On the Reduction of Many-Body Dielectric Theories to the Onsager Equation

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An approximate theory for the dielectric constant \( \epsilon \) of a dense polar fluid was derived by Ramshaw, Schaefer, Waugh, and Deutch (RSWD). In the present article, the RSWD theory is generalized and made rigorous by another method of derivation. The result is a rigorous expression for \( \epsilon \) which differs from the RSWD expression by the presence of a fluctuation term. Both the rigorous expression and the RSWD expression are then specialized to the Onsager model. It is found that the rigorous expression for \( \epsilon \) reduces to the Onsager equation, but that the RSWD expression does not because the fluctuation term is nonzero (and nonnegligible) for the Onsager model. The well-known discrepancy between the Onsager equation and the theory of Harris and Alder is found to have the same origin.

I. INTRODUCTION

The first reasonably successful theory for the dielectric constant \( \epsilon \) of a dense polar fluid was the Onsager theory,\(^1\) which was based upon a single-molecule local-field model. Soon thereafter Kirkwood\(^2\) formulated the many-body statistical-mechanical theory of polar dielectrics. A number of authors have subsequently modified and extended the statistical theory.\(^3\)\(^-\)\(^9\)

The primary purpose of the present article is to clarify the relation between the Onsager theory and the statistical theory. Our attention will be restricted to the question of how to properly specialize a statistical expression for \( \epsilon \) to the Onsager model. We shall not consider the more difficult question of whether there exists a well-defined physical limit (e.g., that of "negligible short-range angular correlations") in which a statistical expression for \( \epsilon \) may reduce to the Onsager equation even though the Onsager model has not itself been adopted. (Several authors have considered this latter question, under the assumption that the molecular surroundings of a molecular sample of macroscopic size may be treated as a continuum for calculational purposes. However, the validity of this assumption for systems of polarizable polar molecules is not at present known.)

Our development is based upon a generalization of the approximate dielectric theory derived by Ramshaw, Schaefer, Waugh, and Deutch (RSWD).\(^8\) The result of this generalization is a rigorous expression for \( \epsilon \) which differs from the RSWD expression by the presence of a fluctuation term \( \Delta \). This term represents the effect of fluctuations in the instantaneous dipole moment of a representative molecule about its mean value (in the molecular frame) in zero applied field. The characteristic features of the RSWD theory, including the emphasis on single-molecule orientation and the introduction of an effective molecular dipole moment and polarizability, are preserved in the rigorous theory.

The rigorous expression for \( \epsilon \) is then specialized to the Onsager model. The proper way to effect this specialization is not altogether obvious, and the most straightforward approach (whose correctness may at first appear self-evident) turns out to be wrong. When the specialization to the Onsager model is properly performed, the rigorous expression for \( \epsilon \) is found to reduce to the Onsager equation. A perhaps more surprising result is that \( \Delta \) is nonzero for the Onsager model, so that the RSWD expression does not reduce to the Onsager equation. (The statement of RSWD to the contrary was based upon the incorrect approach mentioned above.) The well-known discrepancy between the Onsager equation and the theory of Harris and Alder\(^4\) is found to have the same origin, namely, the unwarranted neglect of fluctuations.

It is also noteworthy that, for the Onsager model at least, \( \Delta \) is comparable in magnitude to the other terms in the equation, and hence may not be neglected. While this behavior is not necessarily to be expected in all cases, it seems clear that the \textit{a priori} neglect of \( \Delta \) in real systems is hazardous and cannot be recommended as a general procedure. Instead, the magnitude of \( \Delta \) should be separately investigated in each particular case. These remarks have particular relevance to the theories of Kirkwood,\(^2\) Harris and Alder,\(^4\) and RSWD,\(^8\) in all of which fluctuations were neglected in a similar manner.

