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Structure of Dielectric Fluids. I. The Two-Particle Distribution Function of Polar Fluids*

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A molecular fluid of identical molecules with a rigid dipole moment in an arbitrarily shaped volume is considered. The volume may or may not be embedded in a dielectric continuum. It is shown that when an arbitrary external field is applied, the constitutive relation $\mathbf{P}=(\epsilon-1)/4\pi\mathbf{E}$ between the local polarization and the local macroscopic electric field is valid under some completely acceptable restrictions. In the establishment of this relation a crucial role is played by a long-range part of the two-particle correlation function, for which an explicit expression is obtained. One term in this long-range part is explicitly dependent on the shape of the sample volume and on the surroundings. The resulting dielectric constant of the molecular fluid can be formally expressed in only the local interactions of the molecules and is thus independent of the surroundings and the shape of the sample.

I. INTRODUCTION

The molecular statistical mechanical theory of static dielectric polarization has been extensively studied by several authors.[1–7] These derivations lead to molecular expressions for the static dielectric constant for systems of molecules which have a permanent dipole moment, a polarizability, or both. A common preliminary assumption in these theories is that the static dielectric constant of the molecular medium is really a constant, i.e., the polarization in the molecular sample is proportional to the macroscopic electric field, and the proportionality constant is the same for any shape of the sample and, in the absence of saturation, for any spatially varying external electric field. Once this assumption is accepted, in order to find a molecular expression for the dielectric constant it is clearly sufficient to consider just one specific situation, with a specific shape of the sample and a specific external field. In fact, it has been customary to perform the derivation for the special case of a spherical sample in a homogeneous external field. The resulting expressions for the dielectric constant contain integrations over the whole volume.

However, a statistical mechanical theory of dielectric polarization cannot be considered as complete, unless it has been shown that an arbitrary external field acting on an arbitrarily shaped sample of the molecular medium with arbitrary surroundings yields a polarization inside the medium which is proportional to the local macroscopic electric field. This property of the polarization suggests that it must be possible to express the dielectric constant in terms of the interactions of a molecule with its neighbors on microscopic distances only.

In the present paper we develop a molecular theory of dielectric polarization without using the preliminary assumption mentioned above. By starting from the statistical mechanical expression for the polarization of an arbitrarily shaped system in an arbitrary static external field, we shall prove that the polarization is proportional to the local macroscopic electric field, apart from some minor and completely acceptable restrictions. The external electric field $\mathbf{E}_0(\mathbf{r})$ is defined as the electric field *in the absence of the molecular medium.* If we bring a molecular sample with an arbitrarily shaped volume V into this field, the total electric field is modified because of the resulting polarization in V. The Hamiltonian is expressed in terms of the external field $\mathbf{E}_0(\mathbf{r})$. Therefore a general statistical mechanical theory leads in a natural way to an expression for the polarization $\mathbf{P}(\mathbf{r})$ in terms of the external field $\mathbf{E}_0(\mathbf{r})$. If we take into consideration the linear term in $\mathbf{E}_0$ only, the expression takes the form

$$\mathbf{P}(\mathbf{r})=\int_V d\mathbf{r}'\mathsf{A}(\mathbf{r},\mathbf{r}')\cdot\mathbf{E}_0(\mathbf{r}'), \qquad (1.1)$$

where $\mathsf{A}(\mathbf{r},\mathbf{r}')$ is an ensemble average of the molecular sample in the absence of the external field. Now we

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want to prove that the relation (1.1) leads with acceptable approximations to a simple proportionality relation

$$\mathbf{P}(\mathbf{r})=\chi\mathbf{E}(\mathbf{r}), \qquad \text{if } \mathbf{r} \text{ in } V, \tag{1.2}$$

between the polarization and the resulting macroscopic electric field $\mathbf{E}(\mathbf{r})$. Equation (1.2) is the well-known basic constitutive relation of the macroscopic theory of dielectrics. The constant χ, which is called the dielectric susceptibility, is related to the dielectric constant ϵ by the simple formula

$$\chi=(\epsilon-1)/4\pi. \tag{1.3}$$

In the present paper we consider a system of molecules with a permanent dipole moment, but with zero polarizability. The extension of the theory to include polarizable molecules will be given in a subsequent paper.

We find from either the macroscopic theory or the microscopic theory that the relation between $\mathbf{P}(\mathbf{r})$ and $\mathbf{E}_0(\mathbf{r})$ is shape dependent and depends upon the nature of the surroundings. On the other hand, the constant of proportionality χ between $\mathbf{P}(\mathbf{r})$ and the macroscopic field $\mathbf{E}(\mathbf{r})$ is independent of sample shape and surroundings. This difference is a manifestation of the long-range nature of the dipole–dipole interaction. There are other important consequences of this long-range nature. For example, it is well known[2,8] from calculation of the polarization of a sphere in a homogeneous external field that

$$\begin{aligned}(\epsilon-1)/4\pi&=\tfrac{1}{3}(\epsilon+2)\tfrac{1}{3}(\beta\rho\mu^2)[1+(N-1)\langle\cos\gamma_{12}\rangle_0]\\&=\tfrac{1}{3}(\epsilon+2)(\beta/3V)\langle\mathbf{M}^2\rangle_0\end{aligned} \tag{1.4}$$

for a system of polar molecules with zero polarizability. Here $\mathbf{M}$ is the total dipole moment of the molecular sample. N denotes the number of molecules, ρ is the particle density, μ is the absolute value of the permanent dipole moment of the particles. γ_{12} is the angle between the permanent dipole moments of molecule 1 and molecule 2. The averaging $\langle\ \rangle_0$ is over a canonical ensemble for a sphere of the molecular medium suspended in vacuum with external field zero. In the derivation of Eq. (1.4) it has been assumed that the molecular medium behaves as a dielectric with dielectric constant ϵ.

For a sphere of the same molecular medium embedded in a continuum fluid of its own dielectric constant an analogous calculation yields[2,8]

$$\begin{aligned}(\epsilon-1)/4\pi&=[3\epsilon/(2\epsilon+1)]\tfrac{1}{3}(\beta\rho\mu^2)[1+(N-1)\langle\cos\gamma_{12}\rangle_\infty]\\&=[3\epsilon/(2\epsilon+1)](\beta/3V)\langle\mathbf{M}^2\rangle_\infty.\end{aligned} \tag{1.5}$$

The averaging $\langle\ \rangle_\infty$ is over a canonical ensemble for a sphere of the molecular medium embedded in an infinite dielectric with the same dielectric constant. The derivations of Eqs. (1.4) and (1.5) are given in Sec. V.

If the dielectric constant of the molecular medium is independent of sample shape and surroundings, then a comparison of Eqs. (1.4) and (1.5) indicates that the equilibrium pair distribution function in the absence of the field must be different for these two cases.

The primary objective of this paper is to examine the behavior of the pair distribution function of a polar fluid. We shall demonstrate that the pair distribution function has a long-range part which depends on the sample shape and the surroundings. This long-range character of the pair distribution function is a consequence of the dipole–dipole interaction and precludes the use of the conventional techniques employed for the analysis of fluids where only short-range interactions are present. We wish to emphasize that the two-particle distribution function refers to the joint distribution of positions and orientations of two dipoles. The marginal distribution function of positions of the two dipoles is referred to as the "position pair distribution function." The position pair distribution function is obtained from the two-particle distribution function by integrating over the orientations of the two dipoles.

II. MACROSCOPIC THEORY OF DIELECTRICS

In this section we derive some exact results from the macroscopic theory of dielectrics, assuming the validity of the constitutive relation (1.2), where the dielectric susceptibility χ is related to the dielectric constant ϵ by (1.3).

We consider an electric field $\mathbf{E}_0(\mathbf{r})$ which is due to a fixed charge distribution, and we refer to $\mathbf{E}_0(\mathbf{r})$ as the external field. If a dielectric sample of arbitrary shape is introduced in the external field, a polarization $\mathbf{P}(\mathbf{r})$ is induced in the dielectric. The fixed charge distribution is unaffected by the change in the total field due to this polarization. The resulting total electric field $\mathbf{E}(\mathbf{r})$ can be readily expressed in terms of $\mathbf{E}_0(\mathbf{r})$ and $\mathbf{P}(\mathbf{r})$. We introduce the dipole tensor $\mathsf{T}(\mathbf{r},\mathbf{r}')$ by requiring that $\mathsf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{p}$ is the electric field at $\mathbf{r}$, due to a dipole $\mathbf{p}$ at $\mathbf{r}'$. Then clearly

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_0(\mathbf{r})+\int_V d\mathbf{r}'\mathsf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{P}(\mathbf{r}'), \tag{2.1}$$

where V is the volume of the dielectric. The dipole tensor is given by

$$\begin{aligned}\mathsf{T}(\mathbf{r},\mathbf{r}')&\equiv-\frac{\partial}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{r}'}|\mathbf{r}-\mathbf{r}'|^{-1}\\&=\frac{3(\mathbf{r}-\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^5}-\frac{\mathsf{U}}{|\mathbf{r}-\mathbf{r}'|^3},\end{aligned} \tag{2.2}$$

where U is the unit dyadic. The singularity in $\mathsf{T}(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}=\mathbf{r}'$ is not integrable in the mathematical sense. Hence, strictly speaking, Eq. (2.1) is defined only if $\mathbf{r}$ is not in V. An expression for $\mathbf{E}(\mathbf{r})$ which is also correct if $\mathbf{r}$ is in V is found by calculating the potential due to the polarization $\mathbf{P}(\mathbf{r})$ and taking the gradient. Thus we are led to

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_0(\mathbf{r})-\frac{\partial}{\partial\mathbf{r}}\int_V d\mathbf{r}'\mathbf{P}(\mathbf{r}')\cdot\frac{\partial}{\partial\mathbf{r}'}|\mathbf{r}-\mathbf{r}'|^{-1}. \tag{2.3}$$

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However, we will use Eq. (2.2) also for the case that $\mathbf{r}$ is in V. We incur no error provided that we calculate the integration over the singularity according to the rule

$$\int_{|\mathbf{r}'-\mathbf{r}|<\Delta} d\mathbf{r}'\mathsf{T}(\mathbf{r},\mathbf{r}') \equiv -\frac{\partial}{\partial \mathbf{r}}\int_{|\mathbf{r}'-\mathbf{r}|<\Delta} d\mathbf{r}'\frac{\partial}{\partial \mathbf{r}'}|\mathbf{r}-\mathbf{r}'|^{-1} = -\frac{4\pi}{3}\mathsf{U} \qquad (2.4)$$

for any distance Δ. For instance, the electric field due to a homogeneously polarized sphere with polarization $\mathbf{P}_0$ equals $-(4\pi/3)\mathbf{P}_0$ inside the sphere.

The validity of Eq. (2.1) does not depend on the constitutive relation (1.2). If we use the relation (1.2) for $\mathbf{r}$ in V, we find from (2.1)

$$\mathbf{P}(\mathbf{r}) = \frac{\epsilon-1}{4\pi}\left[\mathbf{E}_0(\mathbf{r}) + \int_V d\mathbf{r}'\mathsf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{P}(\mathbf{r}')\right], \quad \text{if } \mathbf{r} \text{ is in } V. \qquad (2.5)$$

Equation (2.5) gives us a relation between the polarization $\mathbf{P}(\mathbf{r})$ in the dielectric in V and the external field $\mathbf{E}_0(\mathbf{r})$ in the absence of the dielectric. It is easy to show that Eq. (2.5) implies the constitutive relation. Let us assume that we fill the volume V with a medium, without knowing whether or not this medium satisfies the local constitutive relation (1.2). Suppose that we find a resulting polarization $\mathbf{P}(\mathbf{r})$ in V which obeys the equation

$$\mathbf{P}(\mathbf{r}) = a\left[\mathbf{E}_0(\mathbf{r}) + \int_V d\mathbf{r}'\mathsf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{P}(\mathbf{r}')\right], \quad \text{if } \mathbf{r} \text{ is in } V. \qquad (2.6)$$

The form between brackets in Eq. (2.6) is known to be the total electric field $\mathbf{E}(\mathbf{r})$ according to (2.1). Hence it follows from (2.6) that the polarization obeys the equality $\mathbf{P}(\mathbf{r}) = a\mathbf{E}(\mathbf{r})$ in the medium. We shall use the equality (2.6) as a test whether or not a medium behaves as a dielectric in the presence of fixed external charges, according to Eq. (1.2).

