dielectric constant could then be explained as being almost entirely associated with the observed density maximum[2] for the system.

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Structure of Dielectric Fluids. II. The Free Energy and the Kerr Effect in Polar Fluids*

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The Helmholtz free energy of a molecular fluid of rigid dipoles in the absence of any external field is studied. An explicit formal expression for the excess free energy due to the dipolar interaction is found. It is shown that the free energy per particle is independent of the shape of the sample, although shape-dependent long-range correlations are present in the fluid. For the special case of the Onsager model of polar fluids an explicit expression is obtained for the contribution to the free energy due to the dipolar interactions. Next, we study the long-range part of the three-particle correlation function for an arbitrarily shaped sample of the molecular fluid in the absence of an external field. This long-range part is dependent on the shape of the sample. The three-particle correlation function arises in the expression for the Kerr constant, which measures the birefringence of the fluid when a strong electric field is applied. We show explicitly that, in the lowest nonvanishing order in the field, the birefringence is proportional to the square of the resulting local macroscopic electric field with a proportionality constant (the Kerr constant) which is independent of the shape of the sample. A formal expression is given for the Kerr constant in terms of the local properties of the fluid.

I. INTRODUCTION

This paper is the second in a series dealing with the structure of dielectric fluids. In the first paper[1] we obtained an explicit expression for the long-range part of the two-particle correlation function for a molecular sample of rigid dipoles in a volume of arbitrary shape V. Included in the analysis was the possibility that the molecular sample V was surrounded by a dielectric continuum of arbitrary shape W. The basic result is that the two-particle correlation function has a long-range part that can be split into two terms. One term involves the dipole–dipole interaction tensor. This term, while not explicitly shape dependent, gives a shape-dependent result when an integration is performed over the volume V. The second term is explicitly dependent on the shape of the sample and the surround-

ings, but it is proportional to the inverse of the volume $(V+W)$. Therefore this second term will vanish in the thermodynamic limit. On the other hand, the contribution of this second term is not negligible when the two-particle correlation function appears in an integral where the range of integration effectively covers the entire volume. Such situations arise in the calculation of the dielectric constant in terms of a fluctuation formula and in the calculation of the reduced two-particle angular correlation function.

Knowledge of the two-particle correlation function may be used to determine the thermodynamic properties of the system. One purpose of the present paper is to examine the statistical thermodynamics of the dipolar fluid. We show how the Helmholtz free energy of a polar fluid may be related to the Helmholtz free energy of a reference fluid once the two-particle dis-

tribution function for the dipolar system is known. In the reference system molecules interact with exactly the same short-range forces present in the dipolar system, but the molecules have zero dipole moment. We restrict our attention to the case where W is zero, i.e., the molecular volume V is in vacuum, and demonstrate that the Helmholtz free energy of the polar fluid does not depend on the shape of the sample. The same is true for the pressure and for the internal energy.

The molecular theory in I demonstrated that a shape-independent dielectric constant ϵ is consistent with a long-range, shape-dependent two-particle correlation function. A formal molecular expression for the dielectric constant was obtained in terms of the shape-independent short-range part of the two-particle correlation function. Alternatively, the dielectric constant may be computed according to

$$(\epsilon-1)/4\pi = \lim_{E\to 0}[\mathbf{P}(\mathbf{r})\cdot\mathbf{e}/|\mathbf{E}(\mathbf{r})|], \quad (1.1)$$

where $\mathbf{E}$ is the average macroscopic field at $\mathbf{r}$, $\mathbf{e}$ is a unit vector in the direction of $\mathbf{E}$, and $\mathbf{P}(\mathbf{r})$ is the polarization defined by

$$\mathbf{P}(\mathbf{r}) = \langle\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\,\boldsymbol{\mu}(\omega_i)\rangle_{\mathbf{E}_0}. \quad (1.2)$$

In Eq. (1.2) $\boldsymbol{\mu}(\omega_i)$ is the dipole moment of molecule i with orientation ω_i, and the angular bracket with subscript $\mathbf{E}_0$ denotes an average over all molecular configurations in the presence of the external electric field $\mathbf{E}_0(\mathbf{r})$. For small $\mathbf{E}_0$, $\mathbf{P}(\mathbf{r})$ involves averages over the one- and two-particle distribution functions in the absence of any external field [see Eqs. (3.5)–(3.7) of I]. In general the relation between $\mathbf{E}_0(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ will be dependent on sample geometry. In I it was demonstrated that the shape dependence of the two-particle distribution function in the absence of $\mathbf{E}_0$ compensates the shape dependence of the relation between $\mathbf{E}_0(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$, so that one recovers, for all geometries, a shape-independent dielectric constant defined in terms of the short-range shape-independent part of the two-particle correlation function.

Another important property of dipolar fluids is manifest in the Kerr effect. The Kerr effect measures the difference in the refractive index for light polarized parallel $n_{||}$ and perpendicular $n_\perp$ to a strong static electric field $\mathbf{E}$. The effect is customarily expressed in terms of the Kerr constant[2-4]

$$K = \lim_{E\to 0}\{[n_{||}(\mathbf{r})-n_\perp(\mathbf{r})]/|\mathbf{E}(\mathbf{r})|^2\}. \quad (1.3)$$

The refractive index $n_p(\mathbf{r})$ at point $\mathbf{r}$ for light propagating at optical frequencies with polarization in the direction $\mathbf{e}_p$ is given by the Clausius–Mossotti formula

$$\frac{n_p^2(\mathbf{r})-1}{n_p^2(\mathbf{r})+2} = \tfrac{4}{3}\pi\langle\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\,\boldsymbol{\alpha}(\omega_i):\mathbf{e}_p\mathbf{e}_p\rangle_{\mathbf{E}_0}. \quad (1.4)$$

Here $\boldsymbol{\alpha}(\omega_i)$ is the anisotropic polarizability tensor of molecule i with orientation ω_i. If the refractive index

is close to unity it follows from Eq. (1.3) that the Kerr constant may be expressed as

$$K = \lim_{E\to 0}2\pi\,|\,\mathbf{E}(\mathbf{r})\,|^{-2}\langle\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\,\boldsymbol{\alpha}(\omega_i):\boldsymbol{\sigma}(\mathbf{r})\rangle_{\mathbf{E}_0}, \quad (1.5)$$

where $\boldsymbol{\sigma}(\mathbf{r}) = \mathbf{e}_{||}(\mathbf{r})\mathbf{e}_{||}(\mathbf{r}) - \mathbf{e}_\perp(\mathbf{r})\mathbf{e}_\perp(\mathbf{r})$, and $\mathbf{e}_{||}(\mathbf{r})$ and $\mathbf{e}_\perp(\mathbf{r})$ are unit vectors parallel and perpendicular to the local macroscopic field $\mathbf{E}(\mathbf{r})$. We may rewrite this expression as

$$K = \lim_{E\to 0}2\pi\,|\,\mathbf{E}(\mathbf{r})\,|^{-2}\,\mathbf{Q}(\mathbf{r}):\boldsymbol{\sigma}(\mathbf{r}) \quad (1.6)$$

with

$$\mathbf{Q}(\mathbf{r}) = \langle\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)[\boldsymbol{\alpha}(\omega_i)-\tfrac{1}{3}\mathbf{I}\,\mathrm{Tr}\,\boldsymbol{\alpha}]\rangle_{\mathbf{E}_0}, \quad (1.7)$$

where, for convenience, the trace of the polarizability tensor is subtracted in the definition of $\mathbf{Q}(\mathbf{r})$ [note that the unit tensor $\mathbf{I}$ obeys $\mathbf{I}:\boldsymbol{\sigma}(\mathbf{r})=0$].

In the limit of small external field $\mathbf{Q}(\mathbf{r})$ is proportional to $|\,\mathbf{E}_0\,|^2$. As in the case of the dielectric constant one may question if the shape-dependent relationship between $\mathbf{E}_0(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ is compensated by the shape dependence of the particle distribution functions that occur in the zero-field averages that arise when $\mathbf{Q}(\mathbf{r})$ is expanded in terms of $\mathbf{E}_0$. The second purpose of this paper is to demonstrate that this compensation does take place and that the Kerr constant for a strongly polar fluid is independent of sample geometry.

The situation is more complicated, however, than that encountered in the case of the dielectric constant. The reason is that when $\mathbf{Q}(\mathbf{r})$ is expanded averages over the two- and three-particle distribution functions are encountered. Thus in order to examine the Kerr constant one must generalize the theory developed in I to the three-particle distribution function and determine the long-range nature of this higher-order distribution function. The analysis of the Kerr constant presented here is an important test of our theory of polar fluids, since it demonstrates that the techniques we have developed may be used to obtain higher-order distribution functions.

It is important to note that the Kerr constant defined according to Eq. (1.5) is closely related to the alignment which is measured in the NMR electric field effect.[4,5] Furthermore, detailed interpretation of Kerr constant experiments for actual systems must take into account the hyperpolarizability.[2,4] We assume the hyperpolarizability to be zero in our model polar fluid, since our intent is to focus on the long-range nature of the zero-field three-particle correlation function. Finally, we wish to emphasize that the definition of the Kerr constant involves the refractive index for light polarized parallel and perpendicular to the local macroscopic field $\mathbf{E}(\mathbf{r})$, *not* the external field $\mathbf{E}_0(\mathbf{r})$. This Kerr constant will be geometry independent. Since the relation between $\mathbf{E}_0$ and $\mathbf{E}$ is in general geometry dependent, one may not in all cases measure these re-

fractive indices parallel and perpendicular to E_0 and expect the resulting quantity to be independent of sample shape.

The reader may wish to know with what confidence we regard the results for the distribution functions in this paper and Paper I. Our view is that, while we are not prepared (or interested) to argue that the derivation is completely rigorous, we feel strongly that the results are exact for large separation, to the order mentioned.

