of one charge impurity $q_a$ and one dipole impurity $\boldsymbol{\mu}_b$. In this case the leading, longest-range contribution to $G_2^{(1)}$ comes from the eight graphs

$$G_2^{(1)} = (1) + (5) + (9) + (13) + (3) + (7) + (11) + (15) \tag{3.17}$$

which have an effective range $|\mathbf{r}_a - \mathbf{r}_b|^{-2}$. The eight integrals corresponding to these graphs may easily be written down in a manner completely analogous to Eq. (3.4) for the charge–charge case. The resulting eight integrals may be reduced by using the short-range property of $G_{2,p}^{(0)}$ and $G_{2,\mu_b}^{(0)}$, the definition

$$\boldsymbol{\mu}_{b,\text{eff}}(\boldsymbol{\omega}_b) = \boldsymbol{\mu}_b(\boldsymbol{\omega}_b) + (V\Omega_b) \int d\mathbf{r} d\omega \\ \times G_{2,\mu_b}^{(0)}(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_b, \boldsymbol{\omega}_b)\boldsymbol{\mu}(\boldsymbol{\omega}) \tag{3.18}$$

and Eqs. (3.5)–(3.7). The result for the asymptotic limit $w_2^{(1)}$ of the potential of mean force is

$$w_2^{(1)}(\mathbf{r}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = -q_a \boldsymbol{\mu}_{b,\text{eff}}(\boldsymbol{\omega}_b) \cdot \Gamma(\mathbf{r}_b, \mathbf{r}_a) - (\tfrac{1}{3}\beta\rho\boldsymbol{\mu} \cdot \boldsymbol{\mu}_{\text{eff}}) \\ \times \int_V d\mathbf{r} q_a \Gamma(\mathbf{r}, \mathbf{r}_a) \cdot F(\mathbf{r}, \mathbf{r}_b) \cdot \boldsymbol{\mu}_{b,\text{eff}}(\boldsymbol{\omega}_b). \tag{3.19}$$

This equation for $w_2^{(1)}$ is completely equivalent to the integral equation

$$w_2^{(1)}(\mathbf{r}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = -q_a \boldsymbol{\mu}_{b,\text{eff}}(\boldsymbol{\omega}_b) \cdot \Gamma(\mathbf{r}_b, \mathbf{r}_a) \\ + \frac{\epsilon - 1}{4\pi} \int_V d\mathbf{r} \Gamma(\mathbf{r}, \mathbf{r}_a) \cdot \nabla_r w_2^{(1)}(\mathbf{r}; \mathbf{r}_b, \boldsymbol{\omega}_b), \tag{3.20}$$

as may be verified by use of the integral equation for F, Eq. (3.9) and Eqs. (3.13), (3.8). The solution of this integral equation, Eq. (3.19), depends upon the geometry of $(V+W)$. For the important special geometry of an infinite volume $V$, $w_2^{(1)}$ is given by

$$w_2^\infty(\mathbf{r}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = (1/\epsilon) q_a \boldsymbol{\mu}_{b,\text{eff}}(\boldsymbol{\omega}_b) \\ \cdot [(\mathbf{r}_a - \mathbf{r}_b)/|\mathbf{r}_a - \mathbf{r}_b|^3]. \tag{3.21}$$

We see that the effective interaction between the impurity charge and the impurity dipole at large separation is similar to the direct charge–dipole interaction, except that the shielding of the polar solvent introduces a factor $\epsilon^{-1}$ and that the impurity dipole moment is changed to $\boldsymbol{\mu}_{b,\text{eff}}$. The effective impurity dipole arises because the short-range forces between the impurity dipole and the fluid modifies the orientation of the surrounding solvent dipoles.

For arbitrary geometries $(V+W)$ the molecular expression Eq. (3.19) or equivalently (3.20) for the potential of mean force is consistent with the potential energy of interaction, $w_m$, of a charge $q_a$ and a dipole $\mathbf{p} = \boldsymbol{\mu}_{b,\text{eff}}$ obtained from the macroscopic Maxwell equations. In a dielectric $V$ with a dielectric constant $\epsilon$, surrounded by a dielectric $W$ with a dielectric constant $\epsilon_0$, the macroscopic electric potential $\psi(\mathbf{r}; \mathbf{r}_b, \boldsymbol{\omega}_b)$ at

point $\mathbf{r}$ due to a dipole $\mathbf{p}$ at $\mathbf{r}_b$ in $V$ with orientation $\boldsymbol{\omega}_b$ is given by the equation

$$\psi(\mathbf{r}; \mathbf{r}_b, \boldsymbol{\omega}_b) = -\mathbf{p}(\boldsymbol{\omega}_b) \cdot \boldsymbol{\Gamma}(\mathbf{r}_b, \mathbf{r})$$

$$+ \frac{\epsilon-1}{4\pi} \int_V d\mathbf{r}' \boldsymbol{\Gamma}(\mathbf{r}', \mathbf{r}) \cdot \nabla_{r'} \psi(\mathbf{r}'; \mathbf{r}_b, \boldsymbol{\omega}_b) \quad (3.22)$$

which follows again by noting that $\psi(\mathbf{r}; \mathbf{r}_b, \boldsymbol{\omega}_b)$ is the sum of the potential due to the dipole $\mathbf{p}(\boldsymbol{\omega}_b)$ in the presence of the dielectric in $W$, and the potential due to the polarization in $V$ in the presence of the dielectric in $W$. Since $w_m = q_a \psi$ it follows that $w_2^{(1)}$ is identical to $w_m$ with the choice $\mathbf{p} = \boldsymbol{\mu}_{b,\mathrm{eff}}$.

## C. Dipole–Dipole

We next consider the case of two dipole impurities $\boldsymbol{\mu}_a$ and $\boldsymbol{\mu}_b$. In this case all sixteen graphs in Fig. 2 contribute to $G_2^{(1)}$ with an effective range $|\mathbf{r}_a - \mathbf{r}_b|^{-3}$. The 16 integrals may be written down for this case. A vast reduction is possible if one uses the short-range property of $G_{2,p}^{(0)}$ and $G_{2,\mu_a}^{(0)}$ and $G_{2,\mu_b}^{(0)}$, the definition $\boldsymbol{\mu}_{b,\mathrm{eff}}$ according to Eq. (3.18) with an analogous definition of $\boldsymbol{\mu}_{a,\mathrm{eff}}$, and Eqs. (3.5)–(3.7). The resulting large separation part of the potential of mean force between the two dipoles is found to be

$$w_2^{(1)}(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = -\boldsymbol{\mu}_{a,\mathrm{eff}}(\boldsymbol{\omega}_a) \cdot \mathbf{F}(\mathbf{r}_a, \mathbf{r}_b) \cdot \boldsymbol{\mu}_{b,\mathrm{eff}}(\boldsymbol{\omega}_b)$$

$$(3.23)$$

which clearly is anticipated from the results of the pure dipole case considered in I.