II. THE RIGOROUS THEORY

We consider the canonical spherical sample of volume \( V \) containing \( N \) identical polarizable polar molecules; the number density \( N/V \) will be denoted by \( \rho \). For simplicity the molecules will be taken to be axially symmetric. The sample is suspended in vacuum and subjected to a uniform static external electric field \( E = E_0 \), where \( E_0 \) is a unit vector which specifies the field direction. We assume that the dielectric constant of the sample is well defined; this is a nontrivial assumption which has been the subject of several recent investigations.\(^10\)\(^-\)\(^14\)

Under these conditions, the polarization (dipole moment per unit volume) \( P \) and the macroscopic Maxwell electric field \( E_0 \) are uniform within the sample, and have the values \((3/4\pi)(\epsilon - 1)/(\epsilon + 2)E\) and \(3E/(\epsilon + 2)\), respectively. Our basic starting expression for \( \epsilon \) is

\[
\left( 3 \over 4\pi \rho \right) \left( \frac{\epsilon - 1}{\epsilon + 2} \right) = \frac{\partial (\mu_0 \cdot E)}{\partial E} \left( \frac{E}{\epsilon} \right)
\]

(1)
Here $\mu_1$ is the instantaneous dipole moment of a representative molecule 1; the brackets $\langle \cdots \rangle$ with subscript $E$ denote an equilibrium statistical-mechanical average over the positions and orientations of all molecules in the sample, taken in the presence of $E$; the subscript zero on the derivative indicates that it is to be evaluated at $E = 0$. Equation (1) is identical to Eq. (2) of RSWD, except that the low-field limit has been made explicit by means of the derivative.

Because the molecules are polarizable, $\mu_1$ depends upon the positions $\mathbf{R}$ and the orientations $\mathbf{\omega}$ of all the molecules in the sample, as well as upon the applied field $E$. We must therefore write $\mu_1$ as $\mu_1(\mathbf{R}, \mathbf{\omega}, E)$. It will be convenient to let the single symbol $\tau$ represent the molecular configuration $(\mathbf{R}, \mathbf{\omega})$. We may then write

$$\langle \mu_1 \cdot \mathbf{e}_s \rangle_E = \int d\tau f_E(\tau) \mu_1(\tau, E) \cdot \mathbf{e}_s,$$  
(2)

where $f_E(\tau)$ is the configurational probability distribution in the presence of $E$. Let the single symbol $\sigma$ denote the partial configuration $(\mathbf{R}, \mathbf{\omega}^{\sigma-1})$, where $\mathbf{\omega}^{\sigma-1} = (\omega_2, \cdots, \omega_N)$. Thus $\sigma$ differs from the complete configuration $\tau$ only by the absence of the orientation $\omega_1$ of molecule 1, so that $\tau = (\omega_2, \sigma)$ and $d\tau = d\omega_1 d\sigma$. We may then make use of the concept of conditional probability to write

$$f_E(\tau) = f_E(\omega_1, \sigma) = f_E(\omega_1) f_E(\sigma | \omega_1),$$  
(3)

where $f_E(\omega_1)$ is the single-molecule orientation distribution function in the presence of $E$,

$$f_E(\omega_1) = \int d\sigma \ f_E(\sigma),$$  
(4)

Equation (3) is the definition of the conditional probability distribution $f_E(\sigma | \omega_1)$, which is the relative probability distribution of $\sigma$ for a given fixed value of $\omega_1$.

Combining Eqs. (2) and (3), we obtain

$$\langle \mu_1 \cdot \mathbf{e}_s \rangle_E = \int d\omega_1 f_E(\omega_1) m_1(\omega_1, E) \cdot \mathbf{e}_s,$$  
(5)

where

$$m_1(\omega_1, E) = \int d\sigma f_E(\sigma | \omega_1) \mu_1(\tau, E).$$  
(6)

The quantity $m_1(\omega_1, E)$ is the average value of $\mu_1$ in the presence of the field under the constraint of fixed $\omega_1$. Its main significance is that it corresponds to a quantity which plays a central role in the Onsager model, as will be seen in the next section. Of immediate interest is the behavior of $m_1(\omega_1, E)$ for the case $E = 0$. Because of the assumed axial symmetry of molecule 1 and the spherical symmetry of the sample, $m_1(\omega_1, 0)$ must lie along the symmetry axis of molecule 1. Therefore

$$m_1(\omega_1, 0) = \mu_s \mathbf{e}_1,$$  
(7)

where $\mu_s$ is a scalar independent of $\omega_1$, and $\mathbf{e}_1$ is the unit vector parallel to the permanent moment of molecule 1 (which must also lie along the symmetry axis). Equation (7) implies that $\mu_s = m_1(\omega_1, 0) \cdot \mathbf{e}_1$. Since $\mu_s$ is independent of $\omega_1$, its value is unchanged by averaging over $\omega_1$, so that