II. STATISTICAL THERMODYNAMICS OF THE DIPOLAR SYSTEM

We consider a system of N rigid dipoles, each with dipole moment $\lambda^{1/2}\mathbf{\mu}$ in a volume V of arbitrary shape. The potential energy of interaction is

$$U(\lambda) = \sum_{i<j}\sum \left[v(\mathbf{r}_i, \omega_i; \mathbf{r}_j, \omega_j) \right.$$
$$\left. - \lambda\mathbf{\mu}(\omega_i)\cdot\mathbf{T}(\mathbf{r}_i, \mathbf{r}_j)\cdot\mathbf{\mu}(\omega_j) \right], \quad (2.1)$$

where $\mathbf{r}_i$, ω_i denote, respectively, the position and orientation of particle i, $v(\mathbf{r}_i, \omega_i; \mathbf{r}_j, \omega_j)$ is a short-ranged pair potential that may depend on orientation, and $\mathbf{T}$ is the dipole–dipole tensor

$$\mathbf{T}(\mathbf{r}, \mathbf{r}') = -\nabla_r\nabla_{r'}|\mathbf{r}-\mathbf{r}'|^{-1}$$
$$= [3(\mathbf{r}-\mathbf{r}')(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^5] - (\mathbf{I}/|\mathbf{r}-\mathbf{r}'|^3), \quad (2.2)$$

where $\mathbf{I}$ is the unit dyadic. If $\lambda=1$, $U(\lambda)$ refers to the potential energy of the dipolar system of interest. If $\lambda=0$, then U is the potential energy of a reference system where the molecules interact exclusively by the short-ranged potential v. For λ between zero and one the configurational free energy $A(\lambda)$ is related to the configurational partition function $Z(\lambda)$ by

$$\exp[-\beta A(\lambda)] = Z(\lambda) = (V\Omega)^{-N}$$
$$\times \int_V d\mathbf{r}^N d\omega^N \exp[-\beta U(\lambda)], \quad (2.3)$$

where $\Omega = \int d\omega$.

It is an easy matter to show by differentiation followed by integration of $\ln Z(\lambda)$ with respect to λ that

$$A(1) - A(0) = (-kT)\int_0^1 d\lambda [Z(\lambda)]^{-1}\frac{\partial Z(\lambda)}{\partial \lambda}$$
$$= -\frac{1}{2}\int_0^1 d\lambda \int_V d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2$$
$$\times n_2(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda)$$
$$\times \mathbf{\mu}(\omega_1)\cdot\mathbf{T}(\mathbf{r}_1, \mathbf{r}_2)\cdot\mathbf{\mu}(\omega_2). \quad (2.4)$$

Here, $n_2(\lambda)$ is the two-particle distribution function for the polar system when the molecules have dipole moment $\lambda^{1/2}\mathbf{\mu}$.

In I the following expression was found for n_2,

$$n_2(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda) = \rho^2/\Omega^2 + G_2^{(0)}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda)$$
$$+ G_2^{(1)}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda), \quad (2.5)$$

where ρ is the particle number density. The function $G_2^{(0)}$ is strictly of short range for every value of λ between zero and unity, and only depends upon the density, temperature, and the value of the dipole moment. The function $G_2^{(1)}$ is the long-range part of the two-particle correlation function and for the case of the molecular sample V in vacuum, $G_2^{(1)}$ is given by

$$G_2^{(1)}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda) = (\beta\rho^2/\Omega^2)\lambda^{1/2}\mathbf{\mu}_{\mathrm{eff}}(\omega_1; \lambda)$$
$$\cdot\mathbf{F}(\mathbf{r}_1, \mathbf{r}_2; \lambda)\cdot\lambda^{1/2}\mathbf{\mu}_{\mathrm{eff}}(\omega_2; \lambda). \quad (2.6)$$

In Eq. (2.6) $\mathbf{F}$ is the effective interaction tensor

$$\mathbf{F}(\mathbf{r}, \mathbf{r}'; \lambda) = [1/\epsilon(\lambda)]\{\mathbf{T}(\mathbf{r}_1\mathbf{r}') + \mathbf{R}_V^*(\mathbf{r}, \mathbf{r}'; \epsilon^{-1}(\lambda))\}$$
$$(2.7)$$

where $\mathbf{R}_V^*\cdot\mathbf{p}$ has the interpretation of the reaction field established at the point $\mathbf{r}$ in V by a dipole $\mathbf{p}$ at $\mathbf{r}'$ in V, when V is empty and the surroundings are filled with a dielectric continuum characterized by the dielectric constant $\epsilon^{-1}(\lambda)$. The dielectric constant of the polar fluid $\epsilon(\lambda)$ is given by

$$[\epsilon(\lambda) - 1]/4\pi = \tfrac{1}{3}\beta\rho\lambda^{1/2}\mathbf{\mu}\cdot\lambda^{1/2}\mathbf{\mu}_{\mathrm{eff}}(\lambda), \quad (2.8)$$

where $\lambda^{1/2}\mathbf{\mu}_{\mathrm{eff}}$ is an effective dipole moment defined by

$$\lambda^{1/2}\mathbf{\mu}_{\mathrm{eff}}(\omega_1; \lambda) = \lambda^{1/2}\mathbf{\mu}(\omega_1) + \mathbf{\kappa}(\omega_1; \lambda). \quad (2.9)$$

The vector $\mathbf{\kappa}(\omega_1, \lambda)$ which appears in the effective dipole moment is defined in terms of $G_2^{(0)}$

$$(\rho/\Omega)\mathbf{\kappa}(\omega_1; \lambda)$$
$$= \int d\mathbf{r}_2 d\omega_2 \lambda^{1/2}\mathbf{\mu}(\omega_2) G_2^{(0)}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda). \quad (2.10)$$

It must be emphasized that the results quoted above for n_2 and $\epsilon(\lambda)$ follow directly from the molecular theory developed in I for the case $W=0$, and the reader is referred to this reference for the derivation.

In order to compute the free energy difference $A(1) - A(0)$, we substitute the expression for n_2, Eq. (2.5) into (2.4)

$$A(1) - A(0) = -\frac{1}{2}\int_0^1 d\lambda \int_V d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 \mathbf{\mu}(\omega_1)\cdot\mathbf{T}(\mathbf{r}_1, \mathbf{r}_2)\cdot\mathbf{\mu}(\omega_2)$$

$$\times \left(G_2^{(0)} + \frac{\beta\rho^2}{\Omega^2}\lambda\mathbf{\mu}_{\mathrm{eff}}(\omega_1; \lambda)\cdot\mathbf{F}(\mathbf{r}_1, \mathbf{r}_2; \lambda)\cdot\mathbf{\mu}_{\mathrm{eff}}(\omega_2; \lambda) \right). \quad (2.11)$$

Since the integrand contains a factor T and since R_V^* is proportional to V^{-1}, one may in general prove that the term R_V^* appearing in F leads to a negligible contribution to the integral as the volume becomes large. It follows that

$$A(1) - A(0) = -\frac{1}{2} \int_0^1 d\lambda \int_V d\mathbf{r}_1 d\omega_1 \int d\mathbf{r}_2 d\omega_2 \mathbf{\mu}(\omega_1) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{\mu}(\omega_2)$$

$$\times \left(G_2^{(0)} + \frac{\beta\rho^2\lambda}{\Omega^2\epsilon(\lambda)} \mathbf{\mu}_{\mathrm{eff}}(\omega_1; \lambda) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{\mu}_{\mathrm{eff}}(\omega_2; \lambda) \right), \quad (2.12)$$

where, due to the short range of $G_2^{(0)}$ and the effective short range of T^2, the integration over $\mathbf{r}_2$ may be extended over all space. Consequently, as V approaches infinity the integral term in Eq. (2.12) will be proportional to V and independent of sample shape. The term $A(0)$ is the Helmholtz free energy of a fluid with short-range interactions and thus may be assumed to be proportional to V in the thermodynamic limit. Thus we find in the thermodynamic limit that our expression for the Helmholtz free energy $A(1)$ of a fluid of molecules with a rigid dipole moment $\mathbf{\mu}$ is proportional to the volume V and independent of the sample shape as required for a thermodynamic system. This calculation cannot be regarded as a *proof* since it depends upon the correctness of the assumptions used in obtaining the expression for the two-particle distribution function n_2. Indeed in the derivation of n_2 in I we assumed uniform density and we assumed in the graphical expansion of n_2, the existence of certain integrals as V becomes large. A *proof* that $A(1)$ is a shape-independent, extensive quantity should not rely on these assumptions. Our calculation simply shows that the long-range shape-dependent n_2 derived in I is *consistent* with the expected thermodynamic character of a polar fluid. Of course it follows that the pressure and the internal energy are also independent of the sample shape, since these quantities are simply related to derivatives of the Helmholtz free energy.

The expression for $A(1) - A(0)$, Eq. (2.12), is also useful because it enables us to relate the free energy of the polar fluid to the free energy of a reference system $A(0)$ where the interactions are exclusively of short range. This is particularly desirable since a good deal is

known about the thermodynamics of systems which interact via short-range forces only. However, in order to proceed to calculate $[A(1) - A(0)]$ explicitly, we need information about $G_2^{(0)}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda)$ for $0 \leq \lambda \leq 1$. [Note that the dielectric constant $\epsilon(\lambda)$ and the unknown vector $\mathbf{\mu}_{\mathrm{eff}}$ are fully determined by $G_2^{(0)}$ according to Eqs. (2.8)–(2.10).] In general it will be difficult to compute $G_2^{(0)}$ and we must resort to approximations or inference from available experimental data. Here we restrict consideration to one possible approximation for $G_2^{(0)}$ to illustrate how $[A(1) - A(0)]$ may be computed. The approximation is based on a molecular picture inferred from Onsager's theory of the dielectric constant.