Once again we may show that the microscopic potential of mean force $w_2^{(1)}$ between the impurity dipoles at large separation may be obtained from the macroscopic calculation, based on Maxwell's equations, of the interaction energy between two dipoles $\mathbf{p}_a = \boldsymbol{\mu}_{a,\mathrm{eff}}$ and $\mathbf{p}_b = \boldsymbol{\mu}_{b,\mathrm{eff}}$. Macroscopically, the field at $\mathbf{r}$ due to a dipole $\mathbf{p}_b$ at $\mathbf{r}_b$ in $V$ with orientation $\boldsymbol{\omega}_b$ is given by the integral equation

$$\mathbf{E}(\mathbf{r}; \mathbf{r}_b, \boldsymbol{\omega}_b) = \mathbf{D}(\mathbf{r}, \mathbf{r}_b) \cdot \mathbf{p}_b(\boldsymbol{\omega}_b)$$

$$+ \frac{\epsilon-1}{4\pi} \int_V d\mathbf{r}' \mathbf{D}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{E}(\mathbf{r}'; \mathbf{r}_b, \boldsymbol{\omega}_b) \quad (3.24)$$

when $V$ is a dielectric region with dielectric constant $\epsilon$, surrounded by another dielectric region $W$ with a dielectric constant $\epsilon_0$. From Eqs. (3.9) and (3.8) one finds immediately that

$$\mathbf{E}(\mathbf{r}; \mathbf{r}_b, \boldsymbol{\omega}_b) = \mathbf{F}(\mathbf{r}, \mathbf{r}_b) \cdot \mathbf{p}_b(\boldsymbol{\omega}_b). \quad (3.25)$$

Since the macroscopic energy of interaction between

$\mathbf{p}_a$ and $\mathbf{p}_b$ is

$$w_m(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = -\mathbf{p}_a(\boldsymbol{\omega}_a) \cdot \mathbf{E}(\mathbf{r}_a; \mathbf{r}_b, \boldsymbol{\omega}_b), \quad (3.26)$$

the identity of $w_m$ and $w_2^{(1)}$, Eq. (3.23), follows immediately from Eqs. (3.25) and (3.26). Here again we see that the impurity dipoles have an interaction energy at large separations exactly as expected from macroscopic electrostatics, except that there is an effective dipole moment for each impurity. The effective dipole moments arise because the short-range forces between the solvent dipoles and the impurities can modify the local polarization around each impurity. In the case of an infinite volume $V$ the potential of mean force is

$$w_2^\infty(\mathbf{r}_a, \boldsymbol{\omega}_a; \mathbf{r}_b, \boldsymbol{\omega}_b) = -\epsilon^{-1} \boldsymbol{\mu}_{a,\mathrm{eff}}(\boldsymbol{\omega}_a) \cdot \mathbf{T}(\mathbf{r}_a, \mathbf{r}_b) \cdot \boldsymbol{\mu}_{b,\mathrm{eff}}(\boldsymbol{\omega}_b).$$

$$(3.27)$$

## D. Quadrupole Impurities

Clearly our considerations may be extended to higher multipole impurities. It is of some interest to consider the case of a quadrupole impurity, for in this case the range of potential of mean force may be greater than the range of the direct interaction. As an example we consider the charge–quadrupole interaction with $q_a$ the charge impurity and $\mathbf{Q}_b$ the quadrupole impurity. The direct potential energy of interaction for a charge and a quadrupole is

$$\tfrac{1}{2} q_a \mathbf{Q}_b : \nabla_{r_b} \nabla_{r_b} \gamma(\mathbf{r}_a, \mathbf{r}_b) \quad (3.28)$$

which is of order $|\mathbf{r}_a - \mathbf{r}_b|^{-3}$. The direct potential energy of interaction between a dipole $\boldsymbol{\mu}$ at $\mathbf{r}$ and the impurity quadrupole is

$$\tfrac{1}{2} \boldsymbol{\mu} \cdot \nabla_r \mathbf{Q}_b : \nabla_{r_b} \nabla_{r_b} \gamma(\mathbf{r}, \mathbf{r}_b) \quad (3.29)$$

which is of order $|\mathbf{r}_b - \mathbf{r}|^{-4}$. In these expressions the effects of the surrounding medium in $W$ are included in $\gamma$.

Although the direct interaction between a charge and a quadrupole is of order $r^{-3}$, we find upon examination of the sixteen graphs contributing to $G_2^{(1)}$ that seven graphs have a leading contribution of order $r^{-2}$. The graphs are

$$G_2^{(1)} = (5) + (9) + (13) + (3) + (7) + (11) + (15).$$

$$(3.30)$$

However, it may be shown that the leading terms of some of these graphs which are formally of order $r^{-2}$ vanish. For example, the contribution of graph (5) is

$$(5) = [V^2 \Omega_a \Omega_b]^{-1} \int_V d\mathbf{r} d\boldsymbol{\omega} \beta q_a \boldsymbol{\mu}(\boldsymbol{\omega}) \cdot \boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a) \frac{\rho}{\Omega} [-\tfrac{1}{2} \beta \boldsymbol{\mu}(\boldsymbol{\omega}) \cdot \nabla_r \mathbf{Q}_b : \nabla_{r_b} \nabla_{r_b} \gamma(\mathbf{r}, \mathbf{r}_b)]. \quad (3.31)$$

Since the term between brackets in Eq. (3.31) is of order $r^{-4}$ and therefore effectively of short range, we may replace $\boldsymbol{\Gamma}(\mathbf{r}, \mathbf{r}_a)$ by $\boldsymbol{\Gamma}(\mathbf{r}_b, \mathbf{r}_a)$. The contribution of (5) is then

$$(5) = -\tfrac{1}{2}[V^2 \Omega_a \Omega_b]^{-1} \tfrac{1}{3} \beta \rho \mu^2 \beta q_a \boldsymbol{\Gamma}(\mathbf{r}_b, \mathbf{r}_a) \cdot \int_V d\mathbf{r} \nabla_r \mathbf{Q}_b : \nabla_{r_b} \nabla_{r_b} \gamma(\mathbf{r}, \mathbf{r}_b), \quad (3.32)$$

where we have performed the integration over $\omega$. Since the integrand has a short-range $|\mathbf{r}-\mathbf{r}_b|^{-4}$, we make an error of higher order if we neglect the effects of the surrounding medium $W$, replacing $\gamma$ by $|\mathbf{r}-\mathbf{r}_b|^{-1}$, and perform the integration over the entire space. The tensor $\int d\mathbf{r}\nabla_r\nabla_{r_b}\nabla_{r_b}|\mathbf{r}-\mathbf{r}_b|^{-1}$ is completely isotropic and symmetric and therefore must be zero, because its rank is not even. We conclude that graph (5) does not contribute to order $r^{-2}$. The same is true for graphs (9) and (13). The expression for $G_2^{(1)}$ obtained from the remaining four graphs is

$$G_2^{(1)} = \frac{\beta q_a}{V\Omega_a}\left(\int_V dr d\omega \mu(\omega)\cdot\Gamma(\mathbf{r},\mathbf{r}_a)G_{2,b}^{(0)}(\mathbf{r},\omega;\mathbf{r}_b,\omega_b) + \int_V dr d\omega dr' d\omega' \mu(\omega)\cdot\Gamma(\mathbf{r},\mathbf{r}_a)\right.$$

$$\times\frac{\rho}{\Omega}\beta\mu(\omega)\cdot\mathbf{D}(\mathbf{r},\mathbf{r}')\cdot\mu(\omega')G_{2,b}^{(0)}(\mathbf{r}',\omega';\mathbf{r}_b,\omega_b) + \int_V dr d\omega dr' d\omega' dr'' d\omega'' \mu(\omega)\cdot\Gamma(\mathbf{r},\mathbf{r}_a)$$

$$\left.\times[G_{2,p}^{(0)}(\mathbf{r},\omega;\mathbf{r}',\omega') + G_{2,p}^{(0)}(\mathbf{r},\omega;\mathbf{r}',\omega')]\beta\mu(\omega')\cdot\mathbf{D}(\mathbf{r}',\mathbf{r}'')\mu(\omega'')G_{2,b}^{(0)}(\mathbf{r}'',\omega'';\mathbf{r}_b,\omega_b)\right). \quad (3.33)$$