We also wish to test the local constitutive relation (1.2) in the case that the sample in V is embedded in a dielectric. Therefore we consider the situation in which the external field $\mathbf{E}_0(\mathbf{r})$ is due to fixed external charges together with a dielectric in a volume W which satisfies by assumption Eq. (1.2) with a dielectric constant ϵ_0. The volumes V and W are assumed not to overlap. If we now bring into V a sample of a certain medium with a polarization $\mathbf{P}_V(\mathbf{r})$, the relation (2.1) between the field $\mathbf{E}_0(\mathbf{r})$ in the absence of the medium in V and the field $\mathbf{E}(\mathbf{r})$ in the presence of this medium does not hold. For now the polarization of the dielectric in W is modified by the electric field due to the polarization $\mathbf{P}_V(\mathbf{r})$ in V. In fact, from the point of view of the dielectric in W, the polarization in V serves as another external source. In order to find a relation between $\mathbf{E}(\mathbf{r})$ and $\mathbf{E}_0(\mathbf{r})$ for this case we consider the situation where the dielectric in W is present only. We take as external sources a fixed charge distribution $\mathfrak{q}_1(\mathbf{r})$. The resulting field is called $\mathbf{E}_1(\mathbf{r})$. This field is the solution of the static Maxwell equations

$$\mathrm{curl}\mathbf{E}_1(\mathbf{r}) = 0, \qquad (2.7\mathrm{a})$$

$$\mathrm{div}\mathbf{E}_1(\mathbf{r}) = 4\pi\mathfrak{q}_1(\mathbf{r}) - 4\pi\,\mathrm{div}\mathbf{P}_W(\mathbf{r}), \qquad (2.7\mathrm{b})$$

$$\mathbf{P}_W(\mathbf{r}) = [(\epsilon_0-1)/4\pi]\mathbf{E}_1(\mathbf{r}), \quad \text{if } \mathbf{r} \text{ is in } W, \qquad (2.7\mathrm{c})$$

where $\mathbf{P}_W(\mathbf{r})$ is the polarization inside W for this situation. Introducing the function $\epsilon_W(\mathbf{r})$ by

$$\begin{aligned}\epsilon_W(\mathbf{r}) &= \epsilon_0, && \text{if } \mathbf{r} \text{ is in } W,\\ \epsilon_W(\mathbf{r}) &= 1, && \text{if } \mathbf{r} \text{ is not in } W,\end{aligned} \qquad (2.8)$$

we may write the Maxwell equations

$$\begin{aligned}\mathrm{curl}\mathbf{E}_1(\mathbf{r}) &= 0,\\ \mathrm{div}\epsilon_W(\mathbf{r})\mathbf{E}_1(\mathbf{r}) &= 4\pi\mathfrak{q}_1(\mathbf{r}).\end{aligned} \qquad (2.9)$$

It follows that the electric field in the case of an external charge distribution $\mathfrak{q}_1(\mathbf{r})+\mathfrak{q}_2(\mathbf{r})$ is equal to $\mathbf{E}_1(\mathbf{r})+\mathbf{E}_2(\mathbf{r})$, where $\mathbf{E}_2(\mathbf{r})$ is the field to which an external charge distribution $\mathfrak{q}_2(\mathbf{r})$ gives rise. The electric field is a linear functional of the external sources. Because of the constitutive relation (2.7c) the same holds for the dielectric polarization in W. The (unknown) polarization $\mathbf{P}_V(\mathbf{r})$ in V may be treated as an external field source. Using the linear dependence of the field on the sources, we may write

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \mathbf{E}_{P_V}(\mathbf{r}), \qquad (2.10)$$

where $\mathbf{E}_{P_V}(\mathbf{r})$ is the electric field in the case that the dielectric in W and the polarization $\mathbf{P}_V(\mathbf{r})$ in V are present, but the fixed external charges are absent. Thus for a sample V with polarization $\mathbf{P}_V(\mathbf{r})$ embedded in a dielectric in the presence of fixed external charges the macroscopic field is the sum of the field $\mathbf{E}_0(\mathbf{r})$ in the absence of $\mathbf{P}_V(\mathbf{r})$ and the field $\mathbf{E}_{P_V}(\mathbf{r})$ arising from $\mathbf{P}_V(\mathbf{r})$ and the surrounding dielectric in the absence of the fixed external charges.

Next we find an expression for $\mathbf{E}_{P_V}(\mathbf{r})$ in terms of $\mathbf{P}_V$. We introduce the tensor $\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)$ by considering the situation where we have the dielectric in W. The volume V is empty and there are no external charges. If we put a dipole $\mathbf{p}$ at a point $\mathbf{r}'$, the resulting field $\mathbf{E}_p(\mathbf{r})$ is linear in $\mathbf{p}$. The tensor R_W is defined by

$$\mathbf{E}_p(\mathbf{r}) = \mathsf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{p} + \mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)\cdot\mathbf{p}. \qquad (2.11)$$

Thus $\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)\cdot\mathbf{p}$ is the field due to the polarization of the dielectric with dielectric constant ϵ_0 in W, if this polarization is caused by the presence of the dipole $\mathbf{p}$. We call $\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)$ the reaction field tensor. For a polarization density $\mathbf{P}_V(\mathbf{r})$ in V, we have

$$\mathbf{E}_{P_V}(\mathbf{r}) = \int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}') + \mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)]\cdot\mathbf{P}_V(\mathbf{r}'), \qquad (2.12)$$

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and it follows that Eq. (2.10) may be written as

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_0(\mathbf{r})+\int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)]\cdot\mathbf{P}_V(\mathbf{r}'). \tag{2.13}$$

This equation is the generalization of Eq. (2.1) for the case that the external field $\mathbf{E}_0(\mathbf{r})$, in the absence of the sample in V, is due to fixed external charges together with a dielectric in W.

The derivation of (2.13) does not depend on the assumption that the sample in V is a dielectric for which the constitutive relation (1.2) holds. If we assume Eq. (1.2) and use

$$\mathbf{P}_V(\mathbf{r})=[(\epsilon-1)/4\pi]\mathbf{E}(\mathbf{r}),\qquad \text{if } \mathbf{r} \text{ is in } V, \tag{2.14}$$

we find from (2.13)

$$\mathbf{P}_V(\mathbf{r})=\frac{\epsilon-1}{4\pi}\left\{\mathbf{E}_0(\mathbf{r})+\int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)]\cdot\mathbf{P}_V(\mathbf{r}')\right\},\qquad \text{if } \mathbf{r} \text{ is in } V, \tag{2.15}$$

and

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_0(\mathbf{r})+(\epsilon-1)/4\pi\int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)]\cdot\mathbf{E}(\mathbf{r}'). \tag{2.16}$$

One notices that the relation

$$\mathbf{P}_V(\mathbf{r})=a\left\{\mathbf{E}_0(\mathbf{r})+\int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)]\cdot\mathbf{P}_V(\mathbf{r}')\right\},\qquad \text{if } \mathbf{r} \text{ is in } V, \tag{2.17}$$

is equivalent with the constitutive relation $\mathbf{P}_V(\mathbf{r})=a\mathbf{E}(\mathbf{r})$ for the sample. Consequently Eq. (2.17) may serve as a test whether a molecular medium in V in the presence of a dielectric in W and fixed external charges does or does not behave as a local dielectric satisfying (2.14). In the special case that W is zero or $\epsilon_0=1$, the tensor $\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)$ is zero, and Eq. (2.13) reduces to (2.1), (2.15) to (2.5) and (2.17) to (2.6).

In the special case that $\epsilon_0=\epsilon$, we can find the solution of Eq. (2.16). One knows that the electric field $\mathbf{E}(\mathbf{r})$ in any system of dielectrics and fixed charges $q(\mathbf{r})$ obeys the Maxwell equations

$$\operatorname{curl}\mathbf{E}(\mathbf{r})=0,$$

$$\operatorname{div}\epsilon(\mathbf{r})\mathbf{E}(\mathbf{r})=4\pi q(\mathbf{r}), \tag{2.18}$$

where $\epsilon(\mathbf{r})$ has the value of the dielectric constant at $\mathbf{r}$. It follows that a solution $\mathbf{E}(\mathbf{r})$ of the Maxwell Eqs. (2.18) remains a solution if we multiply the dielectric constant everywhere with the same constant c, provided that we replace the charge distribution $q(\mathbf{r})$ by $cq(\mathbf{r})$.

We use this property of Maxwell's equations in two cases. In case I the sample V and the surrounding region W are filled with a dielectric with local dielectric constant ϵ. When we multiply the dielectric constant everywhere and the external sources with ϵ^{-1}, we arrive at a situation I′ where V and W are empty, i.e., a region of vacuum with dielectric constant unity, and the external region has a dielectric constant ϵ^{-1}. In case II the sample V is empty, and the region W is filled with a dielectric with dielectric constant ϵ. When we multiply the dielectric constant everywhere and the external charges with ϵ^{-1}, we arrive at the situation II′ where W is empty, i.e., its dielectric constant is unity, and the sample V and the external region have a dielectric constant ϵ^{-1}. These situations are illustrated in Fig. 1.

Recall that the field arising from fixed charges for case II is $\mathbf{E}_0(\mathbf{r})$ and the field arising from the same fixed charges in case I is $\mathbf{E}(\mathbf{r})$. These two fields are related by Eq. (2.16). We define $\mathbf{E}_0'(\mathbf{r})$ to be the field arising from the same fixed charges (multiplied by ϵ^{-1}) in case I′. The field arising in case II′ from the same fixed charges (multiplied by ϵ^{-1}) is defined to be $\mathbf{E}'(\mathbf{r})$. The same reasoning that led to Eq. (2.16) yields the relation

$$\mathbf{E}'(\mathbf{r})=\mathbf{E}_0'(\mathbf{r})+\left(\frac{\epsilon^{-1}-1}{4\pi}\right)\int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})]\cdot\mathbf{E}'(\mathbf{r}'). \tag{2.19}$$

In this case $\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})\cdot\mathbf{p}$ is the reaction field at $\mathbf{r}$ arising from the polarization induced in the region external to $(V+W)$ of dielectric constant ϵ^{-1} by a dipole $\mathbf{p}$ at $\mathbf{r}'$.

The property of the Maxwell equations discussed above leads to the conclusion that

$$\mathbf{E}_0(\mathbf{r})=\mathbf{E}'(\mathbf{r}) \tag{2.20}$$

and

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_0'(\mathbf{r}). \tag{2.21}$$

Hence, we find the relation between the fields $\mathbf{E}_0(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$

$$\mathbf{E}_0(\mathbf{r})=\mathbf{E}(\mathbf{r})+\left(\frac{\epsilon^{-1}-1}{4\pi}\right)\int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})]\cdot\mathbf{E}_0(\mathbf{r}'), \tag{2.22}$$

which is an explicit expression for $\mathbf{E}(\mathbf{r})$ in terms of $\mathbf{E}_0(\mathbf{r})$ in the case that $\epsilon_0=\epsilon$. This relation is important because it provides a relation between $\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon)$ and $\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})$ which we shall have occasion to employ in the microscopic theory. If Eq. (2.22) is used to substitute for $\mathbf{E}(\mathbf{r})$ in Eq. (2.16) for the case $\epsilon_0=\epsilon$, we obtain a relation in terms of $\mathbf{E}_0(\mathbf{r})$ which in the macroscopic theory is valid for arbitrary $\mathbf{E}_0(\mathbf{r})$. It follows that

$$\begin{aligned}\epsilon^{-1}[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})]&=[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon)]\\&+\frac{\epsilon-1}{4\pi}\int_V d\mathbf{r}''[\mathsf{T}(\mathbf{r},\mathbf{r}'')+\mathsf{R}_W(\mathbf{r},\mathbf{r}'';\epsilon)]\\&\cdot\epsilon^{-1}[\mathsf{T}(\mathbf{r}'',\mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r}'',\mathbf{r}';\epsilon^{-1})].\end{aligned} \tag{2.23}$$

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Although it shall not be necessary to our further development, we give the expression for $\mathbf{P}_V(\mathbf{r})$ which follows from (2.22)

$$\mathbf{P}_V(\mathbf{r})=\frac{\epsilon-1}{4\pi}\mathbf{E}_0(\mathbf{r})+\frac{(\epsilon-1)^2}{16\pi^2\epsilon}\int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})]\cdot\mathbf{E}_0(\mathbf{r}'),\quad \text{if } \mathbf{r} \text{ is in } V, \tag{2.24}$$

which is the solution of Eq. (2.15) in the case that $\epsilon_0=\epsilon$. In the special case that the region W is not present, one obtains the relation

$$\mathbf{P}_V(\mathbf{r})=\frac{\epsilon-1}{4\pi}\mathbf{E}_0(\mathbf{r})+\frac{(\epsilon-1)^2}{16\pi^2\epsilon}\int_V d\mathbf{r}'[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_V{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})]\cdot\mathbf{E}_0(\mathbf{r}'),\quad \text{if } \mathbf{r} \text{ is in } V, \tag{2.25}$$

which is the solution of Eq. (2.5).

In these macroscopic considerations we assumed the existence of a local dielectric constant in V according to the relation (1.2) or equivalently (2.14). The microscopic theory will result in an expression for the polarization $\mathbf{P}_V(\mathbf{r})$ in the form of Eq. (1.1). In the linear region, this expression is valid for arbitrary spatially varying $\mathbf{E}_0(\mathbf{r})$. If the macroscopic expression for $\mathbf{P}_V(\mathbf{r})$ (2.24) is valid for arbitrary spatially varying $\mathbf{E}_0(\mathbf{r})$ a necessary consequence is that the molecular expression for $\mathsf{A}(\mathbf{r},\mathbf{r}')$ be

$$\mathsf{A}(\mathbf{r},\mathbf{r}')=[(\epsilon-1)/4\pi]\mathsf{U}\delta(\mathbf{r}-\mathbf{r}')+[(\epsilon-1)^2/16\pi^2\epsilon]\times[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})] \tag{2.26}$$

when the medium in W has dielectric constant ϵ. Our molecular considerations show that A cannot be exactly expressed in the form of Eq. (2.26). It follows that Eq. (2.24) cannot be correct for arbitrary spatially varying $\mathbf{E}_0(\mathbf{r})$, which in turn implies that the constitutive relation (2.14) cannot be correct for arbitrary $\mathbf{E}_0(\mathbf{r})$. However, we will show that, for cases where $\mathbf{E}_0(\mathbf{r})$ does not vary sharply over microscopic distances, the macroscopic expression (2.17) and the microscopic expression (1.1) are consistent. The form of $\mathsf{A}(\mathbf{r},\mathbf{r}')$ will differ significantly from Eq. (2.26) for small separations.