The Onsager model for a dielectric fluid implies that the two-particle distribution function n_2 has the form[1]

$$n_2(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda) = 0 \qquad \text{if } |\mathbf{r}_1 - \mathbf{r}_2| < a,$$

$$n_2(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda) = \rho^2/\Omega^2 + G_2^{(1)}(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \lambda)$$
$$\text{if } |\mathbf{r}_1 - \mathbf{r}_2| > a \quad (2.13)$$

for the case when the molecular core is considered to be a hard sphere. More complicated core geometries, e.g., ellipsoids, can be considered within the context of the Onsager model, but we shall not investigate these possibilities here. It follows from Eq. (2.5) that for the Onsager model

$$G_2^{(0)} = -[(\rho^2/\Omega^2) + G_2^{(1)}] \qquad \text{if } |\mathbf{r}_1 - \mathbf{r}_2| < a,$$

$$G_2^{(0)} = 0 \qquad \text{if } |\mathbf{r}_1 - \mathbf{r}_2| > a, \quad (2.14)$$

so that Eq. (2.12) becomes

$$V^{-1}[A(1) - A(0)] = -\frac{1}{2} \int_0^1 d\lambda \int_{|\mathbf{r}_2 - \mathbf{r}_1| > a} d\omega_1 d\mathbf{r}_2 d\omega_2 \mathbf{\mu}(\omega_1) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{\mu}(\omega_2)$$

$$\times \frac{\beta\rho^2}{\epsilon(\lambda)\Omega^2} \lambda \mathbf{\mu}_{\mathrm{eff}}(\omega_1; \lambda) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{\mu}_{\mathrm{eff}}(\omega_2; \lambda). \quad (2.15)$$

The quantities $\mathbf{\mu}_{\mathrm{eff}}(\omega; \lambda)$ and $\epsilon(\lambda)$ may also be computed according to this model. From Eqs. (2.10), (2.6), and (2.14) one finds

$$\frac{\rho}{\Omega} \mathbf{\kappa}(\omega_1; \lambda) = -\lambda^{1/2} \int_{|\mathbf{r}_2 - \mathbf{r}_1| < a} d\mathbf{r}_2 d\omega_2 \mathbf{\mu}(\omega_2) \frac{\beta\rho^2}{\epsilon(\lambda)\Omega^2} \lambda \mathbf{\mu}_{\mathrm{eff}}(\omega_1; \lambda) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{\mu}_{\mathrm{eff}}(\omega_2; \lambda), \quad (2.16)$$

where because of the restricted region of integration the $R_V{}^*$ term in $G_2{}^{(1)}$ has been neglected. The singularity in T is taken into account in this integral according to the usual prescription[1]

$$\int_{|r'-r|<a} dr'T(r_1 r') = -\tfrac{4}{3}\pi I, \qquad (2.17)$$

so that Eq. (2.16) becomes

$$\kappa(\omega_1;\lambda) = [\beta\rho/\epsilon(\lambda)](\lambda)^{3/2}(4\pi/9)\,\mathbf{\mu}\cdot\mathbf{\mu}_{\mathrm{eff}}(\lambda)\,\mathbf{\mu}_{\mathrm{eff}}(\omega_1;\lambda), \qquad (2.18)$$

which according to Eq. (2.8) may be expressed as

$$\kappa(\omega;\lambda) = \{[\epsilon(\lambda)-1]/3\epsilon(\lambda)\}\lambda^{1/2}\mathbf{\mu}_{\mathrm{eff}}(\omega;\lambda)$$

$$= \{[\epsilon(\lambda)-1]/3\epsilon(\lambda)\}[\lambda^{1/2}\mathbf{\mu}(\omega)+\kappa(\omega;\lambda)], \qquad (2.19)$$

so that κ and $\mathbf{\mu}_{\mathrm{eff}}$ are parallel to $\mathbf{\mu}$. From Eqs. (2.19) and (2.8) we obtain the Onsager formula for the dielectric constant

$$\tfrac{1}{3}\beta\rho\lambda\mu^2 = [\epsilon(\lambda)-1][2\epsilon(\lambda)+1]/12\pi\epsilon(\lambda). \qquad (2.20)$$

The quantity $A(1)-A(0)$ may now be computed for this model. The integral over ω_2 in Eq. (2.15) is performed, followed by the integration over $\mathbf{r}_2$ where one uses the fact that

$$\int_{|r_2-r_1|>a} dr_2 T(r_1, r_2)\cdot T(r_2, r_1) = \frac{8\pi}{3a^3} I. \qquad (2.21)$$

The result is

$$\frac{A(1)-A(0)}{V} = \frac{-4\pi\beta\rho^2}{a^3} \int_0^1 d\lambda \frac{\lambda}{\epsilon(\lambda)} [\tfrac{1}{3}\mathbf{\mu}\cdot\mathbf{\mu}_{\mathrm{eff}}(\lambda)]^2. \qquad (2.22)$$

With the use of Eqs. (2.8) and (2.20) this expression can be put in the form

$$\frac{A(1)-A(0)}{V} = -\frac{\rho\mu^2}{a^3} \int_0^1 d\lambda \frac{\epsilon(\lambda)-1}{2\epsilon(\lambda)+1}, \qquad (2.23)$$

which is the exact result for $A(1)-A(0)$ when the Onsager model is used for the two-particle distribution function. The quadrature in Eq. (2.23) may be performed only after Eq. (2.20) is solved for $\epsilon(\lambda)$ in terms of λ at every density and temperature. The result is

$$\frac{A(1)-A(0)}{V} = -\frac{\rho\mu^2}{2a^3} \int_0^1 d\lambda \frac{9\lambda\alpha\phi(\lambda\alpha)}{3+9\lambda\alpha\phi(\lambda\alpha)}, \qquad (2.24)$$

where

$$\alpha = (4\pi/9)\beta\rho\mu^2 \qquad (2.25)$$

and $\phi(x)$ is the function[6]

$$\phi(x) = \tfrac{1}{2}([1-(3x)^{-1}] + \{[1-(3x)^{-1}]^2 + (\delta/9^x)\}^{1/2}). \qquad (2.26)$$

We may gain an impression for the behavior of the integral in Eq. (2.24) for the case of strongly polar fluids. For fluids with large dielectric constant

$$\epsilon(1) \approx (9/2)\alpha + \tfrac{1}{2}. \qquad (2.27)$$

In these systems the function $\phi(\lambda\alpha)$ will rapidly reach its asymptotic value for large $\lambda\alpha$ in the integral in Eq. (2.24). We incur only a negligible error if we replace $\phi(\lambda\alpha)$ by its asymptotic form for large argument

$$\phi(\lambda\alpha) \approx [1-(1/9\lambda\alpha)] \qquad (2.28)$$

in the region of integration $1/\alpha \leq \lambda \leq 1$ and ignore the contribution to the integral for the region of integration $0 \leq \lambda \leq 1/\alpha$. For this limiting approximation, $\epsilon(1)\gg 5$,

$$\frac{A(1)-A(0)}{V} \approx -\frac{kT}{2\pi a^3} \int_5^\epsilon d\zeta \frac{\zeta-1}{2\zeta+1}$$

$$= -(kT/4\pi a^3)\{(\epsilon-5) - \tfrac{3}{2}\ln[(2\epsilon+1)/11]\}, \qquad (2.29)$$

where $\epsilon(1)$ is the dielectric constant of the polar fluid at the particular density and temperature of interest. Thus Eq. (2.29) gives an idea of the contribution to the Helmholtz free energy due to dipolar forces when the dielectric constant is large and the Onsager model is considered to be adequate. For the Onsager model it is clear that $A(0)$ must be taken to be the free energy of a hard sphere fluid.

The chief defect of the Onsager model is that it does not adequately take into account the short-range angular dependent forces present in real molecular liquids. Of course it is not necessary to limit attention to the approximation of $G_2{}^{(0)}$, Eq. (2.14), implied by this model. For example, it might be argued that an adequate approximation to $n_2(\lambda)$ in Eq. (2.4) is simply $n_2(0)$, i.e., that the major contribution to the integral occurs at distances where the angular dependent short-range forces dominate the dipolar interactions. Under
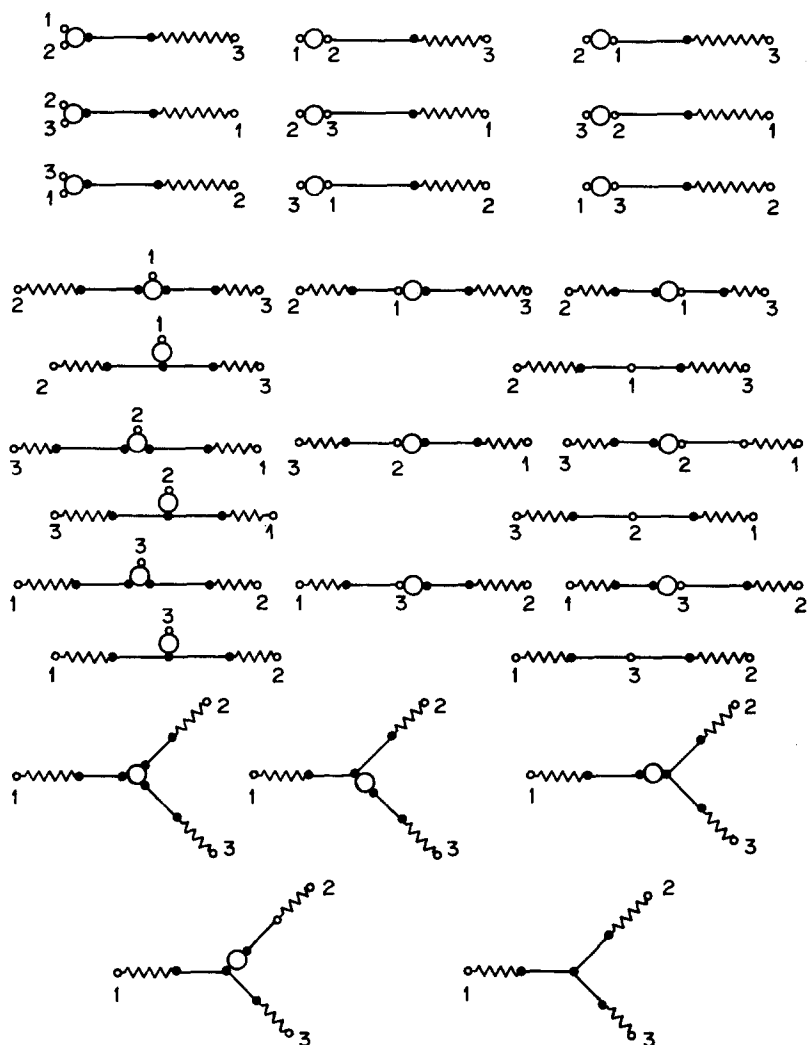
FIG. 1. Graphs contributing to $G_3^{(1)}$. An open circle with two points attached to it represents a factor $G_2^{(0)}$, an open circle with three points attached to it represents a factor $G_3^{(0)}$. A wiggled bond stands for a factor H_2, and a straight solid bond is a b bond. An integration is performed over the unlabeled points. A basic building star S_0 in an original composite graph is represented in these new graphs by a solid bond, or it is a part of a wiggled H_2 bond.

these circumstances $A(1) - A(0)$ may be approximated by

$$[A(1) - A(0)/V] = -\tfrac{1}{2} \int d\mathbf{r}_2 d\omega_1 d\omega_2 n_2(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; 0) \, \mathbf{\mu}(\omega_1) \cdot \mathbf{T}(\mathbf{r}_1, \mathbf{r}_2) \cdot \mathbf{\mu}(\omega_2). \qquad (2.30)$$

In order to proceed with this approximation scheme it is necessary to obtain information about the two-particle distribution function of the reference system.