The function $G_{2,b}^{(0)}$ is of short range, so we introduce the dipole vector $\mathbf{p}_Q$ by the definition

$$(1/V\Omega_b)\mathbf{p}_Q(\omega_b) = \int dr d\omega \mu(\omega)G_{2,b}^{(0)}(\mathbf{r},\omega;\mathbf{r}_b,\omega_b) \quad (3.34)$$

in analogy to the definition of $\kappa$ in Eq. (3.7). We may reduce the expression for $G_2^{(1)}$ by taking into account the short-range nature of $G_{2,b}^{(0)}$ and $G_{2,p}^{(0)}$ and the definition of $\kappa$ and $\mathbf{p}_Q$. The result is

$$G_2^{(1)} = \frac{\beta q_a}{V^2\Omega_a\Omega_b}\left(\Gamma(\mathbf{r}_b,\mathbf{r}_a)\cdot\mathbf{p}_Q(\omega_b) + (\tfrac{1}{3}\beta\rho\mu\cdot\mu_{\text{eff}})\int_V dr\Gamma(\mathbf{r},\mathbf{r}_a)\cdot\mathbf{D}(\mathbf{r},\mathbf{r}_b)\cdot\mathbf{p}_Q(\omega_b)\right.$$

$$\left.+ (\tfrac{1}{3}\beta\rho\mu\cdot\mu_{\text{eff}})^2\int_V dr dr''\Gamma(\mathbf{r},\mathbf{r}_a)\cdot\mathbf{F}(\mathbf{r},\mathbf{r}')\cdot\mathbf{D}(\mathbf{r}',\mathbf{r}_b)\cdot\mathbf{p}_Q(\omega_b)\right), \quad (3.35)$$

where we have used the expression for $G_{2,p}^{(1)}$, Eq. (3.5). The integral equation for $\mathbf{F}$, Eq. (3.9), may be used to simplify this equation and we find for the potential of mean force between the impurity charge and the impurity quadrupole in the asymptotic limit

$$w_2^{(1)}(\mathbf{r}_a;\mathbf{r}_b,\omega_b) = -q_a\mathbf{p}_Q(\omega_b)\cdot\Gamma(\mathbf{r}_b,\mathbf{r}_a) - q_a(\tfrac{1}{3}\beta\rho\mu\cdot\mu_{\text{eff}})\int_V dr\Gamma(\mathbf{r},\mathbf{r}_a)\cdot\mathbf{F}(\mathbf{r},\mathbf{r}_b)\cdot\mathbf{p}_Q(\omega_b). \quad (3.36)$$

This expression for the potential of mean force is identical to the expression obtained for the charge–dipole case in Eq. (3.19) if we replace $\mu_{b,\text{eff}}$ by $\mathbf{p}_Q$. If the short-range forces between the impurity quadrupole and the solvent dipoles are such that a local dipole moment $\mathbf{p}_Q$ arises, the leading effective long-range interaction with the impurity charge will be determined by the induced dipole moment and not by the quadrupole–charge interaction.

If we consider the case of an impurity dipole and an impurity quadrupole an analogous analysis leads us to an expression for the potential of mean force identical to the potential of mean force determined for two impurity dipoles, Eq. (3.23), except for the replacement of $\mu_{b,\text{eff}}$ by $\mathbf{p}_Q$. The case of two impurity quadrupoles $\mathbf{Q}_a$ and $\mathbf{Q}_b$ also leads to a potential of mean force identical to that obtained in Eq. (3.23) for two impurity dipoles, except for the replacement of $\mu_{a,\text{eff}}$ by $\mathbf{p}_{Q_a}$ and $\mu_{b,\text{eff}}$ by $\mathbf{p}_{Q_b}$. In all these cases of impurity quadrupoles (or higher multipole impurities) our formalism will lead to the quadrupole impurity appearing to another distant impurity as an effective dipole. This occurs because our molecular model allows the possibility that the short-range quadrupole–solvent dipole forces induce a local dipole moment.

It may, with some justification, be argued that for molecular impurities such a model is unrealistic. For if the short-range forces are such that solvent dipoles around a molecular impurity are oriented, then the lack of symmetry of the interaction means it is likely, but not necessary, that the impurity will have a nonvanishing dipole moment. However, our model suggests an interesting intermediate situation. Consider an impurity molecule that has a large molecular quadrupole moment $\mathbf{Q}_b$, but a very small dipole moment $\mu_b$, e.g., toluene. At very large distances the dipole moment dominates the potential. At smaller separations the quadrupole moment dominates the potential. At large separations the interaction with another impurity is determined by the effective dipole moment $\mu_{b,\text{eff}}$, not by $\mu_b$ or $\mathbf{Q}_b$, because of the effects of the short-range forces.

## IV. DIELECTRIC SATURATION

In this section we turn attention to the problem of dielectric saturation. Our objective is to obtain expressions for the polarization $\mathbf{P}_V(\mathbf{r})$ of the polar fluid and the macroscopic electric field $\mathbf{E}(\mathbf{r})$ to all orders in the external field $\mathbf{E}_0(\mathbf{r})$. We accomplish this by computing
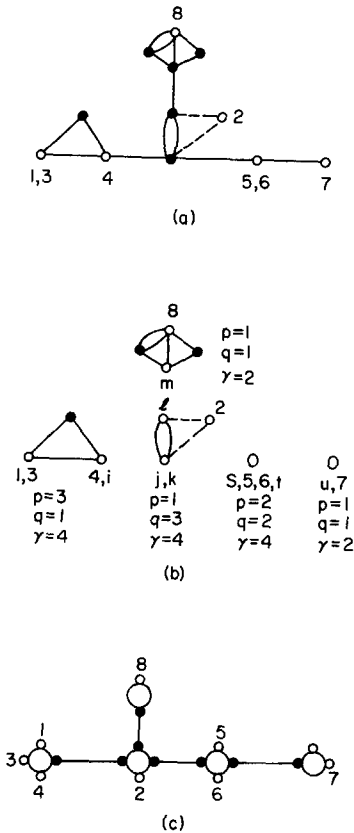
FIG. 3. Example of an old composite graph (a) contributing to $H_8$. The graphs shown in (b) are the disconnected parts resulting from the graph in (a) if we erase the solid bonds in the building stars $S_0$. For each resulting $H_\gamma^{(0)}$ graph we indicate the numbers $p$, $q$ and $\gamma = p+q$. In (c) we show the new $H_8$ graph which contains in it the graph in (a).

an expression for the one-particle distribution function in the presence of the field.

We consider a polar fluid of $N$ rigid dipoles in an arbitrary volume $V$. The potential energy $U$ of the fluid in the presence of the external field $\mathbf{E}_0(\mathbf{r})$ is expressed as

$$U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0) = \sum_{i<j}^N \sum v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)$$

$$-\tfrac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j)$$

$$- \sum_{i=1}^N \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{E}_0(\mathbf{r}_i), \quad (4.1)$$

where $\mathbf{D}$ is defined by Eq. (2.2), and the other symbols have the meaning discussed in the previous sections. We include the possibility that the sample volume $V$ is surrounded by the dielectric continuum in $W$. The pair interaction $v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)$ is assumed to be of short range. The canonical ensemble configurational distribu-

tion function $f$ is given by

$$f(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0) = \exp[-\beta U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0)]$$

$$\times \left\{ \int_V \exp[-\beta U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0)] d\mathbf{r}^N d\boldsymbol{\omega}^N \right\}^{-1}. \quad (4.2)$$

The one-particle distribution function in the presence of the field $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$ is customarily defined as

$$n_1(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{E}_0) = N \int_V d\mathbf{r}^{N-1} d\boldsymbol{\omega}^{N-1} f(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0). \quad (4.3)$$

The polarization $\mathbf{P}_V(\mathbf{r})$ of the molecular sample is microscopically expressed by the relation

$$\mathbf{P}_V(\mathbf{r}) = \int d\boldsymbol{\omega} n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0) \boldsymbol{\mu}(\boldsymbol{\omega}). \quad (4.4)$$

The macroscopic field $\mathbf{E}(\mathbf{r})$ is related to $\mathbf{P}_V(\mathbf{r})$ and $\mathbf{E}_0(\mathbf{r})$ according to the defining relation

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \int_V d\mathbf{r}' \mathbf{D}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{P}_V(\mathbf{r}'). \quad (4.5)$$

The integral over the singularity in $\mathbf{D}(\mathbf{r}, \mathbf{r}')$ at $\mathbf{r} = \mathbf{r}'$ must be computed according to the usual prescription[1]

$$\int_{|\mathbf{r}'-\mathbf{r}|<a} d\mathbf{r}' \mathbf{T}(\mathbf{r}, \mathbf{r}') = -\tfrac{4}{3}\pi \mathbf{I} \quad (4.6)$$

for every distance $a>0$. We emphasize that within the framework of the canonical ensemble the relations (4.4) and (4.5) are exact to all orders in the external field. In order to investigate Eqs. (4.4) and (4.5) we wish to express $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$ in terms of the distribution functions of the fluid in the absence of the external field.