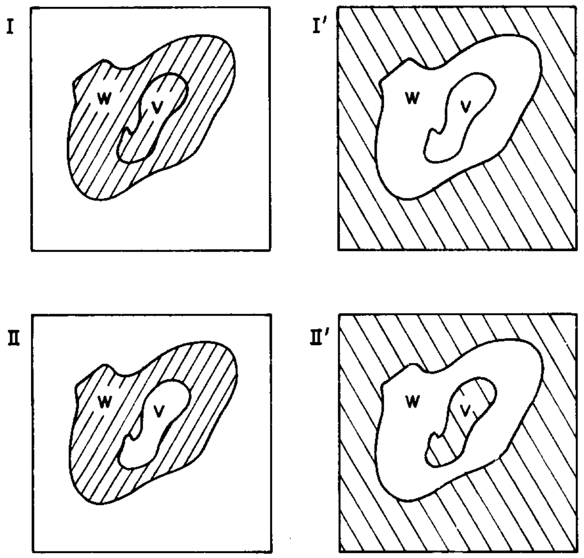

FIG. 1. Illustrative dielectric geometries. Shadings leaning to the right indicate regions with dielectric constant ϵ; shadings leaning to the left indicate regions with dielectric constant ϵ^{-1}. Blank regions have dielectric constant 1. Case I′ is the inverse of I and case II′ is the inverse of II.

III. THE MICROSCOPIC THEORY

Our molecular considerations begin with consideration of a sample of volume V and of arbitrary shape filled with N identical molecules with a permanent dipole moment $\boldsymbol{\mu}$. Surrounding the sample is an arbitrary region of volume W which consists of a macroscopic dielectric continuum with dielectric constant ϵ_0. In the presence of an external field $\mathbf{E}_0(\mathbf{r})$ arising from fixed external charges the potential energy of the molecular sample may be expressed as

$$U(\mathbf{r}^N,\boldsymbol{\omega}^N;\mathbf{E}_0)=V_0(\mathbf{r}^N,\boldsymbol{\omega}^N)-\sum_{i<j}^{N}\sum\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{T}(\mathbf{r}_i,\mathbf{r}_j)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)-\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{R}_W(\mathbf{r}_i,\mathbf{r}_j;\epsilon_0)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)-\sum_{i=1}^{N}\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathbf{E}_0(\mathbf{r}_i), \tag{3.1}$$

if we neglect radiation and retardation effects. Here the first term denotes the short-range interactions between the N molecules. We assume that V_0 consists of pair interactions only

$$V_0(\mathbf{r}^N,\boldsymbol{\omega}^N)=\sum_{i<j}^{N}\sum v(\mathbf{r}_i,\boldsymbol{\omega}_i;\mathbf{r}_j,\boldsymbol{\omega}_j). \tag{3.2}$$

The second term in U is the dipole–dipole interaction between the molecules in the sample with T the dipole–dipole tensor given in Eq. (2.2). The position of particle i is $\mathbf{r}_i$, and the orientation is denoted by the set of Euler angles $\boldsymbol{\omega}_i$. The third term in U is the interaction energy between each dipole in the sample and the reaction field arising from the surrounding dielectric continuum in W. According to Eq. (2.11) each dipole leads to a field at $\mathbf{r}$ arising from the region W of the form $\mathsf{R}_W(\mathbf{r},\mathbf{r}_i;\epsilon_0)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_i)$, which gives rise to a total interaction energy of the form of this third term. The simple form of this term results from the assumption that the region W is filled with a macroscopic dielectric continuum. If the surrounding W were treated as a molecular medium the direct molecular dipole–dipole interactions between the two regions and within W would have to be explicitly considered. Roughly speaking, treating W as a macroscopic dielectric corresponds to ignoring molecular fluctuations in W. We do not prove that these fluctuations may be ignored. The last term in U, Eq. (3.1), consists of the direct interactions

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between the dipoles and the external field $\mathbf{E}_0(\mathbf{r})$. This field $\mathbf{E}_0(\mathbf{r})$ is the electric field due to fixed external charges in the absence of the molecular sample V, but in the presence of the surrounding dielectric in W.

The polarization $\mathbf{P}_V(\mathbf{r})$ at the point $\mathbf{r}$ within the region V is given by

$$\mathbf{P}_V(\mathbf{r}) = \langle \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i)\, \boldsymbol{\mu}(\boldsymbol{\omega}_i) \rangle \tag{3.3}$$

where the bracket denotes an average over the canonical ensemble coordinate space distribution function

$$f(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0) = \exp[-\beta U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0)] \times \left(\int_V d\mathbf{r}^N d\boldsymbol{\omega}^N \exp[-\beta U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0)] \right)^{-1}. \tag{3.4}$$

It is an easy matter to show that up to terms linear in $\mathbf{E}_0(\mathbf{r})$ the polarization is

$$\mathbf{P}_V(\mathbf{r}) = \mathsf{A}_1(\mathbf{r}) \cdot \mathbf{E}_0(\mathbf{r}) + \int_V d\mathbf{r}' \mathsf{A}_2(\mathbf{r}, \mathbf{r}') \cdot \mathbf{E}_0(\mathbf{r}'), \qquad \mathbf{r} \text{ in } V, \tag{3.5}$$

where we have assumed that there is no polarization in the absence of the field $\mathbf{E}_0$. In Eq. (3.5)

$$\mathsf{A}_1(\mathbf{r}) = \beta \int d\boldsymbol{\omega}_1 n_1(\mathbf{r}, \boldsymbol{\omega}_1)\, \boldsymbol{\mu}(\boldsymbol{\omega}_1)\, \boldsymbol{\mu}(\boldsymbol{\omega}_1) \tag{3.6}$$

and

$$\mathsf{A}_2(\mathbf{r}, \mathbf{r}') = \beta \int d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2 n_2(\mathbf{r}, \boldsymbol{\omega}_1; \mathbf{r}', \boldsymbol{\omega}_2)\, \boldsymbol{\mu}(\boldsymbol{\omega}_1)\, \boldsymbol{\mu}(\boldsymbol{\omega}_2), \tag{3.7}$$

where $n_s(\mathbf{r}^s, \boldsymbol{\omega}^s)$, $s = 1, 2, \cdots$, denotes the reduced s-particle distribution function in the presence of W, and in the absence of the external charges

$$n_s(\mathbf{r}^s, \boldsymbol{\omega}^s) = \frac{N!}{(N-s)!} \int_V d\mathbf{r}^{N-s} d\boldsymbol{\omega}^{N-s} f(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{0}). \tag{3.8}$$

In order to compute the polarization $\mathbf{P}_V(\mathbf{r})$ we must obtain an expression for the one- and two-particle distribution function n_1 and n_2. We shall accomplish this by linear graph theory in a form slightly modified from that presented by Uhlenbeck and Ford.[9] The modification is required since the potential of interaction in the absence of the field $U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{0})$ includes a single particle potential of the form $-\frac{1}{2}\boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathsf{R}_W(\mathbf{r}_i, \mathbf{r}_i; \epsilon_0) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_i)$ for each particle arising from the interaction with the surrounding medium W.

The theory of linear graphs[9–11] leads in a well-known way to a graphical expansion of n_s in powers of the fugacity. From this expansion one finds a graphical representation of the virial expansion of n_s in powers of the one-particle distribution n_1. For our purpose it is sufficient to consider the virial expansion of n_2 only.

First, we briefly mention some concepts in the theory of linear graphs which we shall use. A linear graph is a collection of points (vertices) with lines (bonds) joining certain pairs of points. A graph is said to be *connected* if there is a path of bonds between any pair of points. A connected graph may or may not have *articulation points*, which have the property that if all the bonds meeting at such a point are detached from it and the point is erased, the graph becomes disconnected. A connected graph is called a *star* if it has no articulation points.

A slight generalization of the formalism presented by Uhlenbeck and Ford[9] to include the single particle potential and the orientational dependence of U leads to the virial expansion of n_2

$$n_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = \sum_{M=2}^{\infty} a_M(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2), \tag{3.9}$$

where

$$a_M(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = [(M-2)!]^{-1} \sum_{(R_M)} \int_V d\mathbf{r}^{M-2} d\boldsymbol{\omega}^{M-2} \times \prod_{R_M} f_{ij} \prod_{k=1}^{M} n_1(\mathbf{r}_k, \boldsymbol{\omega}_k). \tag{3.10}$$

The summation in Eq. (3.10) is over all different linear graphs R_M with M points labeled $1, 2, \cdots, M$, which become a star when an additional bond between the points labeled 1 and 2 is inserted, if not already present. Between each pair of points there is either one or no bond. A bond between the points i and j contributes a factor f_{ij}, which is the Mayer function defined by

$$1 + f_{ij} \equiv \exp\{-\beta v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j) + \beta \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot [\mathsf{T}(\mathbf{r}_i, \mathbf{r}_j) + \mathsf{R}_W(\mathbf{r}_i, \mathbf{r}_j; \epsilon_0)] \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j)\} \tag{3.11}$$

for $i \neq j$. Each point k contributes a factor $n_1(\mathbf{r}_k, \boldsymbol{\omega}_k)$ to the integrand in Eq. (3.10). Graphs which become a star when a bond between the points labeled 1 and 2 is inserted are called *irreducible*. Otherwise a graph is *reducible*.

Strictly speaking, the derivation of the expansion (3.9) in the canonical ensemble is valid only in the thermodynamic limit, provided that this limit exists. However, it is reasonable to believe that the derivation is valid also for a finite sample volume V, provided that V is of macroscopic size.[12] The expansion (3.9) together with Eqs. (3.10) and (3.11) is the starting point of our investigation of the long-range correlations between the molecules.

First, we make the simplifying assumption that $n_1(\mathbf{r}, \boldsymbol{\omega})$ is constant, independent of position $\mathbf{r}$ and orientation $\boldsymbol{\omega}$. Outside a microscopic boundary region this is most probably a good approximation. Hence, we take

$$n_1(\mathbf{r}, \boldsymbol{\omega}) = \rho \Omega^{-1}, \tag{3.12}$$

where $\rho = NV^{-1}$ is the particle density and Ω is defined by

$$\int d\boldsymbol{\omega} = \Omega. \tag{3.13}$$

If a molecule requires three Eulerian angles to specify its orientation, one finds $\Omega = 8\pi^2$. If the molecules have an axis of rotational symmetry, its orientation may be specified by two angles, and $\Omega = 4\pi$.

Next, we notice that the only irreducible graph in the expansion (3.9) which is disconnected is represented by

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two single points labeled 1 and 2. The contribution of this graph is $\rho^2\Omega^{-2}$. If we introduce the two-particle correlation function G_2 by

$$n_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = \rho^2\Omega^{-2} + G_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2), \quad (3.14)$$

we find that G_2 can be written as a sum of contributions of all different labeled irreducible *connected* graphs.

Next, we examine the various graphs contributing to G_2. According to Eq. (2.2) the dipole–dipole interaction is proportional to the third power of the inverse distance and is therefore of long range. The reaction field tensor R_W has also a long range, and it can be shown that it is proportional to the inverse of the volume V. This property of R_W follows readily from its definition (2.11) and the properties of T, and will be illustrated in Appendix A for the special case of a spherical volume V. Hence, the two-particle interaction can be split into a short-range part $v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)$ and a long-range part $-\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{D}(\mathbf{r}_i, \mathbf{r}_j)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)$, where

$$\mathsf{D}(\mathbf{r}_i, \mathbf{r}_j) = \mathsf{T}(\mathbf{r}_i, \mathbf{r}_j) + \mathsf{R}_W(\mathbf{r}_i, \mathbf{r}_j; \epsilon_0). \quad (3.15)$$

We separate the effects of these two parts of the interaction in a similar way as it has been done by Hemmer[13] in the case of the van der Waals gas and by Lebowitz, Stell, and Baer,[14] in the case of weak long-range forces.