$$\mu_s = \int d\omega_1 f_0(\omega_1) \int d\sigma f_0(\sigma | \omega_1) \mu_1(\tau, 0) \cdot \mathbf{e}_1$$  
$$= \int d\tau f_0(\tau) \mu_1(\tau, 0) \cdot \mathbf{e}_1 = \langle \mu_1(\tau, 0) \cdot \mathbf{e}_1 \rangle_0,$$  
(8)

where the angle brackets with subscript zero denote a statistical average over $\tau$ in zero applied field. We see that $\mu_s$ is identical to the effective molecular dipole moment introduced intuitively by RSWD.

We now combine Eqs. (1), (5), and (7) to obtain

$$\left( \frac{3}{4\pi \epsilon} \left( \epsilon - 1 \right) \right) \left( \frac{\epsilon}{\epsilon + 2} \right) = \mu_s \left( \frac{\partial \cos \theta}{\partial E} \right)_0 + A,$$  
(9)

where $\theta_1$ is the angle between $\mathbf{e}_1$ and $\mathbf{e}_s$, and

$$A = \int d\omega_1 f_0(\omega_1) \left( \frac{\partial m_1(\omega_1, E)}{\partial E} \right)_0 \mathbf{e}_1.$$  
(10)

Equation (9), with $A$ given by Eq. (10), is one form of our rigorous result for $\epsilon$. Alternative expressions for the quantity $A$ are also of interest. If Eqs. (6) and (10) are combined, one obtains

$$A = \overline{\alpha}_s + \Delta,$$  
(11)

where

$$\overline{\alpha}_s = \int d\tau f_0(\tau) \left( \frac{\partial \mu_1(\tau, E)}{\partial E} \right)_0 \mathbf{e}_1 = \frac{1}{3} \left( \int \frac{\partial \mu_1}{\partial E} \right)_0 \mathbf{e}_s,$$  
(12)

$$\Delta = \int d\omega_1 f_0(\omega_1) \int d\sigma \left( \frac{\partial f_0(\sigma | \omega_1)}{\partial E} \right)_0 \mu_1(\tau, 0) \cdot \mathbf{e}_s.$$  
(13)

The second equality in Eq. (12) follows from the spherical symmetry. The quantity $\overline{\alpha}_s$ is seen to be identical to the effective molecular polarizability introduced by RSWD. The significance of $\Delta$ is not apparent from Eq. (13). However, Eq. (13) can be algebraically transformed into the following form:

$$\Delta = \left[ \delta \left( \mu_1(\tau, 0) \cdot \mathbf{e}_s \right) / \partial E \right]_0,$$  
(14)

where

$$\delta \mu_1(\tau) = \mu_1(\tau, 0) - \mu_s \mathbf{e}_1.$$

Thus we see that $\Delta$ is a fluctuation term, which would vanish if the instantaneous dipole moment of molecule 1 in zero applied field were always equal to its effective value $\mu_s \mathbf{e}_1$.

In order to compare our results to those of RSWD, we combine Eqs. (9) and (11) to obtain

$$\left( \frac{3}{4\pi \epsilon} \left( \epsilon - 1 \right) \right) \left( \frac{\epsilon}{\epsilon + 2} \right) = \mu_s \left( \frac{\partial \cos \theta}{\partial E} \right)_0 + \overline{\alpha}_s + \Delta.$$  
(16)

Equation (16) is a rigorous expression for $\epsilon$ which preserves, as far as is possible, the structure, physical insight, and intuitive appeal of the RSWD theory. The quantities $\mu_s$ and $\overline{\alpha}_s$ retain their interpretations as the effective molecular dipole moment and polarizability. If the fluctuation term $\Delta$ is simply neglected, Eq. (16) reduces to Eq. (3) of RSWD. However, as will be discussed in the next section, the validity of this approximation now appears questionable.

We remark parenthetically that the use of the conditional probability distribution is in no way necessary to the derivation of Eq. (16). In fact, Eq. (16), with $\Delta$ given by Eq. (14), could have been obtained almost immediately by combining Eqs. (1) and (2) and introducing Eq. (15) into the result. Our main reason for using the conditional probability approach is that it leads naturally...
to the introduction of the quantity \( m_0(\omega_1, E) \), which in turn greatly facilitates the specialization to the Onsager model.