For simplicity we shall denote the coordinates $(\mathbf{r}_i, \boldsymbol{\omega}_i)$ of particle $i$ by $(i)$, and we write $d(i)$ for the integration element $d\mathbf{r}_i d\boldsymbol{\omega}_i$. We introduce the reduced $s$-particle distribution functions $n_s(\mathbf{r}^s, \boldsymbol{\omega}^s)$ in the absence of the external field by the definition

$$n_s(\mathbf{r}^s, \boldsymbol{\omega}^s) = \frac{N!}{(N-s)!} \int_V d\mathbf{r}^{N-s} d\boldsymbol{\omega}^{N-s} f(\mathbf{r}^N, \boldsymbol{\omega}^N; 0),$$

$$s = 1, 2, 3, \cdots. \quad (4.7)$$

Further we will employ the special distribution function $k_s(\mathbf{r}^s, \boldsymbol{\omega}^s)$, the $s$-particle correlation functions $G_s(\mathbf{r}^s, \boldsymbol{\omega}^s)$ and the special correlation functions $H_s(\mathbf{r}^s, \boldsymbol{\omega}^s)$, which are defined by the sets of relations

$$k_1(1) = n_1(1),$$
$$k_2(12) = n_1(1)\delta(12) + n_2(12),$$
$$k_3(123) = n_1(1)\delta(12)\delta(23) + n_2(12)\delta(23)$$
$$+ n_2(23)\delta(31) + n_2(31)\delta(12) + n_3(123),$$
$$\cdots, \quad (4.8)$$

and

$$n_1(1) = G_1(1),$$
$$n_2(12) = G_1(1)G_1(2) + G_2(12),$$
$$n_3(123) = G_1(1)G_1(2)G_1(3) + G_2(12)G_1(3)$$
$$+ G_2(23)G_1(1) + G_2(31)G_1(2) + G_3(123),$$
$$\cdots, \quad (4.9)$$

and

$$k_1(1) = H_1(1),$$

$$k_2(12) = H_1(1)H_1(2) + H_2(12),$$

$$k_3(123) = H_1(1)H_1(2)H_1(3) + H_2(12)H_1(3)$$
$$+ H_2(23)H_1(1) + H_2(31)H_1(2) + H_3(123),$$

$$\cdots. \qquad (4.10)$$

One may show that the relations between the functions $H_s$ and $G_s$ are the same as between $k_s$ and $n_s$

$$H_1(1) = G_1(1),$$

$$H_2(12) = G_1(1)\delta(12) + G_2(12),$$

$$H_3(123) = G_1(1)\delta(12)\delta(23) + G_2(12)\delta(23)$$
$$+ G_2(23)\delta(31) + G_2(31)\delta(12) + G_3(123),$$

$$\cdots. \qquad (4.11)$$

A relation between $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$ and the functions $H_s$ in the absence of the external field $\mathbf{E}_0$ can be found if we employ functional derivative techniques. We introduce the modified potential energy $U(\mathbf{E}_0; \phi)$ by adding a single particle potential $\phi(\mathbf{r}, \boldsymbol{\omega})$ to $U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0)$,

$$U(\mathbf{E}_0; \phi) = U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0) + \sum_{i=1}^{N} \phi(\mathbf{r}_i, \boldsymbol{\omega}_i). \quad (4.12)$$

The configurational partition function $Z(\mathbf{E}_0; \phi)$ corresponding to $U(\mathbf{E}_0; \phi)$ is

$$Z(\mathbf{E}_0; \phi) = \frac{1}{(V\Omega)^N} \int_V d\mathbf{r}^N d\boldsymbol{\omega}^N \exp[-\beta U(\mathbf{E}_0; \phi)]$$

$$(4.13)$$

so that $Z(\mathbf{E}_0; \phi)$ is a functional of the external field $\mathbf{E}_0(\mathbf{r})$ and of the potential $\phi(\mathbf{r}, \boldsymbol{\omega})$. One readily shows that $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$ is related to the functional $Z(\mathbf{E}_0; \phi)$ by

$$n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0) = -\beta^{-1}[Z(\mathbf{E}_0; 0)]^{-1}[\delta Z(\mathbf{E}_0; \phi)/\delta\phi(\mathbf{r}, \boldsymbol{\omega})]|_{\phi=0}$$

$$= -\beta^{-1}[\delta \ln Z(\mathbf{E}_0; \phi)/\delta\phi(\mathbf{r}, \boldsymbol{\omega})]|_{\phi=0}. \qquad (4.14)$$

On the other hand, we find by expanding $Z(\mathbf{E}_0; \phi)$ in powers of $(\boldsymbol{\mu} \cdot \mathbf{E}_0 - \phi)$

$$\frac{Z(\mathbf{E}_0; \phi)}{Z(0; 0)} = 1 + \sum_{\alpha=1}^{\infty} \frac{\beta^\alpha}{\alpha!} \int_V d(1)d(2)\cdots d(\alpha) k_\alpha(12\cdots\alpha)[\boldsymbol{\mu}(\boldsymbol{\omega}_1) \cdot \mathbf{E}_0(\mathbf{r}_1) - \phi(\mathbf{r}_1, \boldsymbol{\omega}_1)]\cdots[\boldsymbol{\mu}(\boldsymbol{\omega}_\alpha) \cdot \mathbf{E}_0(\mathbf{r}_\alpha) - \phi(\mathbf{r}_\alpha, \boldsymbol{\omega}_\alpha)].$$

$$(4.15)$$

If we take the logarithm of Eq. (4.15) and use the relations (4.10) between $k_\alpha$ and $H_\alpha$, we find according to Kubo[9]

$$\ln Z(\mathbf{E}_0; \phi) - \ln Z(0; 0) = \sum_{\alpha=1}^{\infty} \frac{\beta^\alpha}{\alpha!} \int_V d(1)d(2)\cdots d(\alpha) H_\alpha(12\cdots\alpha)$$

$$\times [\boldsymbol{\mu}(\boldsymbol{\omega}_1) \cdot \mathbf{E}_0(\mathbf{r}_1) - \phi(\mathbf{r}_1, \boldsymbol{\omega}_1)]\cdots[\boldsymbol{\mu}(\boldsymbol{\omega}_\alpha) \cdot \mathbf{E}_0(\mathbf{r}_\alpha) - \phi(\mathbf{r}_\alpha, \boldsymbol{\omega}_\alpha)]. \quad (4.16)$$

By taking the functional derivative of this equation with respect to $\phi(\mathbf{r}, \boldsymbol{\omega})$ and by using Eq. (4.14), we obtain

$$n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0) = \sum_{\alpha=1}^{\infty} \frac{\beta^{\alpha-1}}{(\alpha-1)!} \int_V d(1)d(2)\cdots d(\alpha) H_\alpha(12\cdots\alpha)\delta(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_1, \boldsymbol{\omega}_1)\boldsymbol{\mu}(\boldsymbol{\omega}_2) \cdot \mathbf{E}_0(\mathbf{r}_2)\cdots\boldsymbol{\mu}(\boldsymbol{\omega}_\alpha) \cdot \mathbf{E}_0(\mathbf{r}_\alpha). \quad (4.17)$$

In order to study $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$ we must investigate $H_\alpha$, $\alpha = 1, 2, \cdots$. We shall develop a suitable graphical expansion of $H_\alpha$, and thus of $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$.