III. THE KERR EFFECT

The birefringence measured in the Kerr effect arises because the molecules tend to be aligned by a static electric field. The effect exists only if the molecules have an anisotropic polarizability or hyperpolarizability. For strongly polar fluids composed of molecules with large permanent dipole moments one expects that the alignment produced by the external field may be calculated neglecting the polarizability and fluctuations in the average dipole moment. Therefore, in order to calculate $\mathbf{Q}(\mathbf{r})$ for a strongly polar fluid we shall assume that the molecules have a rigid dipole moment and

interact via the dipole–dipole interaction. In addition there is a short-range angular dependent pair potential $v(\mathbf{r}_i, \omega_i; \mathbf{r}_j, \omega_j)$ between the molecules. Thus the molecular model of the fluid is identical to the model considered in I. In the following we demonstrate that the quantity $\mathbf{Q}(\mathbf{r})$ is proportional to the square of the macroscopic field with a constant of proportionality that is independent of sample geometry and may be computed on the basis of certain short-range distribution functions. It follows according to Eq. (1.6) that the Kerr constant is independent of sample shape.

The molecular sample of N identical molecules with permanent dipole moment $\mathbf{\mu}$ in a volume V will be considered to be surrounded by an arbitrary region W (which might be zero) filled with a dielectric continuum with dielectric constant ϵ_0. As in I we add these hypo-

thetical continuum surroundings in order to investigate the effect of the surroundings as well as the shape of V on the quantity $\mathbf{Q}(\mathbf{r})$.

The total potential energy of the molecular sample in the presence of an external field due to fixed charges and the induced polarization in W is

$$U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0) = \sum_{i_1 < j}^{N} v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)$$

$$-\sum_{i_1 < j}^{N} \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{T}(\mathbf{r}_i, \mathbf{r}_j) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j)$$

$$-\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{R}_W(\mathbf{r}_i, \mathbf{r}_j; \epsilon_0) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j)$$

$$-\sum_{i=1}^{N} \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{E}_0(\mathbf{r}_i), \quad (3.1)$$

where for simplicity the constant energy of interaction between the continuum W and $\mathbf{E}_0$ has been omitted. The external field $\mathbf{E}_0$ is the electric field in the absence of the molecular fluid in V, but in the presence of the continuum in W and fixed external charges. The tensor

$\mathbf{R}_W$ is the reaction field tensor, defined in I, which gives the additional interaction energy between the molecules in the sample due to the polarization induced in W from the molecular dipole moments.

To compute $\mathbf{Q}(\mathbf{r})$, Eq. (1.7), we perform an average over the canonical ensemble coordinate space distribution function

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

$$\times \left(\int_V d\mathbf{r}^N d\boldsymbol{\omega}^N \exp[-\beta U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0)] \right). \quad (3.2)$$

In the low-field limit we expand $f(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0)$ in powers of $\mathbf{E}_0$ and substitute in Eq. (1.7). To accomplish this reduction it is useful to introduce several auxiliary quantities. The reduced s-particle distribution function n_s, in the absence of the external field, $\mathbf{E}_0 = 0$, is defined by

$$n_s(\mathbf{r}^s, \boldsymbol{\omega}^s) = \frac{N!}{(N-s)!} \int_V d\mathbf{r}^{N-s} d\boldsymbol{\omega}^{N-s} f(\mathbf{r}^N, \boldsymbol{\omega}^N; 0). \quad (3.3)$$

These reduced distribution functions are related to the s-particle correlation functions $G_s(\mathbf{r}^s, \boldsymbol{\omega}^s)$ and the special correlation functions $H_s(\mathbf{r}^s, \boldsymbol{\omega}^s)$ by

$$n_1(\mathbf{r}_1, \boldsymbol{\omega}_1) = G_1(\mathbf{r}_1, \boldsymbol{\omega}_1),$$

$$n_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = G_1(\mathbf{r}_1, \boldsymbol{\omega}_1)G_1(\mathbf{r}_2, \boldsymbol{\omega}_2) + G_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2),$$

$$n_3(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3) = G_1(\mathbf{r}_1, \boldsymbol{\omega}_1)G_1(\mathbf{r}_2, \boldsymbol{\omega}_2)G_1(\mathbf{r}_3, \boldsymbol{\omega}_3) + G_1(\mathbf{r}_1, \boldsymbol{\omega}_1)G_2(\mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3) + G_1(\mathbf{r}_2, \boldsymbol{\omega}_2)G_2(\mathbf{r}_3, \boldsymbol{\omega}_3; \mathbf{r}_1, \boldsymbol{\omega}_1)$$

$$+ G_1(\mathbf{r}_3, \boldsymbol{\omega}_3)G_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) + G_3(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3), \cdots \quad (3.4)$$

and

$$H_1(\mathbf{r}_1, \boldsymbol{\omega}_1) = G_1(\mathbf{r}_1, \boldsymbol{\omega}_1),$$

$$H_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = G_1(\mathbf{r}_1, \boldsymbol{\omega}_1)\delta(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) + G_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2),$$

$$H_3(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3) = G_1(\mathbf{r}_1, \boldsymbol{\omega}_1)\delta(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)\delta(\mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3) + G_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)\delta(\mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3)$$

$$+ G_2(\mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3)\delta(\mathbf{r}_3, \boldsymbol{\omega}_3; \mathbf{r}_1, \boldsymbol{\omega}_1) + G_2(\mathbf{r}_3, \boldsymbol{\omega}_3; \mathbf{r}_1, \boldsymbol{\omega}_1)\delta(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)$$

$$+ G_3(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3), \cdots. \quad (3.5)$$

To second order in $\mathbf{E}_0$ we find for $\mathbf{Q}(\mathbf{r})$

$$\mathbf{Q}(\mathbf{r}) = [Z(0)/Z(\mathbf{E}_0)][\mathbf{Q}_\mathrm{I} + \mathbf{Q}_\mathrm{II} + \mathbf{Q}_\mathrm{III}], \quad (3.6)$$

where

$$Z(\mathbf{E}_0) = \int_V d\mathbf{r}^N d\boldsymbol{\omega}^N \exp[-\beta U(\mathbf{r}^N, \boldsymbol{\omega}^N; \mathbf{E}_0)], \quad (3.7)$$

and

$$\mathbf{Q}_\mathrm{I} = \int_V d\mathbf{r}_1 d\boldsymbol{\omega}_1 \delta(\mathbf{r} - \mathbf{r}_1) \mathbf{\Delta}(\boldsymbol{\omega}_1) n_1(\mathbf{r}_1, \boldsymbol{\omega}_1), \quad (3.8)$$

$$\mathbf{Q}_\mathrm{II} = \int_V d\mathbf{r}_1 d\boldsymbol{\omega}_1 \delta(\mathbf{r} - \mathbf{r}_1) \mathbf{\Delta}(\boldsymbol{\omega}_1) \beta \boldsymbol{\mu}(\boldsymbol{\omega}_1) \cdot \mathbf{E}_0(\mathbf{r}_1) n_1(\mathbf{r}_1, \boldsymbol{\omega}_1)$$

$$+ \int_V d\mathbf{r}_1 d\boldsymbol{\omega}_1 d\mathbf{r}_2 d\boldsymbol{\omega}_2 \delta(\mathbf{r} - \mathbf{r}_1) \mathbf{\Delta}(\boldsymbol{\omega}_1) \beta \boldsymbol{\mu}(\boldsymbol{\omega}_2) \cdot \mathbf{E}_0(\mathbf{r}_2) n_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2), \quad (3.9)$$

$$\mathbf{Q}_\mathrm{III} = \frac{1}{2}\beta^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \langle \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{\Delta}(\boldsymbol{\omega}_i) \boldsymbol{\mu}(\boldsymbol{\omega}_j) \cdot \mathbf{E}_0(\mathbf{r}_j) \boldsymbol{\mu}(\boldsymbol{\omega}_k) \cdot \mathbf{E}_0(\mathbf{r}_k) \rangle_0, \quad (3.10)$$

with

$$\boldsymbol{\Delta}(\boldsymbol{\omega}_i) = \boldsymbol{\alpha}(\boldsymbol{\omega}_i) - \tfrac{1}{3}\mathbf{I}\,\mathrm{Tr}\,\boldsymbol{\alpha}. \qquad (3.11)$$

In Eq. (3.10) the angular bracket with subscript zero indicates an average over configurations in the absence of $\mathbf{E}_0$.