The function f_{ij} defined by Eq. (3.11) can be written as

$$\begin{aligned} f_{ij} = {} & \{\exp[-\beta v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)] - 1\} \\ & \times \exp\{\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{D}(\mathbf{r}_i, \mathbf{r}_j)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)\} \\ & + \sum_{\alpha=1}^{\infty} (\alpha!)^{-1}[\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{D}(\mathbf{r}_i, \mathbf{r}_j)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)]^{\alpha} \\ = {} & a_{ij} + \sum_{\alpha=1}^{\infty}\cdot(\alpha!)^{-1}(b_{ij})^{\alpha}, \end{aligned} \quad (3.16)$$

where

$$\begin{aligned} a_{ij} = {} & \{\exp[-\beta v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)] - 1\} \\ & \times \exp\{\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{D}(\mathbf{r}_i, \mathbf{r}_j)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)\} \end{aligned} \quad (3.17)$$

and

$$b_{ij} = \beta\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{D}(\mathbf{r}_i, \mathbf{r}_j)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j). \quad (3.18)$$

One notices that the function a_{ij} is of short range and the function b_{ij} is of long range. If we represent a factor a_{ij} by a dotted line (a short-range bond) between the points i and j, and a factor $(1/\alpha!)(b_{ij})^{\alpha}$ by α solid lines (long-range bonds) between the points i and j, then an f bond in the graphs contributing to a_M [cf. Eq. (3.10)] can be written as the sum of one short-range bond a_{ij}, one long-range bond b_{ij}, two long-range bonds, etc.:

$$f_{ij} = a_{ij} + b_{ij} + (2!)^{-1}(b_{ij})^2 + (3!)^{-1}(b_{ij})^3 + \cdots. \quad (3.19)$$

If we replace each f_{ij} in Eq. (3.10) by the expansion (3.19) 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. By replacing each f bond in the graphical expansion of G_2 by the expansion (3.19), we are led to the expansion

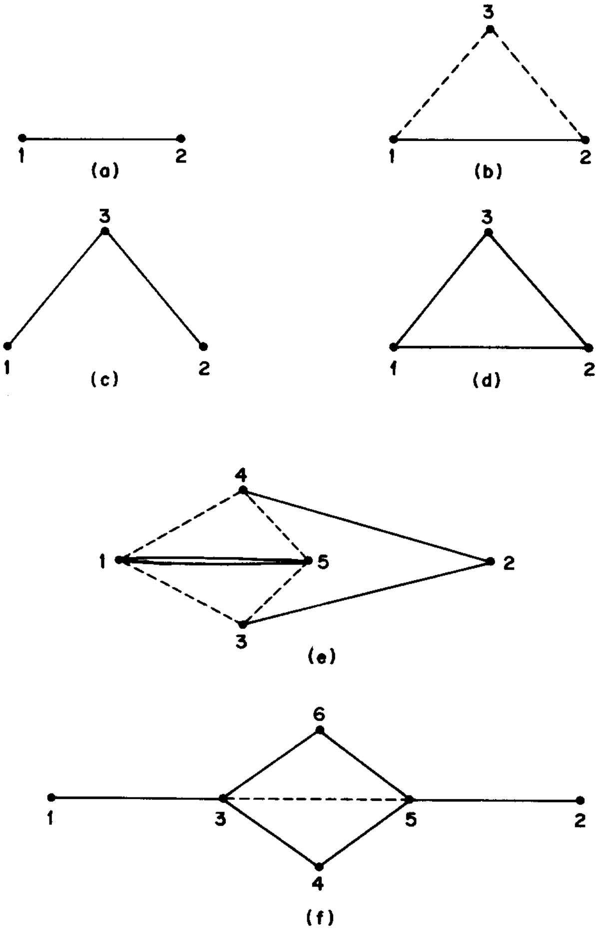

FIG. 2. Some examples of irreducible connected composite graphs, which contribute to the two-particle correlation function $G_2(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2)$.

$$G_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = \sum_{L=2}^{\infty} b_L(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)\rho^L\Omega^{-L}, \quad (3.20)$$

where the functions b_L can be graphically represented as

$$\begin{aligned} b_L(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = {} & [(L-2)!]^{-1} \sum_{(C_L)} \int_V d\mathbf{r}^{L-2} d\boldsymbol{\omega}^{L-2} \\ & \times \prod_{C_L} a_{ij} \prod_{C_L} [(1/\alpha!)(b_{pq})^{\alpha}]. \end{aligned} \quad (3.21)$$

The sum is over all different connected irreducible composite graphs C_L with L points labeled $1, 2, \cdots L$. The indices (i,j) and (p,q) refer to pairs of points in a graph C_L. Between each pair of points in a graph we have three possibilities: (a) one or several solid bonds, (b) one dotted bond, and (c) no bonds. A dotted bond between the points i and j contributes a factor a_{ij} to the

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integrand in Eq. (3.21), a number α of solid bonds between the points p and q contributes a factor $(1/\alpha!)(b_{pq})^{\alpha}$. In Fig. 2 we give some examples of composite graphs contributing to G_2.

In order to estimate the order of magnitude of the various graphs contributing to the expansion (3.20) of the two-particle correlation function G_2, we introduce a dimensionless parameter of smallness δ by putting

$$\delta=\beta\mu^2\Lambda^{-3}. \tag{3.22}$$

Here Λ is a typical macroscopic distance in our system which is very large compared with the average distance between two neighboring molecules $\rho^{-1/3}$. One expects the quantity $\frac{1}{3}\beta\rho\mu^2$ to be of the order of the dielectric susceptibility $(\epsilon-1)/4\pi$ of the molecular medium. For polar fluids the susceptibility is typically between zero and ten. Hence the parameter δ is much smaller than unity for real systems under a wide variety of conditions of density and temperature.

The bond b_{pq} is of the order δ and therefore small if the distance $|\mathbf{r}_p-\mathbf{r}_q|$ is macroscopic. However, for a very small microscopic distance $|\mathbf{r}_p-\mathbf{r}_q|$ the value of b_{pq} is not small and must be considered to be of zeroth order in δ. Due to the short range of a_{ij} the contribution to G_2 of a graph where two points are connected by a path of short-range bonds arises only from configurations where the points are within molecular distance from each other. Hence any number of long-range bonds between two points which are connected by a path of short-range bonds is of zeroth order in δ. The factor $\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{R}_W(\mathbf{r}_i,\mathbf{r}_j;\epsilon_0)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)$ is of order δ for any distance $|\mathbf{r}_i-\mathbf{r}_j|$ (cf. Appendix A). Thus this term is negligible compared to $\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathsf{T}(\mathbf{r}_i,\mathbf{r}_j)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)$ if $\mathbf{r}_i$ and $\mathbf{r}_j$ are close together but of equal importance when $\mathbf{r}_i$ and $\mathbf{r}_j$ are far apart.

The order of magnitude of various graphs may be estimated from these considerations. For example, the contribution of all the graphs in Fig. 2, if $\mathbf{r}_1$ and $\mathbf{r}_2$ are on microscopic distance from each other, has a leading term of zeroth order in δ. If $\mathbf{r}_1$ and $\mathbf{r}_2$ are separated by a macroscopic distance Λ then graph (a) is of order δ and graph (b) is zero because of the short range of a_{ij}. Graph (c) is of order δ, for if $|\mathbf{r}_3-\mathbf{r}_2|$ is microscopic, the bond b_{32} is of zeroth order, and the bond b_{13} is of first order in δ, and vice versa. Moreover, the region in which b_{13} and b_{32} are both of order δ is of the order of the volume V, and hence of order δ^{-1}. Consequently, this region also has a leading contribution of order δ. In a similar way one finds that graph (d) is of order δ^2. In (e) the contribution comes only from configurations in which 1, 3, 4, and 5 are separated from each other by microscopic distances, and therefore this group of particles is on macroscopic distance from 2. This graph is of order δ^2. Graph (f) has a leading term of order δ since the coordinates $\mathbf{r}_3$ and $\mathbf{r}_5$ must be separated by a microscopic distance and the integrations over $\mathbf{r}_6$ and $\mathbf{r}_4$ give a contribution of zeroth order in δ.

The contribution of a graph clearly does not depend on the labeling of the points other than the points 1 and 2. This property enables us to express b_L in terms of irreducible graphs in which only the points 1 and 2 are labeled. The symmetry number σ of a graph in which two points are labeled 1 and 2 is the number of automorphisms of the graph.[9] An automorphism is a permutation of points other than the pair labeled 1 or 2 which leaves the bonds between pairs of points unchanged. For example, in Fig. 2 the graphs (a), (b), (c), and (d) have a symmetry number 1, (e) and (f) have a symmetry number 2. In a graph with L points labeled from 1 to L there are $(L-2)!/\sigma$ ways of labeling the points which are not labeled 1 or 2. Hence we may write Eq. (3.21) as

$$b_L(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2)=\sum_{(S_L)}\sigma^{-1}\int_V d\mathbf{r}^{L-2}d\boldsymbol{\omega}^{L-2}\times\prod_{S_L}a_{ij}\prod_{S_L}[(1/\alpha!)(b_{pq})^{\alpha}], \tag{3.23}$$

where the sum is now over all different connected irreducible composite graphs S_L with L points in which only the points 1 and 2 are labeled.

First, we consider irreducible connected composite graphs which are stars. For microscopic separation of $\mathbf{r}_1$ and $\mathbf{r}_2$ each star has a leading contribution of zeroth order in δ. Now it is not difficult to see that the only star which has a contribution to G_2 of first order in δ for a macroscopic distance between $\mathbf{r}_1$ and $\mathbf{r}_2$ is the star (a) in Fig. 2. We call this star S_0. Each other star is at least of order δ^2 if $\mathbf{r}_1$ and $\mathbf{r}_2$ are far apart.

Next, we consider an irreducible composite graph contributing to G_2 which is not a star. Such a graph is built out of a set of stars which are hung together at the articulation points of the graph. An irreducible graph must become a star if one inserts an additional direct bond between the points labeled 1 and 2. For an irreducible graph it must be the case that each building star which does not contain either the point 1 or the point 2 is hung to precisely two other stars and that the stars which do contain either the point 1 or the point 2 are hung to precisely one other star. For if there were any other star attached to only one star or attached to more than two stars, the resulting graph would be reducible. Each articulation point of the graph is called an endpoint of the two stars to which it belongs, and the points 1 and 2 are called endpoints of the end stars. Thus the graph must be a chain of stars hung together at the end points, with the two stars which contain either the point 1 or the point 2 at the two ends of the chain. Each building star itself is an irreducible graph contributing to G_2. For example, the graph (f) in Fig. 2 is a chain of three stars with the star S_0 as the two end stars.

If $\mathbf{r}_1$ and $\mathbf{r}_2$ are on microscopic distance any star chain has a contribution of zeroth order in δ. If $\mathbf{r}_1$ and $\mathbf{r}_2$ are on macroscopic distance from each other, each graph has a leading term of the same order in δ as the building star in the chain with the lowest order in δ for macro-

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scopic separation of its end points. This can be seen by noting that there is a region in configuration space in which the end points of this star are separated by a macroscopic distance, and points not belonging to this star are either microscopically close to point 1 or point 2. This region in configuration space gives a contribution which is of the same order in δ as the contribution from the star under consideration if its end points were labeled 1 and 2 and were macroscopically separated. Any other configuration is of higher order. For if the end points of this star are close to each other, there must be at least one other star in the chain whose end points are macroscopically separated, because the end points 1 and 2 of the complete graph are far apart. But this configuration by assumption must give a higher-order contribution to the graph. One may conclude that the only graphs which give a first-order contribution to G_2 for large separation of $\mathbf{r}_1$ and $\mathbf{r}_2$ are those where the chain of stars contains at least once the star S_0. Any graph which is a chain exclusively of stars not of the type S_0 gives, for macroscopic distance between $\mathbf{r}_1$ and $\mathbf{r}_2$, a contribution to G_2 of at least second order in δ.

The set of composite irreducible graphs which do not have the star S_0 as one of its building stars is called Z. The irreducible graphs which are a star other than S_0 are also included in Z including those graphs which are completely free of b bonds. The contribution to G_2 of the graphs in Z is of zeroth order if $\mathbf{r}_1$ and $\mathbf{r}_2$ are separated by a microscopic distance, and of second order if $\mathbf{r}_1$ and $\mathbf{r}_2$ are separated by a macroscopic distance. The zeroth-order term of the contributions of the graphs in Z to G_2 is called $G_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)$. Then $G_2^{(0)}$ has a range of microscopic size. Actually, the leading contribution to G_2 of the graphs in Z is proportional to $\beta^2\mu^4 |\mathbf{r}_1-\mathbf{r}_2|^{-6}$ if $|\mathbf{r}_1-\mathbf{r}_2|$ tends to a macroscopic size. Hence the contribution is of second order in δ if $|\mathbf{r}_1-\mathbf{r}_2|=\mathcal{O}(\Lambda)$, of zeroth order if $|\mathbf{r}_1-\mathbf{r}_2|=\mathcal{O}(\rho^{-1/3})$, and of first order in the intermediate region $|\mathbf{r}_1-\mathbf{r}_2|=\mathcal{O}(\Lambda^{1/2}\rho^{-1/6})$. Since $G_2^{(0)}$ is defined as the zeroth-order contribution for any separation, it must be zero in this intermediate region. Hence the range of $G_2^{(0)}$ must be smaller than $\Lambda^{1/2}\rho^{-1/6}$.

We wish to emphasize that $G_2^{(0)}$ is not the complete zeroth order of G_2. The irreducible graphs which are not in Z have a zeroth-order part for small separation. Thus the graphs that contribute to order δ for large separation, also contribute to order unity for small separation. It is this feature that forces us to employ an unwieldy graphical expansion, since a single parameter of smallness is not valid for all separations.