Our starting point is the expansion of $G_\alpha$, $\alpha = 2, 3, \cdots$ in terms of irreducible connected composite graphs.[2] As in I and II we assume that in the absence of the external field the system is homogeneous and isotropic

$$H_1(1) = G_1(1) = n_1(1) = \rho/\Omega. \qquad (4.18)$$

If $\alpha \geq 2$, we find from the basic theory of linear graphs, in a manner similar to that employed in I and II, that $G_\alpha$ can be represented as the sum over all different $\alpha$-irreducible, connected, composite graphs with $\alpha$ root points labeled $1, 2, \cdots, \alpha$ and any number of unlabeled field points. It is customary to represent a field point by a small black circle, a root point by a small open circle. Each point contributes a factor $\rho/\Omega$. Between any pair of points we have one dotted bond, any number of solid bonds or no bonds. A dotted bond between the

points $i$ and $j$ contributes a short-range factor $a_{ij}$ given by

$$a_{ij} = \{\exp[-\beta v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)] - 1\}$$

$$\times \exp[\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j)]. \quad (4.19)$$

A number $\alpha$ of solid bonds between the points $i$ and $j$ contributes a factor $(1/\alpha!)(b_{ij})^\alpha$, where

$$b_{ij} = \beta\boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j). \qquad (4.20)$$

The contribution of a graph has an extra factor $\sigma^{-1}$, where $\sigma$ is the symmetry number of the graph, that gives the number of permutations of field points in the graphs which leave the bonds between pairs of points invariant. An integration is performed over the coordinates of the field points. The difference in the ground rules for the graphical expansion in this section and in the previous section is only the designation in the previous section of root points as impurities.

A similar expansion of $H_\alpha$, $\alpha \geq 2$, is found as the sum over all different connected composite $\gamma$-irreducible graphs, $1 \leq \gamma \leq \alpha$, with $\gamma$ root points and any number of unlabeled field points.[7] Each root point is labeled by a subset out of the set of numbers $(1, 2, \cdots, \alpha)$. The subsets labeling the root points in a graph are disjoint and exhaust the set of numbers $(1, 2, \cdots, \alpha)$. If $\gamma = 1$, the only irreducible graph is said to be the graph consisting of one root point and no field points. The contribution of the field points and the bonds are the same as for $G_\alpha$ graphs. A root point labeled $\{i_1, i_2, \cdots, i_n\}$ contributes a factor $(\rho/\Omega)\delta(i_1, i_2)\delta(i_2, i_3)\cdots\delta(i_{n-1}, i_n)$.

From the discussion in earlier sections and in I and II we know that we can split the $H_\alpha$ graphs in two classes. The graphs in one class do not contain the basic star $S_0$ as a building star. As previously, the star $S_0$ consists of a single solid bond with its two end points. The sum of the $H_\alpha$ graphs which do not contain the star $S_0$ as a building star is called $H_\alpha^{(0)}$. We know that $H_\alpha^{(0)}$ is of short range and does not depend on the shape of the sample and the surroundings. The contribution of the other graphs, i.e., the $H_\alpha$ graphs which contain the star $S_0$ at least once as a building star, is called $H_\alpha^{(1)}$. Any graph contributes either to $H_\alpha^{(0)}$, or it has at least one building star $S_0$, and therefore contributes to $H_\alpha^{(1)}$. If we erase in a $H_\alpha^{(1)}$ graph the solid bonds in the constituent stars $S_0$, we are left with a number of disconnected parts, none of which contains a building star $S_0$. Each of these remaining disconnected parts may be considered to be a $H_\gamma^{(0)}$ graph, $\gamma = p + q$, where $p$ is the total number of labels attached to the root points in this disconnected part and $q$ is the number of stars $S_0$ attached to this disconnected part in the original graph. In order to illustrate how the number $\gamma$ is determined for a remaining disconnected part in a graph, we give an example in Fig. 3. Figure 3(a) gives a graph contributing to $H_8^{(1)}$. After erasing the solid bonds in the building stars $S_0$, we are left with five disconnected parts, which are shown in Fig. 3(b). For every resulting disconnected part we indicate the numbers $p$, $q$, and $\gamma = p + q$. A resulting disconnected graph is considered to be a $H_\gamma^{(0)}$ graph with an additional label assigned to each point for every star $S_0$ which has been removed in the original graph, as shown in Fig. 3(b). Field points with stars $S_0$ attached to it in the original graph become labeled root points in the $H_\gamma^{(0)}$ graphs which result after erasing the solid bonds in the building stars $S_0$.

We can find a simpler graphical expansion of $H_\alpha$ by representing a factor $H_\gamma^{(0)}$ by a hypervertex consisting of a large open circle with $\gamma$ small circles attached to its circumference. We use ideas introduced by Lebowitz, Stell, and Baer,[7] but our expansion here is not identical to any of the expansions these authors use. By resummation we find that $H_\alpha$, $\alpha \geq 2$ is given as the sum over all connected irreducible graphs consisting of $H_\gamma^{(0)}$ hypervertices, $\gamma \geq 2$, and single solid bonds which are stars $S_0$. The small circles in the $H_\gamma^{(0)}$ hypervertices are either black (field points) or open (root points). The

total graph must have precisely $\alpha$ small open circles labeled $1, 2, \cdots, \alpha$. To each small black circle precisely one solid bond is attached, and no solid bond is attached to any of the root points. Each solid bond must be a constituent star $S_0$, and the total graph must be irreducible. In determining whether or not a graph is irreducible, each hypervertex is to be thought of as a single point, which is considered a root point if the hypervertex contains one or more small open circles, and which is considered a field point otherwise. In Fig. 3(c) we show the new graph contributing to $H_8$ which contains in it the contribution of the old graph, Fig. 3(a). The number $q$ of (black) field points in a hypervertex in a new graph is equal to the number $q$ of the corresponding $H_\gamma^{(0)}$ graph in an old graph, and the number $p$ of (open) root points in a hypervertex in a new graph is equal to the number $p$ of the corresponding $H_\gamma^{(0)}$ graph in an old graph. Every old $H_\alpha$ graph may be found by substituting $H_\gamma^{(0)}$ graphs for the $H_\gamma^{(0)}$ hypervertices in a new $H_\alpha$ graph. Reversely, if we substitute $H_\gamma^{(0)}$ graphs for the $H_\gamma^{(0)}$ hypervertices in a new $H_\alpha$ graph, we find an old $H_\alpha$ graph. It will be clear that one new graph represents the sum over an infinite number of old graphs. Furthermore, the new graphs contributing to $H_\alpha$ cannot contain an $H_\gamma^{(0)}$ hypervertex with $\gamma > \alpha$, otherwise the resulting new graph would be reducible. We may forget about the symmetry numbers of the new graphs, because they are always equal to unity.

It is not hard to verify that by using the new graphical representation of $H_\alpha$ each old graph is effectively taken into account once and not more than once, and that the symmetry numbers of the old graphs are properly accounted for. The contribution to $H_8$ from the new graph in Fig. 3(c) is

$$\int_V d(i) d(j) d(k) d(l) d(m) d(s) d(t) d(u)$$
$$\times H_4^{(0)}(134i) b_{ij} H_4^{(0)}(j2kl) b_{lm} H_2^{(0)}(m8)$$
$$\times b_{ks} H_4^{(0)}(s56t) b_{tu} H_2^{(0)}(u7). \quad (4.21)$$

The new graphical expansion of $H_2$ is given by



$$= H_2^{(0)}(12) + \int_V d(3) d(4) H_2^{(0)}(13) b_{34} H_2^{(0)}(42)$$

$$+ \int_V d(3) d(4) d(5) d(6) H_2^{(0)}(13) b_{34}$$
$$\times H_2^{(0)}(45) b_{56} H_2^{(0)}(62) + \cdots. \quad (4.22)$$

This expansion of $H_2$ is equivalent to the result for $G_2$ obtained in I and quoted in Sec. II.