We assume as in I that the fluid is uniform in the absence of $\mathbf{E}_0$,

$$n_1(\mathbf{r}_1, \boldsymbol{\omega}_1) = G_1(\mathbf{r}_1, \boldsymbol{\omega}_1) = H_1(\mathbf{r}_1, \boldsymbol{\omega}_1) = \rho/\Omega, \quad (3.12)$$

where Ω is introduced in Eq. (2.3). It follows since

$$\Omega^{-1}\int_V d\mathbf{r}_1 d\boldsymbol{\omega}_1 \delta(\mathbf{r}-\mathbf{r}_1)\boldsymbol{\alpha}(\boldsymbol{\omega}_1) = \tfrac{1}{3}\mathbf{I}\,\mathrm{Tr}\,\boldsymbol{\alpha}, \qquad (3.13)$$

that $\mathbf{Q}_\mathrm{I}=0$. Furthermore since $\boldsymbol{\alpha}$ is symmetric the first term of $\mathbf{Q}_\mathrm{II}$ will vanish.

In order to compute the remaining term of $\mathbf{Q}_\mathrm{II}$ we use the results of I, quoted in Sec. II of the present paper. The two-particle distribution function can be separated according to Eq. (2.5)

$$n_2(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) = (\rho^2/\Omega^2) + G_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)$$
$$+ G_2^{(1)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2) \quad (3.14)$$

with an explicit expression for $G_2^{(1)}$ given by Eq. (2.6) for $\lambda = 1$. If the external continuum has the same dielectric constant as the molecular medium, then the explicit expression for $G_2^{(1)}$ is given by Eq. (2.6) together with Eq. (2.7) for $\lambda = 1$ except that $\mathbf{R}_V{}^*$ is replaced by $\mathbf{R}_{(V+W)}{}^*$. If the dielectric constant ϵ_0 of W differs from that of the molecular medium, the interaction term $\mathbf{F}(\mathbf{r}, \mathbf{r}'; 1)$ appearing in Eq. (2.6) is given by the solution of the integral equation

$$\mathbf{F}(\mathbf{r}, \mathbf{r}'; 1) = \mathbf{D}(\mathbf{r}, \mathbf{r}') + \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot\boldsymbol{\mu}_\mathrm{eff}$$
$$\times \int_V d\mathbf{r}''\mathbf{D}(\mathbf{r}, \mathbf{r}'')\cdot\mathbf{F}(\mathbf{r}'', \mathbf{r}'), \quad (3.15)$$

where

$$\mathbf{D}(\mathbf{r}, \mathbf{r}') = \mathbf{T}(\mathbf{r}, \mathbf{r}') + \mathbf{R}_W(\mathbf{r}, \mathbf{r}'; \epsilon_0) \qquad (3.16)$$

and $\boldsymbol{\mu}_\mathrm{eff} = \boldsymbol{\mu}(\omega) + \boldsymbol{\kappa}(\omega; 1)$ is defined by Eq. (2.9). From Eqs. (3.9), (3.14), and (2.6) it follows that

$$\mathbf{Q}_\mathrm{II} = \int_V d\boldsymbol{\omega}_1 d\mathbf{r}_2 d\boldsymbol{\omega}_2 \boldsymbol{\Delta}(\boldsymbol{\omega}_1)\left(G_2^{(0)}(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2)\right.$$
$$\left. + \frac{\beta\rho^2}{\Omega^2}\boldsymbol{\mu}_\mathrm{eff}(\boldsymbol{\omega}_1)\cdot\mathbf{F}(\mathbf{r}, \mathbf{r}_2)\cdot\boldsymbol{\mu}_\mathrm{eff}(\boldsymbol{\omega}_2)\right)\beta\boldsymbol{\mu}(\boldsymbol{\omega}_2)\cdot\mathbf{E}_0(\mathbf{r}_2).$$
$$(3.17)$$

If $\mathbf{E}_0$ does not vary appreciably over a distance of the order of the range of $G_2^{(0)}$ and $\boldsymbol{\alpha}$ is symmetric, it is an easy matter to show that this term vanishes identically. Consequently, the leading term in the enumerator of Eq. (3.6) is $\mathbf{Q}_\mathrm{III}$ which is proportional to $\mathbf{E}_0{}^2$. To lowest order $Z(\mathbf{E}_0)$ may be replaced by $Z(\mathbf{0})$ in the denominator in Eq. (3.6), and one finds after some

simplifications that to second order in $\mathbf{E}_0$

$$\mathbf{Q}(\mathbf{r}) = \int_V d\mathbf{r}_1 d\boldsymbol{\omega}_1 d\mathbf{r}_2 d\boldsymbol{\omega}_2 d\mathbf{r}_3 d\boldsymbol{\omega}_3 \delta(\mathbf{r}-\mathbf{r}_1)\boldsymbol{\Delta}(\boldsymbol{\omega}_1)$$
$$\times\tfrac{1}{2}\beta^2\boldsymbol{\mu}(\boldsymbol{\omega}_2)\cdot\mathbf{E}_0(\mathbf{r}_2)\boldsymbol{\mu}(\boldsymbol{\omega}_3)$$
$$\times\mathbf{E}_0(\mathbf{r}_3)H_3(\mathbf{r}_1, \boldsymbol{\omega}_1; \mathbf{r}_2, \boldsymbol{\omega}_2; \mathbf{r}_3, \boldsymbol{\omega}_3), \quad (3.18)$$

where H_3 is given by Eq. (3.5). Hence in order to investigate $\mathbf{Q}(\mathbf{r})$ we must study the special correlation function H_3. This function involves both G_2 and G_3. The correlation function G_2 has been obtained, so that here it remains to investigate the three-particle correlation function G_3. We shall use a graphical expansion to investigate G_3 similar to the graphical expansion employed in I to obtain G_2.

IV. THE GRAPHICAL EXPANSION OF G_2 AND G_3

Our starting point is the graphical representation of G_2 and G_3 according to the formalism of Uhlenbeck and Ford.[7] The linear graphs which are used by these authors consist of labeled points with bond lines joining certain pairs of points. A connected graph may have *articulation points*, which are defined by the property that if all the bonds meeting at the point are cut and the point is erased, the graph becomes disconnected. A connected graph is called a *star* if it has no articulation points. A graph with L points labeled $1, 2, \cdots, L$ is said to be *s irreducible* $(s \leq L)$ if the graph becomes a star when additional bonds are inserted between every pair of points out of the set $1, 2, \cdots, s$, insofar as these bonds are not already present. According to the well-known graphical expansion theory,[7,8] we can represent the virial expansion of G_s by

$$G_s(\mathbf{r}^s, \boldsymbol{\omega}^s) = \sum_{M=s}^{\infty} C_M(\mathbf{r}^s, \boldsymbol{\omega}^s)\left(\frac{\rho}{\Omega}\right)^M, \qquad (4.1)$$

where

$$C_M(\mathbf{r}^s, \boldsymbol{\omega}^s) = [(M-s)!]^{-1}\sum_{(R_M)}\int_V d\mathbf{r}^{M-s}d\boldsymbol{\omega}^{M-s}\prod_{R_M} f_{ij}.$$
$$(4.2)$$

The sum is over all different connected s-irreducible graphs R_M with M points labeled $1, 2, \cdots, M$. Between any pair of points there is either one or no bond. A bond between the points i and j contributes a factor f_{ij} to the integrand in Eq. (4.2), where

$$f_{ij} = \exp[-\beta v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)$$
$$+ \beta\boldsymbol{\mu}(\boldsymbol{\omega}_i)\cdot\mathbf{D}(\mathbf{r}_i, \mathbf{r}_j)\cdot\boldsymbol{\mu}(\boldsymbol{\omega}_j)] - 1. \quad (4.3)$$

As we did in I, we expand the factor f_{ij} in the standard way[9,10]

$$f_{ij} = a_{ij} + \sum_{\alpha=1}^{\infty}(\alpha!)^{-1}(b_{ij})^\alpha, \qquad (4.4)$$

where

$$a_{ij} = \{\exp[-\beta v(\mathbf{r}_i, \boldsymbol{\omega}_i; \mathbf{r}_j, \boldsymbol{\omega}_j)] - 1\}$$
$$\times \exp[\beta \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j)] \quad (4.5)$$

and

$$b_{ij} = \beta \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j). \quad (4.6)$$

The factor a_{ij} is of short range, and will be represented by a dotted bond between the points i and j in a graph. The factor $(1/\alpha!)(b_{ij})^\alpha$ will be represented by α solid bonds. If we replace each factor f_{ij} in Eq. (4.2) by the expansion (4.4), we can write $C_M(\mathbf{r}^s, \boldsymbol{\omega}^s)$ as an expansion in terms of composite graphs, which have either one dotted bond, or any number of solid bonds, or no bond at all between each pair of points:

$$C_M(\mathbf{r}^s, \boldsymbol{\omega}^s) = [(M-s)!]^{-1} \sum_{(S_M)} \int_V d\mathbf{r}^{M-s} d\boldsymbol{\omega}^{M-s}$$
$$\times \prod_{S_M} a_{ij} \prod_{S_M} (\alpha!)^{-1}(b_{pq})^\alpha. \quad (4.7)$$

The sum is now over all different connected s-irreducible composite graphs S_M with M points labeled $1, 2, \cdots, M$. A dotted bond between the points i and j contributes a factor a_{ij}, a number α of solid bonds between the points p and q contributes a factor $(1/\alpha!)(b_{pq})^\alpha$ to the integrand in Eq. (4.7).

We reduce the graphical expansion one more step by noticing that the contribution of an s-irreducible graph to G_s does not depend on the labeling of the points other than the points $1, 2, \cdots, s$. We introduce the symmetry number σ of an s-irreducible graph as the number of permutations of the points other than these s points which leave the bonds between pairs of points unchanged. If the graph has M points, $M \geq s$, there are $(M-s)!/\sigma$ different ways of labeling the other points $s+1, s+2, \cdots, M$. Thus we may expand $C_M(\mathbf{r}^s, \boldsymbol{\omega}^s)$ as

$$C_M(\mathbf{r}^s, \boldsymbol{\omega}^s) = \sum_{(T_M)} \sigma^{-1} \int_V d\mathbf{r}^{M-s} d\boldsymbol{\omega}^{M-s}$$
$$\times \prod_{T_M} a_{ij} \prod_{T_M} (\alpha!)^{-1}(b_{pq})^\alpha, \quad (4.8)$$

where the sum is now over all different connected composite s-irreducible graphs T_M with M points, in which only the points $1, 2, \cdots, s$ are labeled.