The contribution to G_2 from the graphs which are not in Z (i.e., which are a star chain which have the star S_0 as at least one of its building stars) has a first-order term for large separation. We introduce the function $G_2^{(1)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)$ which is the zeroth order of this contribution for microscopic separation and the first order for macroscopic separation. Hence for microscopic values of $|\mathbf{r}_1-\mathbf{r}_2|$ the function $G_2^{(0)}+G_2^{(1)}$ is the zeroth-order term of G_2; for macroscopic values of $|\mathbf{r}_1-\mathbf{r}_2|$ the zeroth-order term of G_2 vanishes, and the first-order term is given by $G_2^{(1)}$. The function $G_2^{(0)}+G_2^{(1)}$ is expected to be a good approximation of G_2 for all separations. Hence

$$G_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)=G_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)+G_2^{(1)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2). \quad (3.24)$$

We consider first the graphs contributing to $G_2^{(1)}$ which contain once the star S_0 as a building link. We have the possibility that either the point 1 is an end point of this star S_0, or there is a graph out of the set Z which connects the point 1 to an end point of this star S_0. The same is true for the point 2. The symmetry number of a star chain is the product of the symmetry numbers of the constituent stars in the chain, where the end points of a star play the role of the points 1 and 2 in determining the symmetry number. From Eqs. (3.20) and (3.23) it follows easily that the contribution to $G_2^{(1)}$ of the graphs which contain exactly once the star S_0 as a constituent star can be written as

$$\int_V d\mathbf{r}_3 d\boldsymbol{\omega}_3 d\mathbf{r}_4 d\boldsymbol{\omega}_4 H_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_3, \boldsymbol{\omega}_3)\beta\boldsymbol{\mu}(\boldsymbol{\omega}_3)\cdot\mathsf{D}(\mathbf{r}_3, \mathbf{r}_4)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_4)H_2^{(0)}(\mathbf{r}_4, \boldsymbol{\omega}_4; \mathbf{r}_2, \boldsymbol{\omega}_2), \quad (3.25)$$

where the function $H_2^{(0)}$ is defined by

$$H_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)=(\rho/\Omega)\delta(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)+G_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2). \quad (3.26)$$

The δ function, defined by the equality

$$\int d\mathbf{r}_2 d\boldsymbol{\omega}_2 \delta(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)f(\mathbf{r}_2, \boldsymbol{\omega}_2)=f(\mathbf{r}_1, \boldsymbol{\omega}_1) \quad (3.27)$$

for every function f of position and orientation, is included to take into account the case where S_0 is attached to point 1, 2 or both.

The graphs contributing to $G_2^{(1)}$ which contain as a basic constituent the star S_0 twice or more times can be built up by starting with a graph out of Z with one of its end points labeled 1, then hanging S_0 to the other end point of this graph of Z, and finally hanging any graph contributing to $G_2^{(1)}$ to the other end point of this star S_0. By taking together the contribution of these graphs with the contribution (3.25), we arrive at the following equation for $G_2^{(1)}$:

$$\begin{aligned}G_2^{(1)}&(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)\\ &=\int_V d\mathbf{r}_3 d\boldsymbol{\omega}_3 d\mathbf{r}_4 d\boldsymbol{\omega}_4 H_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_3, \boldsymbol{\omega}_3)\beta\boldsymbol{\mu}(\boldsymbol{\omega}_3)\cdot\mathsf{D}(\mathbf{r}_3, \mathbf{r}_4)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_4)H_2^{(0)}(\mathbf{r}_4, \boldsymbol{\omega}_4; \mathbf{r}_2, \boldsymbol{\omega}_2)\\ &\quad+\int_V d\mathbf{r}_3 d\boldsymbol{\omega}_3 d\mathbf{r}_4 d\boldsymbol{\omega}_4 H_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_3, \boldsymbol{\omega}_3)\beta\boldsymbol{\mu}(\boldsymbol{\omega}_3)\cdot\mathsf{D}(\mathbf{r}_3, \mathbf{r}_4)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_4)G_2^{(1)}(\mathbf{r}_4, \boldsymbol{\omega}_4; \mathbf{r}_2, \boldsymbol{\omega}_2). \quad (3.28)\end{aligned}$$

Lebowitz, Stell, and Baer[14] have shown that in the thermodynamic limit an integral equation equivalent to Eq. (3.28) is exact when the pair potential is sepa-

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rated into two contributions provided that $G_2^{(0)}$ is interpreted to be the entire contribution of the graphs in Z and $G_2^{(1)}$ is interpreted to be the entire contribution of the graphs not in Z. Our derivation leads to Eq. (3.28) for finite volume but should not be considered rigorous [see Footnote (12)]. The parameter δ is introduced in order to display the relative order of magnitude of the graphs for large and small interparticle separation. For large interparticle separation the graphs in Z are of order δ^2 or higher. The term $G_2^{(0)}$ includes only the zeroth order in δ contribution of the graphs in Z so that $G_2^{(0)}$ vanishes for large interparticle separation.

In Eq. (3.28) we have taken into account only the zeroth-order term $G_2^{(0)}$ of the graphs in Z, since we intend only to find an equation for the lowest-order term $G_2^{(1)}$ for macroscopic separation.

The range of $H_2^{(0)}$ is the same as the range of $G_2^{(0)}$, which is microscopic. We assume that we make a negligible error if we replace $\mathbf{D}(\mathbf{r}_3,\mathbf{r}_4)$ by $\mathbf{D}(\mathbf{r}_1,\mathbf{r}_2)$ in the first term of Eq. (3.28) and by $\mathbf{D}(\mathbf{r}_1,\mathbf{r}_4)$ in the last term. For the first term this is certainly justified for configurations where $|\mathbf{r}_1-\mathbf{r}_2|$ is much larger than the range of $G_2^{(0)}$. For the second term the replacement is only justified when $\mathbf{r}_1$ and $\mathbf{r}_4$ are well separated. For small separations we must expect to incur an error. With this replacement we may write Eq. (3.28) as

$$\begin{aligned}G_2^{(1)}(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2)&=(\beta\rho^2/\Omega^2)[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]\\&\quad\cdot\mathbf{D}(\mathbf{r}_1,\mathbf{r}_2)\cdot[\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)]\\&\quad+\frac{\beta\rho}{\Omega}\int_V d\mathbf{r}_4d\boldsymbol{\omega}_4[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]\\&\quad\cdot\mathbf{D}(\mathbf{r}_1,\mathbf{r}_4)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_4)G_2^{(1)}(\mathbf{r}_4,\boldsymbol{\omega}_4;\mathbf{r}_2,\boldsymbol{\omega}_2),\end{aligned}\tag{3.29}$$

where we have used the definition (3.26) of $H_2^{(0)}$, and where the vector $\boldsymbol{\kappa}(\boldsymbol{\omega})$ is defined by

$$\frac{\rho}{\Omega}\boldsymbol{\kappa}(\boldsymbol{\omega}_1)=\int_V d\mathbf{r}_2d\boldsymbol{\omega}_2G_2^{(0)}(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_2).\tag{3.30}$$

Equation (3.29) is the principal result of the microscopic analysis. It is an integral equation of the Dyson form for the long-range part of the two-particle correlation function valid to lowest order in δ.

In order to examine $\boldsymbol{\kappa}(\boldsymbol{\omega})$, we must examine the function $G_2^{(0)}$ which is nonvanishing only for small separations, but involves the interaction $-\boldsymbol{\mu}\cdot\mathbf{D}\cdot\boldsymbol{\mu}$ as well as the short-range interaction v. We recall that $\beta\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathbf{R}_W(\mathbf{r}_i,\mathbf{r}_j;\epsilon_0)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)$ is of first order in δ for any separation. Furthermore, one readily checks that

$$\int d\mathbf{r}_3\mathbf{T}(\mathbf{r}_1,\mathbf{r}_3)\cdot\mathbf{T}(\mathbf{r}_3,\mathbf{r}_2)=-4\pi\mathbf{T}(\mathbf{r}_1,\mathbf{r}_2),\tag{3.31}$$

if $\mathbf{r}_3$ is integrated over the whole three-dimensional space, and that

$$\int_V d\mathbf{r}_3\mathbf{T}(\mathbf{r}_1,\mathbf{r}_3)\cdot\mathbf{T}(\mathbf{r}_3,\mathbf{r}_2)=-4\pi\mathbf{T}(\mathbf{r}_1,\mathbf{r}_2)+\mathcal{O}(1/V),\tag{3.32}$$

if $\mathbf{r}_1$ and $\mathbf{r}_2$ in V, and if $\mathbf{r}_3$ is integrated over V only. The property (3.32) of $\mathbf{T}$ reflects the fact that the square of the dipole–dipole interaction is effectively of short range (being proportional to r^{-6}). The same is true *a fortiori* for higher powers of $\mathbf{T}$. One may conclude that in order to calculate $G_2^{(0)}$ it is sufficient to calculate the contributions of the graphs in Z by replacing $\mathbf{D}(\mathbf{r}_i,\mathbf{r}_j)$ by $\mathbf{T}(\mathbf{r}_i,\mathbf{r}_j)$ [neglecting $\mathbf{R}_W(\mathbf{r}_i,\mathbf{r}_j;\epsilon_0)$] and by performing the space integrations over the entire three-dimensional space instead of over V only. So we arrive at the following conclusions: (i) $G_2^{(0)}(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2)$ has a microscopic range and (ii) $G_2^{(0)}(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2)$ depends only upon the relative positions and orientations of the particles 1 and 2. Strictly speaking, the conclusion (ii) is not justified in a microscopic region at the boundary of V. For then $\beta\boldsymbol{\mu}\cdot\mathbf{R}\cdot\boldsymbol{\mu}$ can become large and also the difference between (3.31) and (3.32) can be nonnegligible. However we neglect the effects of this boundary region. Because of the short range of $G_2^{(0)}$ we may extend the region of integration in Eq. (3.30) over all space, provided that $\mathbf{r}_1$ is outside a negligible boundary region. It follows that the vector $\boldsymbol{\kappa}(\boldsymbol{\omega}_1)$, which has the dimension of a dipole moment, is a vector fixed to particle 1 and independent of $\mathbf{r}_1$.

The two-particle correlation function G_2 will be approximated by $G_2^{(0)}+G_2^{(1)}$, which is correct up to zeroth order in δ for microscopic distance, and up to first order in δ for macroscopic distance between $\mathbf{r}_1$ and $\mathbf{r}_2$. In the next section we examine the consequences of the two-particle correlation function for the dielectric properties of the fluid.

IV. LONG-RANGE CORRELATIONS AND DIELECTRIC PROPERTIES

We are now in a position to give a molecular equation for the polarization $\mathbf{P}_V(\mathbf{r})$. From Eq. (3.5) one finds

$$\begin{aligned}\mathbf{P}_V(\mathbf{r})&=\beta\rho\Omega^{-1}\int d\boldsymbol{\omega}_1\boldsymbol{\mu}(\boldsymbol{\omega}_1)\boldsymbol{\mu}(\boldsymbol{\omega}_1)\cdot\mathbf{E}_0(\mathbf{r})+\beta\int_V d\mathbf{r}'d\boldsymbol{\omega}_1d\boldsymbol{\omega}_2\\&\quad\times G_2(\mathbf{r},\boldsymbol{\omega}_1;\mathbf{r}',\boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_1)\boldsymbol{\mu}(\boldsymbol{\omega}_2)\cdot\mathbf{E}_0(\mathbf{r}').\end{aligned}\tag{4.1}$$

In order to calculate $\mathbf{P}_V(\mathbf{r})$ to zeroth order in δ, we need G_2 up to first order for large separation, since when $\mathbf{r}'$ is integrated over the volume V, the order is reduced by one. Now we assume that the external field $\mathbf{E}_0(\mathbf{r})$ does not vary appreciably over a distance of the order of the range of $G_2^{(0)}$. Using this assumption we find from Eq. (4.1)

$$\begin{aligned}\mathbf{P}_V(\mathbf{r})&=\beta\rho\Omega^{-1}\int d\boldsymbol{\omega}_1\boldsymbol{\mu}(\boldsymbol{\omega}_1)[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]\cdot\mathbf{E}_0(\mathbf{r})\\&\quad+\beta\int_V d\mathbf{r}'d\boldsymbol{\omega}_1d\boldsymbol{\omega}_2G_2^{(1)}(\mathbf{r},\boldsymbol{\omega}_1;\mathbf{r}',\boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_1)\boldsymbol{\mu}(\boldsymbol{\omega}_2)\cdot\mathbf{E}_0(\mathbf{r}')\end{aligned}\tag{4.2}$$

or

$$\begin{aligned}\mathbf{P}_V(\mathbf{r})&=\tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot(\boldsymbol{\mu}+\boldsymbol{\kappa})\mathbf{E}_0(\mathbf{r})+\beta\int_V d\mathbf{r}'d\boldsymbol{\omega}_1d\boldsymbol{\omega}_2\\&\quad\times G_2^{(1)}(\mathbf{r},\boldsymbol{\omega}_1;\mathbf{r}',\boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_1)\boldsymbol{\mu}(\boldsymbol{\omega}_2)\cdot\mathbf{E}_0(\mathbf{r}')\end{aligned}\tag{4.3}$$

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provided that $\mathbf{r}$ is not in a microscopic boundary region of the volume V. Here we have used the separation of G_2 according to Eq. (3.24) and the definition of the vector $\boldsymbol{\kappa}$ Eq. (3.30). We substitute Eq. (3.29) in Eq. (4.3) and we find

$$\begin{aligned}\mathbf{P}_V(\mathbf{r}) = \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot(\boldsymbol{\mu}+\boldsymbol{\kappa})\Bigg[\mathbf{E}_0(\mathbf{r}) &+ \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot(\boldsymbol{\mu}+\boldsymbol{\kappa}) \\ &\times \int_V d\mathbf{r}'\mathsf{D}(\mathbf{r},\mathbf{r}')\cdot\mathbf{E}_0(\mathbf{r}') + \beta\int_V d\mathbf{r}'d\boldsymbol{\omega}_2 d\mathbf{r}_4 d\boldsymbol{\omega}_4 \\ &\times G_2^{(1)}(\mathbf{r}_4,\boldsymbol{\omega}_4;\mathbf{r}',\boldsymbol{\omega}_2)\mathsf{D}(\mathbf{r},\mathbf{r}_4)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_4)\boldsymbol{\mu}(\boldsymbol{\omega}_2)\cdot\mathbf{E}_0(\mathbf{r}')\Bigg]. \end{aligned} \tag{4.4}$$

This equation can be written as

$$\mathbf{P}_V(\mathbf{r}) = \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot(\boldsymbol{\mu}+\boldsymbol{\kappa})\left[\mathbf{E}_0(\mathbf{r}) + \int_V d\mathbf{r}'\mathsf{D}(\mathbf{r},\mathbf{r}')\cdot\mathbf{P}_V(\mathbf{r}')\right], \tag{4.5}$$

as may easily be verified by substitution of Eq. (4.3) for $\mathbf{P}_V$ in the last term of Eq. (4.5). Recall that $\mathsf{D}(\mathbf{r},\mathbf{r}')=\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_W(\mathbf{r},\mathbf{r}';\epsilon_0)$.