We use the new graphical expansion of $H_\alpha$, $\alpha = 2$, $3, \cdots$, in order to obtain a graphical expansion of $n_1(\mathbf{r}, \boldsymbol{\omega}; E_0)$, Eq. (4.17). The contribution of a new $H_\alpha$ graph to $n_1(\mathbf{r}, \boldsymbol{\omega}; E_0)$ clearly does not depend on the labeling of the root points other than the point 1.

Hence the factor $1/(\alpha-1)!$ in Eq. (4.17) can be taken into account by summation over new $H_\alpha$ graphs in which only the root point 1 is labeled. The other root points are unlabeled, and a factor $1/\tau$ is included instead of the factor $1/(\alpha-1)!$, where the symmetry number $\tau$ is the number of permutations of the $(\alpha-1)$ unlabeled root points which leave the graph invariant. Permutations of unlabeled root points within a hypervertex must be included in determining $\tau$. From the foregoing and Eq. (4.17) it follows immediately

$n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$

$= (\rho/\Omega) +$ (sum over all different connected irreducible graphs built out of $H_\gamma^{(0)}$ hypervertices, $\gamma \geq 2$, and building stars $S_0$, with two or more open root points and any number of black field points. One root point is labeled 1, the other root points and the field points are unlabeled. To every field point one and not more than one solid $b$ bond is attached, no $b$ bond is attached to a root point).

$$(4.23)$$

The contribution of a graph in Eq. (4.23) is found by assigning a weight $H_\gamma^{(0)}$ to each hypervertex with $\gamma$ points, a weight $b_{ij}$ to each solid bond, a weight $\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{E}_0(\mathbf{r}_i)$ to each unlabeled root point, a weight $\delta(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_1, \boldsymbol{\omega}_1)$ to the root point labeled 1. The field points contribute no extra factor. An integration is performed over both field points and root points, including the root point 1. An additional factor $1/\tau$ is included in the contribution of each graph, where $\tau$ is the symmetry number of the graph, defined above as the number of permutations of the unlabeled root points which leave the graph invariant. The graphs consisting of one hypervertex with $\alpha$ root points, no field points and no solid bonds must be included in the expansion (4.23).

In the graphs in Eq. (4.23) the hypervertex containing the point 1 has two or more points. The contribution to $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$ of the graphs in which the hypervertex containing the point 1 has $(s+1)$ points (i.e., $s$ points other than the point 1) is called $n_1^{(s)}(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$. Hence we may write

$$n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0) = \frac{\rho}{\Omega} + \sum_{s=1}^{\infty} n_1^{(s)}(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0). \quad (4.24)$$

The graphs contributing to $n_1^{(s)}$ all begin with a hypervertex that has $s$ points other than the point labeled 1. In order to build up the graphs contributing to $n_1^{(s)}$ we must exhaustively consider all possible combinations in the hypervertex of unlabeled root points and field points, whose total number is $s$. Thus we start with the hypervertex containing the point 1. A certain number $m_0$ of the $s$ points other than the point 1 are chosen to be root points, the remaining points are field points. To the field points we attach a $b$ bond, and at the other end of the $b$ bond we attach one of the graphs contributing to $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$. Each graph contributing to $n_1^{(s)}$ can be built up in this way. The symmetry number $\tau$ of the total resulting graph can be shown to be

$$\tau = (\Pi\tau_i)m_0!m_{g1}!m_{g2}! \cdots, \quad (4.25)$$

where $\tau_i$ is the symmetry number of the $n_1(\mathbf{E}_0)$ graph which we hung to the $b$ bond attached to the field point $i$ in the hypervertex, $m_0$ is the number of root points other than the point 1 in the hypervertex, $m_{g1}$ is the number of identical $n_1(\mathbf{E}_0)$ graphs $g_1$ which we hung to $b$ bonds attached to field points in the hypervertex, etc. By definition

$$m_0 + m_{g1} + m_{g2} + \cdots = s. \quad (4.26)$$

If we sum over all possible sets $\{m_0; m_{g1}, m_{g2}, \cdots\}$ obeying Eq. (4.26), then we find that $n_1^{(s)}$ satisfies the relation

$$n_1^{(s)}(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0) = (s!)^{-1} \int_V d(1)d(2)\cdots d(s+1) H_{(s+1)}^{(0)}(12\cdots s+1)\delta(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_1, \boldsymbol{\omega}_1)$$

$$\times \left\{ \beta\boldsymbol{\mu}(\boldsymbol{\omega}_2) \cdot \left[ \mathbf{E}_0(\mathbf{r}_2) + \int_V d\mathbf{r}_2' d\boldsymbol{\omega}_2' \mathbf{D}(\mathbf{r}_2, \mathbf{r}_2') \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_2') n_1(\mathbf{r}_2', \boldsymbol{\omega}_2'; \mathbf{E}_0) \right] \right\} \times \cdots$$

$$\times \left\{ \beta\boldsymbol{\mu}(\boldsymbol{\omega}_{s+1}) \cdot \left[ \mathbf{E}_0(\mathbf{r}_{s+1}) + \int_V d\mathbf{r}_{s+1}' d\boldsymbol{\omega}_{s+1}' \mathbf{D}(\mathbf{r}_{s+1}, \mathbf{r}_{s+1}') \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_{s+1}') n_1(\mathbf{r}_{s+1}', \boldsymbol{\omega}_{s+1}'; \mathbf{E}_0) \right] \right\}. \quad (4.27)$$

This result may be understood qualitatively in the following manner: Choose $(s-q)$ points of the $s$ points other than the point 1 in the hypervertex as root points, and add to each of the $q$ remaining points by a $b$ bond the sum of the contributions from attaching all the graphs which compose $n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0)$; then sum over $q$ from zero to $s$. In Eq. (4.27) the root points appear as factors $\beta\boldsymbol{\mu} \cdot \mathbf{E}_0$, the $b$ bonds appear as factors $\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{D}(\mathbf{r}_i, \mathbf{r}_i') \cdot \boldsymbol{\mu}\omega_i'$. The factors $1/\tau_i$ in the inverse of the symmetry number of the total graph $1/\tau$, are taken into account in the term $n_1(\mathbf{r}_i', \boldsymbol{\omega}_i'; \mathbf{E}_0)$ in Eq. (4.27). The product $(m_0!m_{g1}! \cdots)^{-1}$ in the inverse symmetry number $1/\tau$ is taken into account by the multinomial factor $s!/m_0!m_{g1}! \cdots$ which arises if we expand $n_1(\mathbf{E}_0)$ in Eq. (4.27) in graphs and take together terms which correspond to identical total graphs.

From Eqs. (4.4) and (4.5) we find

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \int_V d\mathbf{r}' d\omega' \mathsf{D}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{\mu}(\omega') n_1(\mathbf{r}', \omega'; \mathbf{E}_0). \qquad (4.28)$$

Hence we can simplify Eq. (4.27) by substituting Eq. (4.28). So the total one-particle distribution function in the presence of the field becomes

$$n_1(\mathbf{r}, \omega; \mathbf{E}_0) = \rho/\Omega + \sum_{s=1}^{\infty} \frac{\beta^s}{s!} \int_V d(1) d(2) \cdots d(s+1) H_{s+1}^{(0)} (12 \cdots s+1) \delta(\mathbf{r}, \omega; \mathbf{r}_1, \omega_1)$$

$$\times [\mathbf{\mu}(\omega_2) \cdot \mathbf{E}(\mathbf{r}_2)] \cdots [\mathbf{\mu}(\omega_{s+1}) \cdot \mathbf{E}(\mathbf{r}_{s+1})]. \qquad (4.29)$$

The equation (4.29) is the primary result of the analysis. It shows that the expression for $n_1(\mathbf{E}_0)$ in terms of the macroscopic electric field $\mathbf{E}$ is simpler than the expression in terms of the external electric field $\mathbf{E}_0$. Within our model defined by the potential energy $U(\mathbf{r}^N, \omega^N; \mathbf{E}_0)$ Eq. (4.29) is valid in all orders in the field. In real systems the effects of higher orders in the field than the first few orders are usually negligible. For fields which are strong enough to cause electrical breakdown the potential energy Eq. (4.1) does not provide a reasonable description of the system. The important fact illustrated by Eq. (4.29) is that one may understand how the particles are aligned and distributed more easily by considering the macroscopic electric field rather than the external electric field.