The graphical expansion of G_2 has been studied in I. Here we are interested in the expansion of G_3, and we use similar techniques to those employed in I. We introduce a dimensionless parameter of smallness δ by

$$\delta = \beta \mu^2 \Lambda^{-3}, \quad (4.9)$$

where Λ is a typical macroscopic distance in the system, which is much larger than the average distance $\rho^{-1/3}$ between neighboring molecules. Then δ is much smaller than unity in real systems. In order to obtain $\mathbf{Q}$, given by Eq. (3.18), to zeroth order in δ we need G_3 up to zeroth order in δ if the three particles are microscopically

close together, up to first order for configurations where two particles are close together and the third one is macroscopically far from them, and up to second order in δ if all three particles are separated by a macroscopic distance from each other, since every position integration which is effective over the entire volume reduces the order in δ by one. We recall[1] that a b bond is of order δ for macroscopic separations, and that it has a zeroth order contribution in δ if the endpoints are microscopically separated. The term $\beta \boldsymbol{\mu}(\boldsymbol{\omega}_i) \cdot \mathbf{R}_W(\mathbf{r}_i, \mathbf{r}_j; \epsilon_0) \cdot \boldsymbol{\mu}(\boldsymbol{\omega}_j)$, which is one of the terms in b_{ij}, is of order δ for every separation of $\mathbf{r}_i$ and $\mathbf{r}_j$ since $\mathbf{R}_W$ is explicitly proportional to V^{-1}.

Now we consider the graphical expansion of G_3. Every 3-irreducible connected graph consists of a number of stars hung together at the articulation points, or the graph itself is a star. In the former case the graph must become a star if we insert additional bonds joining the points 1, 2, and 3. As we did in I, we introduce again the simple star S_0 consisting of two points joined by one solid b bond. One easily checks that a graph out of the expansion of G_3 which is a star, is of zeroth order in δ if the three points are microscopically separated from each other, at least of second order in δ if two points are close together and the third one is macroscopically far from both, and at least of third order in δ if all three points are far from each other. The same holds for graphs which are built out of stars other than the star S_0. We introduce the set Y of graphs contributing to G_3 which either are a star, or which are built by hanging together any stars other than the star S_0. The zeroth order term of the total contribution of the graphs in Y to G_3 is called $G_3^{(0)}$. According to the foregoing, $G_3^{(0)}$ is zero unless the three particles are microscopically close together, so that $G_3^{(0)}$ has a microscopic range. This definition of $G_3^{(0)}$ is completely analogous to the definition of $G_2^{(0)}$ in I. By a similar argument one shows that $G_3^{(0)}$ depends only on the relative positions and orientations of the three particles, and thus is independent of the shape of the sample and the surroundings. In order to calculate $G_3^{(0)}$ we may entirely neglect the effects of the $\mathbf{R}_W$ terms in the b bonds, and we may extend all integrations over the entire space.

We are left with the contributions of the connected composite 3-irreducible graphs which are not in Y, i.e., which contain at least once the star S_0 as a constituent star. We introduce the function $G_3^{(1)}$ as the contribution of the graphs not included in Y. The lowest order contribution to $G_3^{(1)}$ will be zeroth order in δ if the three particles are close together, first order if two of the particles are close together, and the third one is far from both, and second order if the particles are far apart. Higher order contributions to $G_3^{(1)}$ will be neglected. Thus $G_3^{(1)}$ contains the lowest nonvanishing contribution to G_3 when two or three of the particles are well separated. For microscopic separation of the three particles both $G_3^{(0)}$ and $G_3^{(1)}$ are of order unity.

The total function $G_3{}^{(0)}+G_3{}^{(1)}$ is an excellent approximation for every configuration of the three particles,

$$G_3(\mathbf{r}_1,\,\omega_1;\,\mathbf{r}_2,\,\omega_2;\,\mathbf{r}_3,\,\omega_3)=G_3{}^{(0)}(\mathbf{r}_1,\,\omega_1;\,\mathbf{r}_2,\,\omega_2;\,\mathbf{r}_3,\,\omega_3)$$

$$+G_3{}^{(1)}(\mathbf{r}_1,\,\omega_1;\,\mathbf{r}_2,\,\omega_2;\,\mathbf{r}_3,\,\omega_3).\quad(4.10)$$

We now find an expression for $G_3{}^{(1)}$. The graphs contributing to $G_3{}^{(1)}$ are found by taking one or more stars S_0 and hanging them together directly or via other graphs which do not contain S_0 as a building star, in such a way that the resulting graph is 3-irreducible. The endpoints of the stars S_0 we consider must be articulation points of the resulting graph, so that closed loops of these stars S_0 are precluded. In other words, the endpoints of a building star S_0 in the resulting graph are connected exclusively by the direct solid bond between them. The different possible combinations may be conveniently summarized by using a new graphical representation, in which the sum of all graphs contributing to H_2 is represented by a single wiggled bond, the sum of the graphs contributing to $G_2{}^{(0)}$ is represented by an open circle with two points attached to it, $G_3{}^{(0)}$ is represented by an open circle with three points attached to it. Only the points 1, 2, and 3 are labeled. The reason that

$$H_2(\mathbf{r}_i,\,\omega_i;\,\mathbf{r}_j,\,\omega_j)=(\rho/\Omega)\delta(\mathbf{r}_i,\,\omega_i;\,\mathbf{r}_j,\,\omega_j)$$

$$+G_2(\mathbf{r}_i,\,\omega_i;\,\mathbf{r}_j,\,\omega_j)$$

arises is because one must include the possibility that the endpoint of the star S_0 might be a labeled root point as well as an unlabeled field point. Then one checks that the graphs contributing to $G_3{}^{(1)}$ are precisely summarized by the new graphs given in Fig. 1. The symmetry numbers of the total graphs are properly taken into account, for the symmetry number of any of the graphs represented by a new graph in Fig. 1 is the product of the symmetry numbers of the parts one is left with after erasing the solid b bonds in the basic stars S_0. An integration is performed over the coordinates of the points which are not labeled. For ease of notation we denote the coordinates $(\mathbf{r}_i,\,\omega_i)$ of particle i by (i). The integration element $d(i)$ is a short-hand notation for $d\mathbf{r}_i d\omega_i$. Further, we introduce the special correlation functions $H_3{}^{(0)}$, $H_2{}^{(0)}$, and $H_3{}^{(1)}$ by

$$H_3{}^{(0)}(123)=(\rho/\Omega)\delta(12)\delta(23)+G_2{}^{(0)}(12)\delta(23)$$

$$+G_2{}^{(0)}(23)\delta(31)+G_2{}^{(0)}(31)\delta(12)+G_3{}^{(0)}(123),$$

$$(4.11)$$

and

$$H_2{}^{(0)}(12)=(\rho/\Omega)\delta(12)+G_2{}^{(0)}(12),\quad(4.12)$$

and

$$H_3{}^{(1)}(123)=G_2{}^{(1)}(12)\delta(23)+G_2{}^{(1)}(23)\delta(31)$$

$$+G_2{}^{(1)}(31)\delta(12)+G_3{}^{(1)}(123).\quad(4.13)$$

Hence,

$$H_3(123)=H_3{}^{(0)}(123)+H_3{}^{(1)}(123).\quad(4.14)$$

An expression of $G_3{}^{(1)}$ is now found by writing down the contribution of the graphs given in Fig. 1. We find

$$G_3{}^{(1)}(123)=\int_V d(4)d(5)[G_3{}^{(0)}(124)+G_2{}^{(0)}(12)\delta(24)+G_2{}^{(0)}(24)\delta(41)]\beta\mathbf{\mu}(\omega_4)\cdot\mathsf{D}(\mathbf{r}_4,\mathbf{r}_5)\cdot\mathbf{\mu}(\omega_5)H_2(53)$$

$$+\int_V d(4)d(5)[G_3{}^{(0)}(234)+G_2{}^{(0)}(23)\delta(34)+G_2{}^{(0)}(34)\delta(42)]\beta\mathbf{\mu}(\omega_4)\cdot\mathsf{D}(\mathbf{r}_4,\mathbf{r}_5)\cdot\mathbf{\mu}(\omega_5)H_2(51)$$

$$+\int_V d(4)d(5)[G_3{}^{(0)}(314)+G_2{}^{(0)}(31)\delta(14)+G_2{}^{(0)}(14)\delta(43)]\beta\mathbf{\mu}(\omega_4)\cdot\mathsf{D}(\mathbf{r}_4,\mathbf{r}_5)\cdot\mathbf{\mu}(\omega_5)H_2(52)$$

$$+\int_V d(4)d(5)d(6)d(7)H_3{}^{(0)}(146)\beta\mathbf{\mu}(\omega_4)\cdot\mathsf{D}(\mathbf{r}_4,\mathbf{r}_5)\cdot\mathbf{\mu}(\omega_5)H_2(52)\beta\mathbf{\mu}(\omega_6)\cdot\mathsf{D}(\mathbf{r}_6,\mathbf{r}_7)\cdot\mathbf{\mu}(\omega_7)H_2(73)$$

$$+\int_V d(4)d(5)d(6)d(7)H_3{}^{(0)}(246)\beta\mathbf{\mu}(\omega_4)\cdot\mathsf{D}(\mathbf{r}_4,\mathbf{r}_5)\cdot\mathbf{\mu}(\omega_5)H_2(53)\beta\mathbf{\mu}(\omega_6)\cdot\mathsf{D}(\mathbf{r}_6,\mathbf{r}_7)\cdot\mathbf{\mu}(\omega_7)H_2(71)$$

$$+\int_V d(4)d(5)d(6)d(7)H_3{}^{(0)}(346)\beta\mathbf{\mu}(\omega_4)\cdot\mathsf{D}(\mathbf{r}_4,\mathbf{r}_5)\cdot\mathbf{\mu}(\omega_5)H_2(51)\beta\mathbf{\mu}(\omega_6)\cdot\mathsf{D}(\mathbf{r}_6,\mathbf{r}_7)\cdot\mathbf{\mu}(\omega_7)H_2(72)$$

$$+\int_V d(4)d(5)d(6)d(7)d(8)d(9)H_3{}^{(0)}(468)\beta\mathbf{\mu}(\omega_4)\cdot\mathsf{D}(\mathbf{r}_4,\mathbf{r}_5)\cdot\mathbf{\mu}(\omega_5)H_2(51)\beta\mathbf{\mu}(\omega_6)\cdot\mathsf{D}(\mathbf{r}_6,\mathbf{r}_7)$$

$$\cdot\mathbf{\mu}(\omega_7)H_2(72)\beta\mathbf{\mu}(\omega_8)\cdot\mathsf{D}(\mathbf{r}_8,\mathbf{r}_9)\cdot\mathbf{\mu}(\omega_9)H_2(93).\quad(4.15)$$