The integral equation (4.5) for $\mathbf{P}_V(\mathbf{r})$ follows from the molecular statistical mechanical theory of the system for any external field $\mathbf{E}_0(\mathbf{r})$, provided that this field does not vary considerably over a distance of the order of the range of $G_2^{(0)}$ in V.

If we compare Eq. (4.5) with the macroscopic considerations in Sec. II, in particular with Eq. (2.17), we find that the molecular medium obeys the constitutive relation of the macroscopic theory of dielectrics for an arbitrary sample volume V surrounded by an arbitrarily shaped macroscopic dielectric with arbitrary dielectric constant ϵ_0 and for any static external field which does not vary too wildly in V. In these circumstances the molecular medium behaves as a dielectric [cf. Eq. (2.17)] with a local static dielectric constant ϵ which is given by

$$(\epsilon-1)/4\pi = \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot(\boldsymbol{\mu}+\boldsymbol{\kappa}). \tag{4.6}$$

It follows from the definition (3.30) of $\boldsymbol{\kappa}$ that the resulting dielectric constant ϵ depends only on the local interactions in the molecular medium, and is independent of the shape of the sample and the surroundings.

We are interested in finding the solution of the integral equation (3.29) for $G_2^{(1)}$. If we assume the solution for $G_2^{(1)}$ to be of the form

$$\begin{aligned}G_2^{(1)}(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2) = \beta\rho^2\Omega^{-2}&[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)] \\ &\cdot\mathsf{F}(\mathbf{r}_1,\mathbf{r}_2)\cdot[\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)]\end{aligned} \tag{4.7}$$

and substitute in Eq. (3.29), we find that the tensor function $\mathsf{F}(\mathbf{r}_1,\mathbf{r}_2)$ must satisfy the equation

$$\begin{aligned}\mathsf{F}(\mathbf{r},\mathbf{r}') = \mathsf{D}(\mathbf{r},\mathbf{r}') &+ \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot(\boldsymbol{\mu}+\boldsymbol{\kappa}) \\ &\times\int_V d\mathbf{r}''\mathsf{D}(\mathbf{r},\mathbf{r}'')\cdot\mathsf{F}(\mathbf{r}'',\mathbf{r}'). \end{aligned} \tag{4.8}$$

If F is determined from Eq. (4.8), the solution Eq. (4.7) for $G_2^{(1)}$ is unique. The tensor D defined by Eq. (3.15) depends upon the dielectric constant ϵ_0 of the surrounding medium in W. Consequently F depends both on the dielectric constant ϵ_0 in W and the constant ϵ which we found to be the dielectric constant of the molecular medium in V. The tensor function $\mathsf{F}(\mathbf{r},\mathbf{r}')$ obeying Eq. (4.8) can be used to write down the solution of Eq. (4.5) for the polarization $\mathbf{P}_V(\mathbf{r})$. One readily verifies that

$$\begin{aligned}\mathbf{P}_V(\mathbf{r}) = \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot(\boldsymbol{\mu}+\boldsymbol{\kappa})\mathbf{E}_0(\mathbf{r}) &+ [\tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot(\boldsymbol{\mu}+\boldsymbol{\kappa})]^2 \\ &\times\int_V d\mathbf{r}'\mathsf{F}(\mathbf{r},\mathbf{r}')\cdot\mathbf{E}_0(\mathbf{r}')\end{aligned} \tag{4.9}$$

obeys Eq. (4.5) if F obeys Eq. (4.8).

In the special case that the dielectric constant ϵ_0 of the medium in W is the same as the dielectric constant ϵ given by Eq. (4.6) of the molecular medium in V, the solution $\mathsf{F}(\mathbf{r},\mathbf{r}')$ of Eq. (4.8) is known. For in the case $\epsilon_0=\epsilon$, Eq. (4.8) for F is precisely the same as the integral equation for $\epsilon^{-1}[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})]$ given in Eq. (2.23). Hence we have proven that

$$\mathsf{F}(\mathbf{r},\mathbf{r}') = \epsilon^{-1}[\mathsf{T}(\mathbf{r},\mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})] \tag{4.10}$$

is the solution of Eq. (4.8) if the surrounding medium in W has dielectric constant ϵ given by Eq. (4.6). Thus we find from Eq. (4.7) that

$$\begin{aligned}G_2^{(1)} = (\beta\rho^2/\epsilon\Omega^2)[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]\cdot&[\mathsf{T}(\mathbf{r},\mathbf{r}') \\ &+\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})]\cdot[\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)]\end{aligned} \tag{4.11}$$

in the special case that the surrounding medium in W and the molecular medium in V have the same dielectric constant. Because we know that

$$\begin{aligned}n_2(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2) = \rho^2\Omega^{-2} &+ G_2^{(0)}(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2) \\ &+ G_2^{(1)}(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2),\end{aligned} \tag{4.12}$$

we now have found an explicit expression for the long-range part of the two-particle distribution function n_2 if $\epsilon=\epsilon_0$.[15]

Note that G_2 contains two long-range contributions. One involving T is itself not dependent on the shape or the surroundings, but will give rise to shape-dependent values when integrated over various geometries. The second term involving $\mathsf{R}_{(V+W)}{}^*(\mathbf{r}_1,\mathbf{r}_2;\epsilon^{-1})$ is explicitly dependent on the shape of V and W, but is also proportional to $(V+W)^{-1}$ (see Appendix A). This term proportional to $(V+W)^{-1}$ may not be omitted since the calculation of angular averages [see Eqs. (1.4) and (1.5) and Sec. V] will involve integrations of $\mathbf{r}_1$ and $\mathbf{r}_2$ throughout the volume.

It is clarifying to describe the long-range correlation in terms of a two-particle potential of mean force Φ, which is defined by the relation

$$n_2(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2) = \rho^2\Omega^{-2}\exp[-\beta\Phi(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2)]. \tag{4.13}$$

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From Eqs. (4.12) and (4.11) it follows that, in the case that $\epsilon_0=\epsilon$, the potential of mean force is given to lowest order in δ by

$$\Phi(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = -\epsilon^{-1}[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)] \cdot[\mathsf{T}(\mathbf{r}_1, \mathbf{r}_2)+\mathsf{R}_{(V+W)}{}^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon^{-1})]\cdot[\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)], \tag{4.14}$$

if $|\mathbf{r}_1-\mathbf{r}_2|>\lambda$.

Here λ is the range of $G_2^{(0)}$. Equation (4.14) corresponds to the picture that each molecule drags with it an additional average dipole moment $\boldsymbol{\kappa}$, defined by Eq. (3.30), which is caused by the average orientation of its near neighbors. This whole configuration of molecule together with its oriented neighbors is embedded in a dielectric with dielectric constant ϵ. Another molecule at $\mathbf{r}$ separated by a distance larger than λ from the first one at $\mathbf{r}'$ feels only the electric field $\mathbf{e}(\mathbf{r})$ due to the total dipole moment

$$\boldsymbol{\mu}(\boldsymbol{\omega})+\boldsymbol{\kappa}(\boldsymbol{\omega})=\boldsymbol{\mu}_{\text{eff}}(\boldsymbol{\omega}) \tag{4.15}$$

in a continuous dielectric with dielectric constant ϵ which fills the total volume $(V+W)$. From the macroscopic considerations in Sec. II one obtains

$$\mathbf{e}(\mathbf{r})=[\mathsf{T}(\mathbf{r}, \mathbf{r}')+\mathsf{R}_{(V+W)}{}^*(\mathbf{r}, \mathbf{r}'; \epsilon^{-1})]\cdot\boldsymbol{\mu}_{\text{eff}}(\boldsymbol{\omega})/\epsilon. \tag{4.16}$$

We may draw another important conclusion from Eq. (4.11), which is valid in the special case that $\epsilon_0=\epsilon$. In this case $G_2^{(1)}$ depends only on the total volume $(V+W)$, and not on the two volumes separately. The short-range function $G_2^{(0)}$ does not depend on the shape of either of the two volumes. Consequently, the expression we obtain for $G_2^{(1)}$ is identical if we consider a molecular sample V surrounded by the continuum W of the same dielectric constant ϵ, or if we consider the total volume $(V+W)$ to be a molecular medium in vacuum. Thus the important conclusion is that to order δ it does not matter for the two-particle distribution function whether the surrounding medium of dielectric constant ϵ is treated as a continuum or on a molecular basis. The equivalent statement is that at large separations the potential of mean force may be computed according to macroscopic electrostatic considerations, as it is shown in Eq. (4.14).

The splitting of Eq. (3.24) for G_2 into the functions $G_2^{(0)}$ and $G_2^{(1)}$ was found by distinguishing between different types of graphs. The dielectric constant ϵ of the molecular medium is expressed in Eq. (4.6) in the vector $\boldsymbol{\kappa}$, which is defined by Eq. (3.30) in terms of $G_2^{(0)}$ only. However, the complete two-particle distribution function n_2 has another short-range part resulting from $G_2^{(1)}$. The zeroth order in δ of this short-range part is given by

$$(\beta\rho^2/\epsilon\Omega^2)[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]\cdot\mathsf{T}(\mathbf{r}_1, \mathbf{r}_2)\cdot[\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)], \tag{4.17}$$

as is illustrated in Eq. (4.11) in the special case that $\epsilon_0=\epsilon$. For short separations the term $\mathsf{R}_{(V+W)}{}^*$ in Eq. (4.11) is negligible compared to T. Thus we may obtain an expression for the dielectric constant ϵ in terms of the entire short-range part of n_2. From Eq. (4.17) we find

$$\int_{|\mathbf{r}_2-\mathbf{r}_1|<\lambda} d\mathbf{r}_2 d\boldsymbol{\omega}_2 G_2^{(1)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_2) = -(\rho/\Omega)[(\epsilon-1)/3\epsilon][\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)], \tag{4.18}$$

where we have made use of Eqs. (2.4) and (4.6). Following Kirkwood[1] we introduce the dipole moment $\bar{\mu}(\boldsymbol{\omega}_1)$ by

$$\bar{\mu}(\boldsymbol{\omega}_1)=\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\frac{\Omega}{\rho}\int_{|\mathbf{r}_2-\mathbf{r}_1|<\lambda} d\mathbf{r}_2 d\boldsymbol{\omega}_2 n_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_2). \tag{4.19}$$

Thus $\bar{\mu}(\boldsymbol{\omega}_1)$ is the average total dipole moment in a microscopic sphere with radius λ in the presence of a molecule with orientation $\boldsymbol{\omega}_1$ at the center of the sphere. The microscopic distance λ is the range of $G_2^{(0)}$. By using Eqs. (4.12), (3.30), and (4.18) we find that

$$\bar{\mu}(\boldsymbol{\omega}_1)=[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]-[(\epsilon-1)/3\epsilon][\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)] =[(2\epsilon+1)/3\epsilon][\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]. \tag{4.20}$$

It follows from Eqs. (4.20) and (4.6) that

$$\tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot\bar{\mu}=(\epsilon-1)(2\epsilon+1)/12\pi\epsilon. \tag{4.21}$$

This equation relates the dielectric constant ϵ to the short-range part of the entire two-particle distribution function n_2. Equation (4.21) was found by Kirkwood[1] in the special case of a spherical sample volume V embedded in an infinite dielectric with the same dielectric constant.

In the special case that $\bar{\mu}=\boldsymbol{\mu}$, Eq. (4.21) reduces to the Onsager formula[16,2]

$$\tfrac{1}{3}\beta\rho\mu^2=(\epsilon-1)(2\epsilon+1)/12\pi\epsilon \tag{4.22}$$

for the dielectric constant ϵ of a polar fluid of rigid dipoles. The formula (4.22) was derived by Onsager by adopting the model that each molecule is a dipole $\boldsymbol{\mu}$ in an impenetrable spherical cavity and that the molecules interact with the medium outside their cavity according to the macroscopic theory of dielectrics. It is interesting to note that we obtain the equality $\bar{\mu}=\boldsymbol{\mu}$ if we assume in Eq. (4.19) that

$$n_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)=0, \qquad \text{if } |\mathbf{r}_1-\mathbf{r}_2|<\lambda,$$
$$n_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)=(\rho^2/\Omega^2)+G_2^{(1)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2), \qquad \text{if } |\mathbf{r}_1-\mathbf{r}_2|>\lambda. \tag{4.23}$$

The assumption (4.23) corresponds to the picture of hard spheres with diameter λ, interacting with each other according to the effective long-range interaction which we found for separations larger than λ. Our molecular expression for $\bar{\mu}(\boldsymbol{\omega}_1)$, Eq. (4.20), gives a formal molecular expression for the Kirkwood "g"

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factor[1] introduced by the definition $\bar{\mu}=g\boldsymbol{\mu}$ completely in terms of short-range quantities.