If we use that $H_{s+1}^{(0)}$ has a microscopic range, and assume that the macroscopic field $\mathbf{E}(\mathbf{r})$ does not vary appreciably over the range of $H_{s+1}^{(0)}$, then the field $\mathbf{E}(\mathbf{r}_i)$ may be replaced by $\mathbf{E}(\mathbf{r})$ in Eq. (4.29). The integrations over positions may be extended over all space and thus we find

$$n_1(\mathbf{r}, \omega; \mathbf{E}_0) = \frac{\rho}{\Omega} \left[ 1 + \sum_{s=1}^{\infty} \frac{\beta^s}{s!} \mathsf{M}^{(s)}(\omega) \odot (\mathbf{E}(\mathbf{r}))^s \right] \qquad (4.30)$$

where $\mathsf{M}^{(s)}(\omega)$ is a tensor of the $s$th rank, fixed to the molecular orientation $\omega$, and defined by

$$\frac{\rho}{\Omega} \mathsf{M}^{(s)}(\omega) = \int_V d(1) d(2) \cdots d(s+1) H_{s+1}^{(0)} (12 - \delta + 1)$$

$$\times \delta(\mathbf{r}, \omega; \mathbf{r}_1, \omega_1) \mathbf{\mu}(\omega_2) \mathbf{\mu}(\omega_3) \cdots \mathbf{\mu}(\omega_{s+1}). \qquad (4.31)$$

The product $\odot$ is an inner product between two tensors of the rank $s$. The product $(\mathbf{E}(\mathbf{r}))^s$ is to be understood as a tensor of the rank $s$.

We obtain an expression for $\mathbf{P}_V(\mathbf{r})$ in terms of the macroscopic field $\mathbf{E}(\mathbf{r})$. It follows from Eqs. (4.4) and (4.30) that

$$\mathbf{P}_V(\mathbf{r}) = \sum_{s=0}^{\infty} \mathsf{X}^{(2s+1)} \odot (\mathbf{E}(\mathbf{r}))^{2s+1} \qquad (4.32)$$

where $\mathsf{X}^{(2s+1)}$ is a tensor of the even rank $(2s+2)$, defined by

$$\mathsf{X}^{(2s+1)} = \frac{\beta^{2s+1}}{(2s+1)!} \frac{\rho}{\Omega} \int d\omega \mathbf{\mu}(\omega) \mathsf{M}^{(2s+1)}(\omega). \qquad (4.33)$$

Only the even rank tensors $\mathsf{X}^{(2s+1)}$ appear in Eq. (4.32), because by definition $\mathsf{X}^{(s)}$ is isotropic and symmetric

for fluid systems. The tensors $\mathsf{X}^{(2s+1)}$ are independent of $\mathbf{r}$ and independent of the sample shape and the surroundings. We conclude from Eq. (4.32) that the polarization is a local position-independent function of the macroscopic field, which may be expressed as

$$\mathbf{P}_V(\mathbf{r}) = \{\epsilon[\mathbf{E}(\mathbf{r})] - 1/4\pi\} \mathbf{E}(\mathbf{r}). \qquad (4.34)$$

The functional form of the dielectric constant $\epsilon[\mathbf{E}(\mathbf{r})]$ is defined by comparison of Eq. (4.34) with (4.32), and this functional form is independent of sample shape and surroundings.

We note that to first order in $\mathbf{E}$

$$n_1(\mathbf{r}, \omega; \mathbf{E}_0) = (\rho/\Omega)[1 + \beta\mathbf{\mu}_{\mathrm{eff}}(\omega) \cdot \mathbf{E}(\mathbf{r})], \qquad (4.35)$$

where $\mathbf{\mu}_{\mathrm{eff}} = \mathsf{M}^{(1)}$ is defined in Eq. (4.31), or equivalently by Eq. (3.6). Equation (4.35) is completely consistent with the low-field results obtained in I.

Finally, we make a few remarks about the electric field contribution to the Helmholtz free energy $A$ of the sample. We define the configurational partition function $Z(\mathbf{E}_0)$ by

$$Z(\mathbf{E}_0) = [1/(V\Omega)^N] \int d\mathbf{r}^N d\omega^N \exp[-\beta U(\mathbf{r}^N, \omega^N; \mathbf{E}_0)] \qquad (4.36)$$

and the configurational free energy is equal to

$$A(\mathbf{E}_0) = -(1/\beta) \ln Z(\mathbf{E}_0). \qquad (4.37)$$

The polarization $\mathbf{P}_V(\mathbf{r})$ of the sample is given by the functional derivative of $A$ with respect to the external field

$$\mathbf{P}_V(\mathbf{r}) = -\delta A(\mathbf{E}_0)/\delta \mathbf{E}_0(\mathbf{r}), \qquad (4.38)$$

as one verifies by using the expression (4.1) for the potential energy. Integration of this equation leads to

$$A(\mathbf{E}_0) - A(0) = -\int_V d\mathbf{r} \int_0^{\mathbf{E}_0(\mathbf{r})} \delta \mathbf{E}_0(\mathbf{r}) \cdot \mathbf{P}_V(\mathbf{r}), \qquad (4.39)$$

where the polarization $\mathbf{P}_V$ is a functional of the external field $\mathbf{E}_0(\mathbf{r})$. Equation (4.39) suggests that

$$-\int_0^{\mathbf{E}_0(\mathbf{r})} \delta \mathbf{E}_0(\mathbf{r}) \cdot \mathbf{P}_V(\mathbf{r}) \qquad (4.40)$$

may be thought of as the density of free energy in the sample. This free energy density appears to be a function of the local external field rather than of the local macroscopic field. However, one should realize that,

although $P_V(\mathbf{r})$ is determined by $\mathbf{E}$ at $\mathbf{r}$, it is not determined by $\mathbf{E}_0$ at $\mathbf{r}$ only since the relation between $\mathbf{E}(\mathbf{r})$ and $\mathbf{E}_0(\mathbf{r}')$ is nonlocal [see Eq. (4.5)]. A more common expression for the free energy density is in terms of the macroscopic electric field[10-12]

$$(4\pi)^{-1} \int_0^{\mathbf{D}(\mathbf{r})} \delta\mathbf{D}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r}), \qquad (4.41)$$

where the dielectric displacement $\mathbf{D}$ is defined by

$$\mathbf{D}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + 4\pi\mathbf{P}(\mathbf{r}). \qquad (4.42)$$

It is not hard to establish the relationship between the expression (4.41) for the free energy density and the expression (4.40), which follows from the statistical-mechanical formalism. By using methods similar to those employed by Jackson[13] one may show that

$$-\int_V d\mathbf{r}\mathbf{P}_V(\mathbf{r})\cdot\delta\mathbf{E}_0(\mathbf{r}) = (4\pi)^{-1}\int d\mathbf{r}\mathbf{E}(\mathbf{r})\cdot\delta\mathbf{D}(\mathbf{r})$$

$$-(4\pi)^{-1}\int d\mathbf{r}\mathbf{E}_0(\mathbf{r})\cdot\delta\mathbf{D}_0(\mathbf{r}). \quad (4.43)$$