In order to simplify Eq. (4.15) we use the fact that the functions $G_2{}^{(0)}$ and $G_3{}^{(0)}$ have a microscopic range. Hence,

we expect to incur a negligible error if we make the replacement

$$\int_V d(j) G_2^{(0)}(ij) f(\mathbf{r}_j, \omega_j) = \int_V d(j) G_2^{(0)}(ij) f(\mathbf{r}_i, \omega_j) \tag{4.16}$$

and

$$\int_V d(j) d(k) G_3^{(0)}(ijk) f(\mathbf{r}_j, \omega_j; \mathbf{r}_k, \omega_k) = \int_V d(j) d(k) G_3^{(0)}(ijk) f(\mathbf{r}_i, \omega_j; \mathbf{r}_i, \omega_k) \tag{4.17}$$

for any function f, provided that f does not vary appreciably over a microscopic distance. By making the approximation (4.17) one shows

$$\int_V d(j) \mathsf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \mathbf{\mu}(\omega_j) H_2(jk) = \mathsf{D}(\mathbf{r}_i, \mathbf{r}_k) \cdot \frac{\rho}{\Omega} \mathbf{\mu}_{\text{eff}}(\omega_k) + \tfrac{1}{3}\beta\rho\mathbf{\mu} \cdot \mathbf{\mu}_{\text{eff}} \int_V d\mathbf{r}_j \mathsf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \mathsf{F}(\mathbf{r}_j, \mathbf{r}_k) \cdot \frac{\rho}{\Omega} \mathbf{\mu}_{\text{eff}}(\omega_k), \quad \tag{4.18}$$

where use has been made of the definition of H_2, Eq. (3.5), and of Eqs. (2.6), (2.9), and (2.10) with $\lambda = 1$. Use of Eq. (3.15) leads to

$$\int_V d(j) \mathsf{D}(\mathbf{r}_i, \mathbf{r}_j) \cdot \mathbf{\mu}(\omega_j) H_2(jk) = \mathsf{F}(\mathbf{r}_i, \mathbf{r}_k) \cdot \frac{\rho}{\Omega} \mathbf{\mu}_{\text{eff}}(\omega_k), \tag{4.19}$$

which permits simplification of several of the terms appearing in the right-hand side of Eq. (4.15). Further simplification results if we introduce the vector $\mathbf{\lambda}(ij)$ by the definition

$$\int d(k) G_3^{(0)}(ijk) \mathbf{\mu}(\omega_k) = (\rho^2/\Omega^2) \mathbf{\lambda}(ij) \tag{4.20}$$

and the tensor $\mathsf{M}(\omega_i)$ by the definition

$$\int d(j) d(k) H_3^{(0)}(ijk) \mathbf{\mu}(\omega_j) \mathbf{\mu}(\omega_k) = (\rho/\Omega) \mathsf{M}(\omega_i). \tag{4.21}$$

The vector $\mathbf{\lambda}(ij)$ depends only on the relative position and orientation of the molecules i and j, and has a short range. The tensor $\mathsf{M}(\omega_i)$ is a tensor fixed to molecule i, and independent of the position $\mathbf{r}_i$. Both $\mathbf{\lambda}$ and M are independent of the sample shape and the surroundings since they involve only the short-range part of the three-particle correlation function. By using the definition (4.11) of $H_3^{(0)}$ we find

$$\mathsf{M}(\omega) = \mathbf{\mu}(\omega) \mathbf{\mu}(\omega) + \mathbf{\mu}(\omega)\mathbf{\kappa}(\omega) + \mathbf{\kappa}(\omega) \mathbf{\mu}(\omega) + \mathsf{B}(\omega) + \mathsf{C}(\omega), \tag{4.22}$$

where

$$(\rho/\Omega) \mathsf{B}(\omega_1) = \int d(2) G_2^{(0)}(12) \mathbf{\mu}(\omega_2) \mathbf{\mu}(\omega_2) \tag{4.23}$$

and

$$(\rho/\Omega) \mathsf{C}(\omega_1) = \int d(2) d(3) G_3^{(0)}(123) \mathbf{\mu}(\omega_2) \mathbf{\mu}(\omega_3) = (\rho/\Omega)^2 \int d(2) \mathbf{\lambda}(12) \mathbf{\mu}(2). \tag{4.24}$$

The tensor M is clearly symmetric. Now we make the approximations (4.16) and (4.17) and use Eqs. (4.19)–(4.21) in the result (4.15) for $G_3^{(1)}$, and we find

$$G_3^{(1)}(123) = \frac{\beta\rho}{\Omega}\left(\frac{\rho^2}{\Omega^2}\mathbf{\lambda}(12) + G_2^{(0)}(12)\left[\mathbf{\mu}(\omega_1) + \mathbf{\mu}(\omega_2)\right]\right) \cdot \mathsf{F}(\mathbf{r}_1, \mathbf{r}_3) \cdot \mathbf{\mu}_{\text{eff}}(\omega_3)$$

$$+ \frac{\beta\rho}{\Omega}\left(\frac{\rho^2}{\Omega^2}\mathbf{\lambda}(23) + G_2^{(0)}(23)\left[\mathbf{\mu}(\omega_2) + \mathbf{\mu}(\omega_3)\right]\right) \cdot \mathsf{F}(\mathbf{r}_2, \mathbf{r}_1) \cdot \mathbf{\mu}_{\text{eff}}(\omega_1)$$

$$+ \frac{\beta\rho}{\Omega}\left(\frac{\rho^2}{\Omega^2}\mathbf{\lambda}(31) + G_3^{(0)}(31)\left[\mathbf{\mu}(\omega_3) + \mathbf{\mu}(\omega_1)\right]\right) \cdot \mathsf{F}(\mathbf{r}_3, \mathbf{r}_2) \cdot \mathbf{\mu}_{\text{eff}}(\omega_2)$$

$$+ \frac{\beta^2\rho^3}{\Omega^3} \mathbf{\mu}_{\text{eff}}(\omega_2) \cdot \mathsf{F}(\mathbf{r}_2, \mathbf{r}_1) \cdot \mathsf{M}(\omega_1) \cdot \mathsf{F}(\mathbf{r}_1, \mathbf{r}_3) \cdot \mathbf{\mu}_{\text{eff}}(\omega_3)$$

$$+ \frac{\beta^2\rho^3}{\Omega^3} \mathbf{\mu}_{\text{eff}}(\omega_3) \cdot \mathsf{F}(\mathbf{r}_3, \mathbf{r}_2) \cdot \mathsf{M}(\omega_2) \cdot \mathsf{F}(\mathbf{r}_2, \mathbf{r}_1) \cdot \mathbf{\mu}_{\text{eff}}(\omega_1)$$

$$+ \frac{\beta^2\rho^3}{\Omega^3} \mathbf{\mu}_{\text{eff}}(\omega_1) \cdot \mathsf{F}(\mathbf{r}_1, \mathbf{r}_3) \cdot \mathsf{M}(\omega_3) \cdot \mathsf{F}(\mathbf{r}_3, \mathbf{r}_2) \cdot \mathbf{\mu}_{\text{eff}}(\omega_2). \tag{4.25}$$

The first term in the right-hand side of Eq. (4.25) is zero unless particles 1 and 2 are microscopically close together, similarly for the next two terms. The last three terms give the three-particle correlation function G_3 up to order δ^2 if the three particles are macroscopically separated one from the others.

In the special case that the dielectric constant ϵ_0 of the surrounding dielectric medium in W is equal to the dielectric constant ϵ of the molecular medium,[1]

$$\epsilon = 1 + 4\pi(\tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot\boldsymbol{\mu}_{\text{eff}}), \tag{4.26}$$

the tensor F is given by

$$\mathsf{F}(\mathbf{r},\mathbf{r}') = \epsilon^{-1}[\mathsf{T}(\mathbf{r},\mathbf{r}') + \mathsf{R}_{(V+W)}{}^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})], \tag{4.27}$$

as we showed in I. Hence, if $\epsilon_0 = \epsilon$, the three-particle distribution function n_3 is the same as if the entire volume $(V+W)$ were filled with the molecular fluid. The implications of this equivalence have been discussed in I.

The major result of our analysis is the explicit expression for the long-range part of the three-particle correlation function presented in Eq. (4.25). This result is a generalization of the analysis presented in I to a higher order distribution function. It is interesting to note that the superposition approximation[11] implies that at large but not infinite separations G_3 vanishes while $G_2 \neq 0$. Since for large separation only the last three terms on the right-hand side of Eq. (4.25) remain, one may regard $G_3{}^{(1)}$ as providing information on the correction to the superposition approximation for polar fluids.