V. ILLUSTRATION FOR SPECIAL GEOMETRIES

When the surrounding continuum in W has the same dielectric constant ϵ as the molecular fluid, the long-range part of the two-particle distribution function involves the reaction field tensor $\mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})$, which for arbitrary geometries is a difficult quantity to compute. However, for favorable geometries $\mathsf{R}_{(V+W)}{}^*$ can be investigated. In this section we explicitly treat a few favorable geometries in order to illustrate the crucial role played by this part of the two-particle distribution function.

We shall show explicitly that the molecular two-particle distribution function when employed to calculate the relation (3.5) between the polarization $\mathbf{P}_V$ and the external field $\mathbf{E}_0$ for some special geometries leads to complete agreement with the relation between $\mathbf{P}_V$ and $\mathbf{E}_0$ according to the macroscopic theory. The two long-range terms T and $\mathsf{R}_{(V+W)}{}^*$ are essential for this agreement. Clearly this agreement must be found in our development since the molecular expression for $G_2{}^{(1)}$, Eq. (4.11), has been shown to be consistent with the constitutive relation Eq. (2.14) with a molecular expression for the dielectric constant that is independent of the sample shape and the surroundings.

A. Sphere in Vacuum

First, we consider a sphere in vacuum with radius a, volume V, filled with the molecular fluid. The external field $\mathbf{E}_0$ in the absence of the sphere arises from fixed external charges and is taken to be uniform. Because the molecular fluid is a dielectric with dielectric constant ϵ, the macroscopic field $\mathbf{E}(\mathbf{r})$ in the presence of the sphere is homogeneous within the sphere. The expression for $\mathbf{E}(\mathbf{r})$ is[17]

$$\mathbf{E}(\mathbf{r})=[3/(\epsilon+2)]\mathbf{E}_0 \qquad \text{for } \mathbf{r} \text{ in the sphere.} \tag{5.1}$$

The total dipole moment of the sphere is given by

$$V\mathbf{P}_V=[(\epsilon-1)/4\pi][3/(\epsilon+2)]V\mathbf{E}_0. \tag{5.2}$$

According to the statistical mechanical theory the expression for the total dipole moment in V is

$$V\mathbf{P}_V=\beta\langle\mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_0\cdot\mathbf{E}_0, \tag{5.3}$$

which follows from Eq. (3.5) for the case that $\mathbf{E}_0$ is homogeneous. Here $\mathbf{M}$ is the total dipole moment of the molecules

$$\mathbf{M}(\boldsymbol{\omega}^N)=\sum_{i=1}^{N}\boldsymbol{\mu}(\boldsymbol{\omega}_i). \tag{5.4}$$

The average $\langle\ \rangle_0$ denotes an average over a canonical ensemble for a fluid in the special geometry of a sphere in vacuum in the absence of the external field $\mathbf{E}_0$. From Eqs. (5.2) and (5.3) it follows that

$$\beta V^{-1}\langle\mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_0=[(\epsilon-1)/4\pi][3/(\epsilon+2)]\mathsf{U}. \tag{5.5}$$

Equation (5.5) is derived by using the property that the fluid is a dielectric with dielectric constant ϵ. One notices that Eq. (1.4) follows if one takes the trace in Eq. (5.5). We shall now show that when our expression for n_2 Eq. (4.12) is used to compute the polarization fluctuation $\langle\mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_0$ for this geometry we obtain exact agreement with Eq. (5.5).

By using Eqs. (3.12) and (3.14) for n_1 and n_2 one easily shows that

$$\beta V^{-1}\langle\mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_0=\tfrac{1}{3}\beta\rho\mu^2\mathsf{U}+\beta\int d\boldsymbol{\omega}_1d\boldsymbol{\omega}_2 \times\psi_2{}^0(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_1)\boldsymbol{\mu}(\boldsymbol{\omega}_2), \tag{5.6}$$

where $\psi_2(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)$ is the angular two-particle correlation function defined by

$$\psi_2(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)=V^{-1}\int_V d\mathbf{r}_1d\mathbf{r}_2G_2(\mathbf{r}_1,\boldsymbol{\omega}_1,\mathbf{r}_2,\boldsymbol{\omega}_2). \tag{5.7}$$

The superscript zero on $\psi_2{}^0$ in Eq. (5.6) indicates that this is the form appropriate to a sphere in vacuum. From Eqs. (3.24) and (4.11) it is clear that to compute ψ_2 we must in general integrate $G_2{}^{(0)}$, T and $\mathsf{R}_{(V+W)}{}^*$ over $\mathbf{r}_1$ and $\mathbf{r}_2$. For the case of a sphere in vacuum the region W is zero and the reaction field tensor $\mathsf{R}_V{}^*$ is given by Eq. (A13) in Appendix A with $\epsilon_0=\epsilon^{-1}$.

$$\mathsf{R}_V{}^*(\mathbf{r}_1,\mathbf{r}_2;\epsilon^{-1})=\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_2}\sum_{l=0}^{\infty}\frac{(1-\epsilon)(l+1)}{[\epsilon l+(l+1)]} \times\frac{r_1{}^lr_2{}^l}{a^{2l+1}}P_l(\cos\theta_{12}). \tag{5.8}$$

If we integrate Eq. (5.8) with respect to $\mathbf{r}_2$ over the sphere, only the term with $l=1$ contributes, and we find

$$\int_{\text{sphere}}d\mathbf{r}_2\mathsf{R}_V{}^*(\mathbf{r}_1,\mathbf{r}_2;\epsilon^{-1})=-\frac{2}{a^3}\frac{\epsilon-1}{\epsilon+2}\frac{4\pi}{3}a^3\mathsf{U} =-\frac{8\pi}{3}\frac{\epsilon-1}{\epsilon+2}\mathsf{U}. \tag{5.9}$$

The integration of T over the sphere is given by

$$\int_{\text{sphere}}d\mathbf{r}_2\mathsf{T}(\mathbf{r}_1,\mathbf{r}_2)=-\frac{4\pi}{3}\mathsf{U}, \qquad \text{if } r_1 \text{ is in the sphere,} \tag{5.10}$$

where the integration over the singularity has been taken into account according to Eq. (2.4). Consequently, for the sphere in vacuum we find

$$\psi_2{}^0(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)=\Gamma(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)-(\beta\rho^2/\Omega^2)[4\pi/(\epsilon+2)] \times[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]\cdot[\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)]. \tag{5.11}$$

Here Γ is the contribution to the angular two-particle

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correlation function due to $G_2^{(0)}$

$$\Gamma(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = V^{-1} \int d\mathbf{r}_1 d\mathbf{r}_2 G_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2). \quad (5.12)$$

Since $G_2^{(0)}$ is of short range the term Γ is strictly independent of sample shape and surroundings. Note that the last term in Eq. (5.11) is shape dependent and contains a finite contribution due to the reaction field tensor R_V^*. If the expression (5.11) is inserted in Eq. (5.6), one obtains the equality (5.5) precisely. In carrying out this step note that from Eq. (3.30) it follows that

$$\int d\boldsymbol{\omega}_2 \Gamma(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2) \boldsymbol{\mu}(\boldsymbol{\omega}_2) = (\rho/\Omega) \boldsymbol{\kappa}(\boldsymbol{\omega}_1) \quad (5.13)$$

and that the dielectric constant ϵ is given by Eq. (4.6). Hence we have shown that our result (4.11) for the long-range part of the two-particle correlation function G_2 leads to perfect agreement with the macroscopic theory for this special case.

B. Sphere Embedded in Continuum

We now consider the case of the same spherical molecular sample of the fluid with radius a, volume V embedded in an infinite continuum W with the same dielectric constant ϵ as the molecular fluid. The externally applied field is taken to be homogeneous and equal to $\mathbf{E}_1$ at large distances from the sphere. If the sphere is filled with the molecular fluid, the dielectric constant is constant all over the space, and the macroscopic electric field is $\mathbf{E}_1$ everywhere. In the absence of the molecular fluid in the sphere, we have a spherical cavity in an infinite dielectric. The field $\mathbf{E}_c$ in the cavity is related to the field $\mathbf{E}_1$ by[17]

$$\mathbf{E}_c = [3\epsilon/(2\epsilon+1)]\mathbf{E}_1. \quad (5.14)$$

One notices that $\mathbf{E}_c$ is the appropriate external field for the molecular sample in the sphere. If the cavity is filled with the fluid, the total dipole moment in the sphere is related to the cavity field by

$$V\mathbf{P}_V = [(\epsilon-1)/4\pi][(2\epsilon+1)/3\epsilon]V\mathbf{E}_c. \quad (5.15)$$

The statistical mechanical theory yields for this case

$$V\mathbf{P}_V = \beta\langle \mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_\infty \cdot \mathbf{E}_c, \quad (5.16)$$

where the average $\langle\ \rangle_\infty$ indicates an average over a canonical ensemble for a fluid in the special geometry of a sphere embedded in an infinite dielectric with the same dielectric constant ϵ. It follows from Eqs. (5.15) and (5.16) that

$$\beta V^{-1}\langle \mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_\infty = [(\epsilon-1)/4\pi][(2\epsilon+1)/3\epsilon]\mathsf{U}. \quad (5.17)$$

This equality follows from the fact that the fluid is a dielectric with dielectric constant ϵ. Equation (1.5) follows from Eq. (5.17) by taking the trace. We shall show that when our expression for n_2 Eq. (4.12) is used to compute the polarization fluctuation for this geometry we obtain exact agreement with Eq. (5.17).

By using Eqs. (3.12) and (3.14) for this case one easily shows

$$\beta V^{-1}\langle \mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_\infty = \tfrac{1}{3}\beta\rho\mu^2\mathsf{U} + \beta \int d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2 \times \psi_2^\infty(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_1)\boldsymbol{\mu}(\boldsymbol{\omega}_2). \quad (5.18)$$

The superscript ∞ on ψ_2 indicates that this is the form appropriate to a sphere embedded in a medium with the same dielectric constant. The surrounding volume W is now the entire space except for the sphere V. So for this case $(V+W)$ fills the entire universe and hence

$$\mathsf{R}_{(V+W)}^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon^{-1}) = 0. \quad (5.19)$$

Thus we find for $G_2^{(1)}$ for this case [cf. Eq. (4.11)]

$$G_{2,\infty}^{(1)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = (\beta\rho^2/\epsilon\Omega^2)[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)] \cdot \mathsf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot [\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)]. \quad (5.20)$$

Hence

$$\psi_2^\infty(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = \Gamma(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2) - (\beta\rho^2/\Omega^2)(4\pi/3\epsilon) \times [\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)] \cdot [\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)]. \quad (5.21)$$

Note that Γ is the same in the expression (5.11) for ψ_2^0 and in Eq. (5.21) for ψ_2^∞, since this quantity is independent of the geometry. If we substitute Eq. (5.21) in Eq. (5.18), we obtain Eq. (5.17) precisely with ϵ given by Eq. (4.6).

C. Infinite Layer

Another simple geometry which is used in calculations is an infinite layer of the molecular fluid with a finite thickness, which fills the region V in space where $0<z<d$. This geometry is an idealization of the experimental situation of a dielectric slab which fills the region between two large plane parallel capacitor plates. If we apply a homogeneous external field $\mathbf{E}_0$, not necessarily along the z axis, one finds from Maxwell's equations that the field $\mathbf{E}$ inside the layer is homogeneous and related to $\mathbf{E}_0$ by

$$\mathbf{E} = \begin{pmatrix} 1 & & \\ & 1 & \\ & & \epsilon^{-1} \end{pmatrix} \cdot \mathbf{E}_0, \qquad \text{inside the layer} \quad (5.22)$$

and the polarization of the layer is given by

$$\mathbf{P}_V = [(\epsilon-1)/4\pi] \begin{pmatrix} 1 & & \\ & 1 & \\ & & \epsilon^{-1} \end{pmatrix} \cdot \mathbf{E}_0. \quad (5.23)$$

If we compare Eq. (5.23) with the molecular theory we obtain

$$\beta V^{-1}\langle \mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_l = [(\epsilon-1)/4\pi] \begin{pmatrix} 1 & & \\ & 1 & \\ & & \epsilon^{-1} \end{pmatrix}, \quad (5.24)$$

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where the average $\langle\ \rangle_l$ denotes an average over a canonical ensemble for a fluid layer in vacuum in the absence of the external field $\mathbf{E}_0$. Strictly speaking, the volume V is infinite for the layer. However, the average $\langle\mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_l$ is proportional to the volume, and if we consider the left-hand side of Eq. (5.24) as the limit of a finite layer, the ratio is finite and the equation will be valid in this limit. In the same way as above we may show that

$$\beta V^{-1}\langle\mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle_l=\tfrac{1}{3}\beta\rho\mu^2\mathbf{U}+\beta\int d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2 \times\psi_2^l(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_1)\boldsymbol{\mu}(\boldsymbol{\omega}_2). \quad (5.25)$$

The angular two-particle correlation function ψ_2^l is defined by

$$\psi_2^l(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)=V^{-1}\int_V d\mathbf{r}_1 d\mathbf{r}_2 G_{2,l}(\mathbf{r}_1,\boldsymbol{\omega}_1;\mathbf{r}_2,\boldsymbol{\omega}_2) \quad (5.26)$$

or, more precisely, the right-hand side of Eq. (5.26) in the limit of an infinite layer. The function $G_{2,l}$ is the two-particle correlation function G_2 for this special geometry. The volume W is zero for this case, and $G_{2,l}$ contains a part with $\mathsf{R}_V^*(\mathbf{r}_1,\mathbf{r}_2;\epsilon^{-1})$. In Appendix A it is shown [see Eq. (A14)] that the contribution of R_V^* to ψ_2^l is zero. The contribution of the integration of T for the layer is given in Appendix A by Eq. (A16). From these equations we obtain the expression for ψ_2^l

$$\psi_2^l(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)=\Gamma(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2)-4\pi(\beta\rho^2/\epsilon\Omega^2) \times[\boldsymbol{\mu}(\boldsymbol{\omega}_1)+\boldsymbol{\kappa}(\boldsymbol{\omega}_1)]_z[\boldsymbol{\mu}(\boldsymbol{\omega}_2)+\boldsymbol{\kappa}(\boldsymbol{\omega}_2)]_z. \quad (5.27)$$

If we substitute Eq. (5.27) in Eq. (5.25), we obtain precisely the relation (5.24).