The displacement $\mathbf{D}_0$ is the form appropriate in the absence of the molecular medium in $V$. Inside the surrounding medium $W$ the displacement $\mathbf{D}_0$ is different from $\mathbf{E}_0$, because of the polarization in $W$. We emphasize that in the right-hand side of Eq. (4.43) the position integrations are performed *over the entire space*, whereas in the left-hand side the integration is performed *over the volume $V$ only*. The differentials $\delta\mathbf{D}(\mathbf{r})$ and $\delta\mathbf{D}_0(\mathbf{r})$ in Eq. (4.43) correspond to the differential $\delta\mathbf{E}_0(\mathbf{r})$. The identity (4.43) shows that if one uses Eq. (4.41) as the expression for the free energy density, one has to realize that also outside $V$ there may be a non-zero free energy density, which has to be taken into account. Substitution of Eq. (4.43) in (4.39) shows that the field-contribution to the Helmholtz free energy is equal to the difference between the total macroscopic field energy in the presence of the medium in $V$ and the total field energy in the absence of the medium in $V$.

$$A(\mathbf{E}_0) - A(0) = (4\pi)^{-1}\int d\mathbf{r}\int_0^{\mathbf{D}(\mathbf{r})}\delta\mathbf{D}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})$$

$$-(4\pi)^{-1}\int d\mathbf{r}\int_0^{\mathbf{D}_0(\mathbf{r})}\delta\mathbf{D}_0(\mathbf{r})\cdot\mathbf{E}_0(\mathbf{r}). \quad (4.44)$$

In the special case that the relation between $\mathbf{P}_V$ and $E$ is linear, we obtain the result

$$A(\mathbf{E}_0) - A(0) = -\frac{1}{2}\int_V d\mathbf{r}\mathbf{E}_0(\mathbf{r})\cdot\mathbf{P}_V(\mathbf{r})$$

$$= (8\pi)^{-1}\int d\mathbf{r}\mathbf{D}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})$$

$$-(8\pi)^{-1}\int d\mathbf{r}\mathbf{D}_0(\mathbf{r})\cdot\mathbf{E}_0(\mathbf{r}). \quad (4.45)$$

In the general case that we take into account nonlinear

terms it is not possible to perform the functional integration in Eqs. (4.39) and (4.44) in such a simple way.

## CONCLUSIONS

In this paper we have extended our molecular theory of polar fluids in two directions. First we have obtained expressions for the potential of mean force at large separations for two impurities which may be either a charge, dipole or quadrupole in the polar fluid. The impurities and the solvent dipoles interact by arbitrary short-range pair potentials in addition to their electrostatic interaction. The important result is that the potential of mean force for large separation obtained from the molecular theory is the same as the interaction energy obtained from macroscopic electrostatics when the supporting polar fluid is treated as dielectric continuum, except that the impurity dipole and quadrupole are replaced by effective dipoles. The dielectric constant of the polar fluid determined in this way is the same as the dielectric constant found in I from the polarization of the polar fluid in an external electric field. The effective dipoles arise around the impurity dipoles and quadrupoles because the short-range impurity–solvent dipole interactions may cause local polarization of the surrounding fluid. Of course, the potential of mean force determined for two impurities will depend on the shape of the sample and the surroundings, as expected from the macroscopic theory.

Our analysis of the two impurities may be extended in a number of interesting ways. First we could consider the case of impurities that must be characterized by more than one multipole moment, e.g., ions which have appreciable dipole moments. Second it would be interesting to consider the case of three impurities, in an analysis similar to the one undertaken here and in II for the three-particle correlation function of pure polar fluids. One could determine whether the molecular theory predicts a three-particle potential of mean force which is not the sum of the two-particle potentials of mean force. Third in our analysis the effective dipole moment of an impurity $\mu_{a,\text{eff}}$ is only formally determined. We consider it likely that $\mu_{a,\text{eff}}$ can be determined from low concentration dielectric measurements of mixtures of the dipolar impurity and the polar solvent. Finally, our considerations may be extended to impurities in the dipolar medium in the presence of external fields.

The second problem we have considered in this article concerns dielectric saturation in the pure polar fluid. We have extended our previous analysis of the polarization induced in the molecular polar fluid beyond the term linear in the external field. The major part of the analysis is concerned with obtaining an expression for the one-particle distribution function in the presence of the field, which determines both the polarization and the average macroscopic electric field. We have demonstrated the important result that this one-particle distribution function has a simple form when it is expressed

in terms of the local macroscopic electric field and not the external field. The resulting polarization is shown to be a local, geometry-independent function of the macroscopic electric field.

The expression for the one-particle distribution function to terms linear in the macroscopic field $\mathbf{E}$ is

$$n_1(\mathbf{r}, \boldsymbol{\omega}; \mathbf{E}_0) = (\rho/\Omega)[1 + \beta\boldsymbol{\mu}_{\mathrm{eff}}(\boldsymbol{\omega}) \cdot \mathbf{E}(\mathbf{r})], \quad (4.35)$$

but higher order terms in $\mathbf{E}$ are not properly obtained from the exponentiated form of this linear result.

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# Infrared Emission at 2.7 $\mu$m from Flowing $CO_2$–$N_2$* Mixtures

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A flow tube has been constructed wherein ground-state $CO_2$ and vibrationally excited $N_2$ molecular streams interact and the combined flow is spectrally investigated at selected downstream stations. The close coupling between the lower vibrational levels of $N_2(X {}^1\Sigma_g{}^+)$ and the $CO_2$ asymmetric stretch mode $(00°v_3)$ allows rapid energy exchange to these levels, followed by internal redistribution among the vibrational states of the various $CO_2$ modes. When emission at the 2.7-$\mu$m bands is monitored, it has been observed that such redistribution produces substantial population of the mixed-mode levels associated with this radiation. Comparison of the observed band profiles with analytically derived counterparts has indicated that for an $N_2$ vibrational temperature of 1900°K, $CO_2$ difference bands at 2.7 $\mu$m contribute approximately 2.5 times as much radiant energy as is emitted in the 10°1–00°0 and 02°1–00°0 summation bands.

## I. INTRODUCTION

The rate of vibrational energy exchange between the 00°1 level of the asymmetric stretch mode of $CO_2$ and the first vibrational level of $N_2$ has been examined by several investigators.[1-3] For molecular translational temperatures below 2000°K, the corresponding rate coefficient lies between $10^{-13}$ and $10^{-12}$ $cm^3$ $sec^{-1}$. Similarly, the near resonance between higher levels of this $CO_2$ mode with corresponding $N_2$ states also allows additional energy exchange between these molecules. The appropriate vibrational level diagram for $N_2$–$CO_2$ energy transfer is shown in Fig. 1. Band intensity measurements for $N_2$ vibrational temperatures below 1400°K have indicated that such transferred energy, redistributed internally among the various states of $CO_2$, produces substantial radiation in the 2.7-$\mu$m spectral region.[4] We have extended these measurements to higher vibrational temperatures and have spectrally resolved the 2.7-$\mu$m band profiles.

At relatively low $N_2$ excitation levels, one would expect the summation bands at 2.7 $\mu$m to represent the major portion of the observed radiation. The intensities of such bands depend on the degree of population of the $CO_2$ Fermi resonance, mixed-mode 10°1 and 02°1 levels. As the $N_2$ is increasingly energized, the difference bands (Fig. 1) associated with higher-lying Fermi resonance states will raise the intensity and alter the observed emission profiles. The summation and lower difference bands in the 2.7-$\mu$m spectral region, together with their band-center wavelengths as calculated from the data of Refs. 5–7, are presented in Table I.

## II. EXPERIMENTAL PROCEDURE

The flow-mixing operation and the subsequent radiation emission are shown in Fig. 2. The infrared radiation emitted at 2.7 $\mu$m was measured at selected locations along a flow tube in order to determine the rate of population of the 10°1 and 02°1 levels of $CO_2$. A primary flow of $N_2$ was vibrationally excited within a quartz tube by an S-band generator. The associated vibrational temperature was monitored as a trace amount of CO was injected into the $N_2$* stream. $CO_2$