We are now in a position to calculate the tensor $\mathsf{Q}(\mathbf{r})$, Eq. (3.18). First, we obtain an equation for $H_3{}^{(1)}$ using the definition of $H_3{}^{(1)}$, Eq. (4.13), and Eq. (4.15) and the relation for $G_2{}^{(1)}$ obtained in I,

$$G_2{}^{(1)}(12) = \int_V d(4)d(5) H_2{}^{(0)}(14)\beta\boldsymbol{\mu}(\omega_4)\cdot\mathsf{D}(\mathbf{r}_4,\mathbf{r}_5)\cdot\boldsymbol{\mu}(\omega_5)H_2(52) \tag{4.28}$$

[see Eq. (3.28) of I]. The resulting equation for $H_3{}^{(1)}$ is

$$H_3{}^{(1)}(123) = \int_V d(4)d(5) H_3{}^{(0)}(124)b(45)H_2(53) + \int_V d(4)d(5) H_3{}^{(0)}(234)b(45)H_2(51)$$

$$+ \int_V d(4)d(5) H_3{}^{(0)}(314)b(45)H_2(52) + X, \tag{4.29}$$

where X denotes the last four terms on the right-hand side of Eq. (4.15) and $b(ij) = b_{ij}$ given in Eq. (4.6). We may simplify Eq. (4.29) by noting that $H_2{}^{(0)}$ and $H_3{}^{(0)}$ are of short range and may be treated in integrals analogously to $G_2{}^{(0)}$ and $G_3{}^{(0)}$ in Eqs. (4.16) and (4.17). With the use of Eq. (4.19) and the definition

$$(\rho^2/\Omega^2)\boldsymbol{\sigma}(12) = \int d(3) H_3{}^{(0)}(123)\boldsymbol{\mu}(\omega_3), \tag{4.30}$$

we find

$$H_3{}^{(1)}(123) = (\beta\rho^3/\Omega^3)\boldsymbol{\sigma}(12)\cdot\mathsf{F}(\mathbf{r}_1,\mathbf{r}_3)\cdot\boldsymbol{\mu}_{\text{eff}}(\omega_3) + (\beta\rho^3/\Omega^3)\boldsymbol{\sigma}(23)\cdot\mathsf{F}(\mathbf{r}_2,\mathbf{r}_1)\cdot\boldsymbol{\mu}_{\text{eff}}(\omega_1)$$

$$+ (\beta\rho^3/\Omega^3)\boldsymbol{\sigma}(31)\cdot\mathsf{F}(\mathbf{r}_3,\mathbf{r}_2)\cdot\boldsymbol{\mu}_{\text{eff}}(\omega_2) + (\beta^2\rho^3/\Omega^3)\boldsymbol{\mu}_{\text{eff}}(\omega_2)\cdot\mathsf{F}(\mathbf{r}_2,\mathbf{r}_1)\cdot\mathsf{M}(\omega_1)\cdot\mathsf{F}(\mathbf{r}_1,\mathbf{r}_3)\cdot\boldsymbol{\mu}_{\text{eff}}(\omega_3)$$

$$+ (\beta^2\rho^3/\Omega^3)\boldsymbol{\mu}_{\text{eff}}(\omega_3)\cdot\mathsf{F}(\mathbf{r}_3,\mathbf{r}_2)\cdot\mathsf{M}(\omega_2)\cdot\mathsf{F}(\mathbf{r}_2,\mathbf{r}_1)\cdot\boldsymbol{\mu}_{\text{eff}}(\omega_1)$$

$$+ (\beta^2\rho^3/\Omega^3)\boldsymbol{\mu}_{\text{eff}}(\omega_1)\cdot\mathsf{F}(\mathbf{r}_1,\mathbf{r}_3)\cdot\mathsf{M}(\omega_3)\cdot\mathsf{F}(\mathbf{r}_3,\mathbf{r}_2)\cdot\boldsymbol{\mu}_{\text{eff}}(\omega_2), \tag{4.31}$$

where $\boldsymbol{\mu}_{\text{eff}}$ is defined by Eq. (2.9) with $\lambda = 1$. Note that $\boldsymbol{\sigma}(ij)$ has a microscopic range and is related to M according to

$$\mathsf{M}(\omega_1) = (\rho/\Omega)\int d(2)\boldsymbol{\sigma}(12)\boldsymbol{\mu}(\omega_2). \tag{4.32}$$

When we introduce for $H_3 = H_3{}^{(0)} + H_3{}^{(1)}$ in the expression for $\mathsf{Q}(\mathbf{r})$, Eq. (3.18) and use Eq. (4.31) for $H_3{}^{(1)}$, we find

$$\mathsf{Q}(\mathbf{r}) = \tfrac{1}{2}\beta^2\frac{\rho}{\Omega}\int d\omega_1\boldsymbol{\Delta}(\omega_1)\left[\mathbf{E}_0(\mathbf{r}) + \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot\boldsymbol{\mu}_{\text{eff}}\int_V d\mathbf{r}_2\mathbf{E}_0(\mathbf{r}_2)\cdot\mathsf{F}(\mathbf{r}_2,\mathbf{r})\right]$$

$$\cdot\mathsf{M}(\omega_1)\cdot\left[\mathbf{E}_0(\mathbf{r}) + \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot\boldsymbol{\mu}_{\text{eff}}\int_V d\mathbf{r}_3\mathsf{F}(\mathbf{r},\mathbf{r}_3)\cdot\mathbf{E}_0(\mathbf{r}_3)\right], \tag{4.33}$$

where use has been made of Eqs. (4.21) and (4.32). But it is not difficult to show from the results in I that the relation between the macroscopic electric field $\mathbf{E}(\mathbf{r})$ and the external field $\mathbf{E}_0(\mathbf{r})$ may be written as[12]

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \tfrac{1}{3}\beta\rho\boldsymbol{\mu}\cdot\boldsymbol{\mu}_{\text{eff}}\int_V d\mathbf{r}_2\mathsf{F}(\mathbf{r}_1\mathbf{r}_2)\cdot\mathbf{E}_0(\mathbf{r}_2). \tag{4.34}$$

From Eqs. (4.33) and (4.34) it follows that

$$\mathsf{Q}(\mathbf{r}) = \tfrac{1}{2}\beta^2(\rho/\Omega)\int d\omega_1\boldsymbol{\Delta}(\omega_1)\mathbf{E}(\mathbf{r})\cdot\mathsf{M}(\omega_1)\cdot\mathbf{E}(\mathbf{r}). \tag{4.35}$$

We now must average a fourth rank tensor ΔM over all orientations, where both second rank tensors Δ and M are fixed to the particle and are symmetric. Furthermore, tensor Δ is traceless. A lengthy but straightforward isotropic average over orientations yields the result[13]

$$Q(r) = \tfrac{1}{10}\beta^2\rho[\mathrm{Tr}(\alpha \cdot M) - \tfrac{1}{3}\mathrm{Tr}(\alpha)\ \mathrm{Tr}M][E(r)E(r) - \tfrac{1}{3}IE^2(r)].\qquad(4.36)$$

Thus we found that $Q(r)$ is proportional to quadratic factors of the local macroscopic field $E(r)$ with a proportionality constant which is independent of sample shape and surroundings by virtue of the definition of M in terms of the local, short-range correlation functions in $H_3^{(0)}$.

From the definitions of the Kerr constant, Eq. (1.6), we find

$$K = 2\pi\tfrac{1}{10}\beta^2\rho[\mathrm{Tr}(\alpha \cdot M) - \tfrac{1}{3}\mathrm{Tr}(\alpha)\ \mathrm{Tr}(M)],\qquad(4.37)$$

so that the Kerr constant of this model dipolar fluid is a property of the fluid, independent of sample shape and surroundings.

V. CONCLUSIONS

In this article we have extended the molecular theory of polar fluids developed in I in two directions. First we have shown how the two-particle distribution function may be used to obtain a molecular expression for the Helmholtz free energy of a polar fluid as a sum of the Helmholtz free energy of a reference fluid and a dipolar interaction energy. If the short-range part of the two-particle correlation function $G_2^{(0)}$ is known for various dipole moment strengths then this interaction energy may be computed exactly. In general, such complete knowledge about $G_2^{(0)}$ is not available and one must resort to approximations. We examine in detail the interaction energy that results when one uses the $G_2^{(0)}$ implied by Onsager's model of dielectric fluids. An expression for the contribution to the Helmholtz free energy due to the dipole–dipole interactions is obtained for this model.

Next, we studied the three-particle correlation function G_3 of the polar fluid in the absence of an external field. We found an explicit expression for the long-range part of G_3 in terms of the interaction tensor $F(r, r')$. In the special case of the molecular sample of arbitrary shape V in vacuum or immersed in a continuum W of the same dielectric constant ϵ as the molecular fluid the interaction tensor F is

$$F(r, r') = \epsilon^{-1}[T(r, r') + R_{(V+W)}^*(r, r'; \epsilon^{-1})].\quad(4.27)$$

Thus G_3 has an analogous long-range character to that of G_2 discussed in I. When G_3 occurs in integrals where the region of integration extends effectively over the entire volume, one obtains shape-dependent results.

The three-particle correlation function arises in the molecular expression for the Kerr constant of the polar fluid. We demonstrate that, when the Kerr constant is defined in terms of the average macroscopic field rather than the external field, there is a compensation in shape-dependent effects so that just as in the case of the dielectric constant, a local Kerr constant independent of sample geometry and surroundings results.

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[12] Equation (4.34) follows from Eq. (4.9) of I

$$P_\pi(r) = [(\epsilon-1)/4\pi]E_0(r) + [(\epsilon-1)/4\pi]^2\int dr'F(r, r')\cdot E_0(r'),$$

the constitutive relation $(\epsilon-1)E(r) = 4\pi P_V(r)$, and the result for the dielectric constant ϵ given by Eq. (4.26).
[13] From the definitions (3.4) one finds $\int d(3)G_3(123) = -2G_2(12)$. By considering the order of $\int d(3)G_3^{(1)}(123)$ and $\int d(3)G_3^{(0)}(123)$ for various separations of 1 and 2, one finds then that $\int d(3)G_3^{(0)}(123) = -2G_2^{(0)}(12)$, $\int d(3)G_3^{(1)}(123) = -2G_2^{(1)}(12)$. If we compare these relations with the explicit expression (4.25) for $G_3^{(1)}$, we have to conclude that M is traceless. Hence the term $\mathrm{Tr}M$ in (4.36) and (4.37) is zero and may be omitted.