Hence we showed explicitly that for these geometries the general result Eq. (4.11) leads to the correct macroscopic behavior. The different long-range parts of the two-particle correlation functions for these cases result in different angular two-particle correlation functions [Eqs. (5.11), (5.21), and (5.27)] and in different values for $\beta V^{-1}\langle\mathbf{M}(\boldsymbol{\omega}^N)\mathbf{M}(\boldsymbol{\omega}^N)\rangle$. However, these differences are just what is required to make the expressions (5.5), (5.17), and (5.24) for different geometries consistent with a single shape-independent dielectric constant, which is defined in a molecular way by Eq. (4.6). The differences in the angular two-particle correlation functions ψ_2 arise from the fact that the term with T in $G_2^{(1)}$ [Eq. (4.11)] is integrated over different volumes, and that the reaction field tensor $\mathsf{R}_{(V+W)}^*$ explicitly depends on the shape of the sample volume V and the surrounding volume W.

VI. CONCLUSIONS

In this article we have developed a molecular theory for strongly polar dielectric fluids of arbitrary sample shape that may or may not be embedded in a dielectric continuum. One important conclusion is that the constitutive relation between the local polarization and the local macroscopic electric field is valid, provided that the molecular sample has macroscopic dimensions and provided that the external field does not vary too strongly over microscopic distances. Consequently, the dielectric constant that appears in the constitutive relation is independent of the sample shape and the nature of the surroundings. We have given a formal molecular expression for the dielectric constant in terms of shape-independent quantities.

The most important result of this investigation is the explicit expression that we have obtained by graphical techniques for the two-particle correlation function G_2 for large separation. This expression applies for the sample V in vacuum or when the sample is embedded in a continuum of arbitrary shape in a volume W, which has the same dielectric constant as the sample. The two-particle correlation function has two long-range terms. One of these terms involves T, the dipole–dipole tensor, which when integrated over particle positions will lead to sample shape-dependent results. The second term involves a tensor which is identified to be the same as the reaction field tensor arising from the region outside $(V+W)$, when it is filled with a dielectric of dielectric constant ϵ^{-1}. This second term is explicitly shape dependent and is proportional to the inverse of the total volume $(V+W)$.

An interesting consequence of the theory is that $G_2^{(1)}$ inside the sample is the same when we consider the sample surrounded by a continuum W and when we consider both the sample volume V and the volume of the surrounding region W to be filled with the molecular fluid. One of the differences between these two situations is that V is an "open" system when $(V+W)$ is filled with the molecular fluid. In general we may expect this difference to give rise to an additional term in n_2 proportional to V^{-1}.[18] This term is not explicitly included in our development because of the thermodynamic limit implicit in our use of the graphical expansion, i.e., $G_2^{(0)}$ contains no terms proportional to V^{-1}.[19] We expect that proper inclusion of this term would not affect our results for the polarization or the dielectric constant because the orientation-dependent part of this term is likely to be of short range.

As the molecular sample becomes larger our theory becomes progressively more exact. In the thermodynamic limit $\mathsf{R}_V^*=0$ and our treatment is exact if one accepts the graphical expansion for the dipolar system. Conversely, as the molecular sample becomes smaller the theory is less exact. Taking into account higher order terms in δ will not be useful since some terms of order V^{-1} have been omitted by use of the graphical expansion. It is likely that corrections of order V^{-1} to the dielectric constant are essentially shape dependent.

For special uniform polarization geometries we have explicitly shown that the long-range terms of G_2 are essential for obtaining results consistent with a shape-independent dielectric constant. The angular two-particle correlation function, obtained from G_2, is shape dependent. On the other hand, the position pair distri-

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bution function, obtained by integrating n_2 over the orientations, contains *no long-range contribution*. This latter part is of particular importance since most experiments designed to probe two-particle distribution functions directly are not sensitive to the orientational dependence and measure therefore only the position pair distribution function.

The long-range part of the two-particle distribution function in the absence of the external field causes the polarization to be a geometry-dependent functional of the external field. This same two-particle distribution function is related to the thermodynamic quantities of the system, such as the Helmholtz free energy, the pressure, the internal energy, when there are no external fields. However, it may be shown that these thermodynamic quantities in the absence of the field are independent of the geometry to lowest order in δ. The thermodynamic properties of polar fluids will not be discussed further here.

In this article we have neglected fluctuations in the dipole moment of the molecules. The inclusion of a polarizability complicates the theory. Nevertheless in a similar way, as we used in this paper, it is possible to show that a system of polarizable molecules with or without a permanent dipole moment obeys the constitutive relation of the macroscopic theory of dielectrics. This will be demonstrated in a subsequent paper.

APPENDIX

We study the reaction field tensor $\mathbf{R}_V^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon_0)$ more explicitly for some special geometries. We consider a spherical cavity with radius a in an infinite dielectric with dielectric constant ϵ_0. We wish to find an expression for the reaction field tensor, and we shall accomplish this in several steps. First, we calculate the potential Φ due to a point charge Q inside the cavity. We choose a coordinate system with the origin in the center of the spherical cavity and with the point charge on the z axis. The distance between the charge and the origin is called b. Because Q is inside the spherical cavity, we know that $b<a$. The geometry is invariant for rotations about the z axis. If we use spherical coordinates (r, ϕ, θ), then Φ does not depend upon the azimuth angle ϕ. From Maxwell's equations it follows that[17]

$$\epsilon(r)\,(\partial\Phi/\partial r) \text{ is continuous at } r=a, \qquad \text{(A1)}$$

where

$$\epsilon(r)=\epsilon_0, \quad \text{if } r>a,$$
$$\epsilon(r)=1, \quad \text{if } r<a, \qquad \text{(A2)}$$

and

$$\Phi \text{ is continuous at } r=a. \qquad \text{(A3)}$$

Moreover, if we introduce the potential Φ_1 by

$$\Phi(r,\theta)=Q[r^2+b^2-2rb\cos\theta]^{-1/2}+\Phi_1(r,\theta), \qquad \text{(A4)}$$

then Φ_1 is the potential due to the polarization in the dielectric which is caused by the presence of the charge Q. This potential Φ_1 must obey the Laplace equation

$$\nabla^2\Phi_1=0 \quad \text{if } r<a \text{ and if } r>a. \qquad \text{(A5)}$$

Laplace's equation is not valid at the boundary $r=a$ because of the discontinuity in the dielectric constant. Because of the axial symmetry of the geometry the potential Φ_1 is of the form[17]

$$\Phi_1(r,\theta)=\sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta), \qquad \text{if } r<a,$$

$$\Phi_1(r,\theta)=\sum_{l=0}^{\infty} B_l r^{-l-1} P_l(\cos\theta), \qquad \text{if } r>a, \qquad \text{(A6)}$$

where the functions P_l are the Legendre polynomials. Note that Φ_1 has no singularities and goes to zero if r tends to infinity. The potential due to the point charge Q can be expanded as

$$Q[r^2+b^2-2rb\cos\theta]^{-1/2} = \sum_{l=0}^{\infty} Qb^l r^{-l-1} P_l(\cos\theta), \qquad \text{if } r>b. \qquad \text{(A7)}$$

The condition (A3) requires that

$$A_l a^l = B_l a^{-l-1}, \qquad \text{(A8)}$$

whereas we obtain from Eq. (A1)

$$\epsilon_0 B_l(l+1)a^{-l-2}+\epsilon_0 Qb^l(l+1)a^{-l-2} = -A_l l a^{l-1}+Qb^l(l+1)a^{-l-2}. \qquad \text{(A9)}$$

In obtaining Eq. (A9) we make use of Eq. (A7) and the fact that $b<a$. From Eqs. (A8) and (A9) one finds

$$A_l=Q\{(1-\epsilon_0)(l+1)b^l/[l+\epsilon_0(l+1)]a^{2l+1}\}. \qquad \text{(A10)}$$

Thus the potential Φ_1 at $\mathbf{r}_1$ due to the polarization of the medium caused by the presence of the charge Q at $\mathbf{r}_0$ is

$$\Phi_1(\mathbf{r}_1)=Q\sum_{l=0}^{\infty}\frac{(1-\epsilon_0)(l+1)}{[l+\epsilon_0(l+1)]}\frac{r_0^l r_1^l}{a^{2l+1}}P_l(\cos\theta_{01}), \qquad \text{(A11)}$$

where θ_{01} is the angle between $\mathbf{r}_0$ and $\mathbf{r}_1$. Hence the potential at $\mathbf{r}_1$ due to the polarization of the medium caused by a dipole $\mathbf{p}$ at $\mathbf{r}_0$ is

$$\mathbf{p}\cdot\frac{\partial}{\partial\mathbf{r}_0}\sum_{l=0}^{\infty}\frac{(1-\epsilon_0)(l+1)}{[l+\epsilon_0(l+1)]}\frac{r_0^l r_1^l}{a^{2l+1}}P_l(\cos\theta_{01})$$
$$\text{if } r_0<a \text{ and } r_1<a. \qquad \text{(A12)}$$

The reaction field tensor is thus given by

$$\mathbf{R}_V^*(\mathbf{r}_1,\mathbf{r}_0;\epsilon_0)=\frac{\partial}{\partial\mathbf{r}_1}\frac{\partial}{\partial\mathbf{r}_0}\sum_{l=0}^{\infty}\frac{(\epsilon_0-1)(l+1)}{[l+\epsilon_0(l+1)]}\frac{r_0^l r_1^l}{a^{2l+1}}P_l(\cos\theta_{01}),$$
$$\text{if } r_0<a \text{ and } r_1<a. \qquad \text{(A13)}$$

This tensor is zero if $\epsilon_0=1$, as it should be. The expansion (A13) converges if $r_0<a$ and $r_1<a$. One easily checks that $\mathbf{R}_V^*$ can get large if $\mathbf{r}_0$ and $\mathbf{r}_1$ are close to the boundary and simultaneously close to each other. If we multiply a and the vectors $\mathbf{r}_0$ and $\mathbf{r}_1$ with a certain factor,

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we find that R_V^* is proportional to the inverse of the volume V of the cavity.

Another geometry of interest is a layer in the region V of space where $0<z<d$. We are interested in the reaction field tensor $\mathsf{R}_V^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon_0)$. Although we shall not write down an explicit formula for this tensor, we shall show that

$$\int_V d\mathbf{r}_2 \mathsf{R}_V^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon_0) = 0. \qquad \text{(A14)}$$

For that purpose we remark that the field $\mathbf{E}_P$ due to a homogeneously polarized layer with polarization $\mathbf{P}_0$ is given by

$$\mathbf{E}_P = \begin{pmatrix} 0 & & \\ & 0 & \\ & & -4\pi \end{pmatrix} \cdot \mathbf{P}_0, \quad \text{in the layer,}$$

and

$$\mathbf{E}_P = 0, \qquad \text{outside the layer.} \qquad \text{(A15)}$$

This follows if we recall that the field due to a homogeneously polarized sample is caused in effect only by a polarization surface charge density which is equal to $-\mathbf{P}_0 \cdot \mathbf{n}$,[17] where $\mathbf{n}$ is the outward unit vector normal to the surface. Because the resulting field $\mathbf{E}_P$ given by Eq. (A15) is zero outside the layer, this field cannot induce a polarization in a dielectric outside the layer V. Hence the reaction field caused by the entire homogeneously polarized layer is zero, which proves Eq. (A14). Moreover, it follows from Eq. (A15) that

$$\int_{\text{layer}} d\mathbf{r}_2 \mathsf{T}(\mathbf{r}_1, \mathbf{r}_2) = \begin{pmatrix} 0 & & \\ & 0 & \\ & & -4\pi \end{pmatrix}, \quad \text{if } \mathbf{r}_1 \text{ is in the layer.} \qquad \text{(A16)}$$

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[15] Related work on the asymptotic form of the two-particle distribution function for polar fluids has been presented by D. W. Jepsen, J. Chem. Phys. **45**, 709 (1966) and F. M. Kuni, Phys. Letters **26A**, 305 (1968). We thank the referee for drawing our attention to this work. Kuni's analysis appears to be restricted to the infinite volume case. Comparison of our result for this special geometry Eq. (5.20) and Kuni's results show that Kuni's result differs from ours by a factor of $[3/2\epsilon+1]$.

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[19] This difference and the question of the applicability of the graphical expansion for finite V discussed in Footnote (12) would formally be resolved if we had carried out the entire analysis in the grand canonical ensemble rather than the canonical ensemble. We were reluctant to adopt the grand canonical ensemble formalism since we regard the question of the equivalence of the two ensembles (not proven for finite dipolar systems) to involve the issues raised in this paper since we find a nonnegligible interaction between the sample and the surroundings.

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