So far nothing has been said about the form of \( f_0(\tau) \). If a canonical distribution is assumed, the statistical averages \( \langle \cdots \rangle_\beta \) can be explicitly expressed in terms of zero-field averages \( \langle \cdots \rangle_0 \). In particular, one readily finds that

\[
\frac{1}{\beta} \frac{\partial \langle \cos \theta \rangle_\beta}{\partial E} \big|_0 = \frac{1}{\beta} \langle \cos \theta \rangle_0 = \frac{1}{2} \langle \beta \mu_1 \cdot M \rangle_0,
\]

where \( \beta = (k_\text{B} T)^{-1} \) and \( M = M(\tau) \) is the total dipole moment of the spherical sample (i.e., the sum of all the individual molecular moments, both permanent and induced) in configuration \( \tau \) in zero applied field. Similarly, Eq. (14) becomes \( \Delta = \frac{1}{2} \beta \langle \mu_1 \cdot M \rangle_\beta \). By using these expressions, Eq. (16) can be transformed into a well-known formula of Buckingham and Pople.\(^6\) This equivalence is expected, since both formulas are rigorous.

It must be emphasized that each term on the right-hand sides of Eqs. (9) and (16) is shape dependent and must therefore be evaluated for a sphere in vacuum (because this is the geometry in which the equations were derived). In particular, this shape dependence must be taken into account in approximating the quantities \( \langle \cos \theta \rangle_\beta, \Delta, \) and/or \( \Delta \). It appears likely that, as suggested by Harris,\(^5\) the quantity \( \mu_\alpha \) is not itself shape dependent. The shape dependence has its origin in long-range intermolecular interactions. The conventional treatment of shape dependence has been the quasi-macroscopic approach of Kirkwood;\(^8\) only recently has there been a better understanding of the underlying long-range molecular effects begun to evolve.\(^16\)-\(^19\) A satisfactory treatment of the shape-dependence problem for dense systems of polarizable polar molecules is not yet available. These questions, while of considerable importance, have only peripheral relevance to the present article and will not be discussed further.

We conclude this section with a few remarks about the high-frequency dielectric constant. Consider the case in which the applied electric field is sinusoidal, with an angular frequency \( \omega \) which is high enough that molecular orientation is negligible. Then \( f_\omega(\tau) \approx f_0(\tau) \), which implies that \( \langle \cos \theta \rangle_\omega \approx \langle \cos \theta \rangle_0 = 0 \) and \( \langle \mu_1 \cdot e \rangle_\omega \approx \langle \mu_1 \cdot e \rangle_0 = 0 \). Thus Eq. (16) reduces to

\[
(3/4\pi) \left\{ \left( \langle \epsilon(\omega) - 1 \rangle / \langle \epsilon(\omega) + 2 \rangle \right) \right\} = \langle \alpha(\omega) \rangle_0.
\]

The symbols \( \epsilon, \alpha \), with no arguments, will always refer to \( \epsilon(0) \) and \( \alpha(0) \), in accordance with the notation in the rest of the paper. Let \( \omega_c \) denote the lowest frequency for which Eq. (18) is applicable; this will be a frequency just above the rotational absorption regime. We may regard \( \epsilon(\omega) \) as the high-frequency dielectric constant which would be measured experimentally by extrapolating the square of the refractive index to infinite wavelength. Henceforth \( \epsilon(\omega) \) will be denoted by the more convenient notation \( \epsilon_\omega \).

Now from the structure of \( \alpha(\omega) \) [see Eq. (12)] one may expect that \( \alpha(\omega) \approx \alpha(0) \). The derivative \( \delta \langle \mu_1 \rangle(\tau, E) / \partial E \big|_0 \) is taken at fixed \( \tau \) and hence can depend upon frequency only through the molecular polarizabilities, which to an excellent approximation are independent of \( \omega \) for \( \omega < \omega_c \). The average over \( \tau \) is weighted by the zero-field distribution function \( f_0(\tau) \), so the averaging cannot introduce any frequency dependence. These considerations, together with Eq. (18), imply that

\[
(3/4\pi) \left\{ \left( \epsilon_\omega - 1 \right) / \left( \epsilon_\omega + 2 \right) \right\} = \alpha(0) = \alpha_\omega.
\]

Thus, according to Eq. (19), a molecular calculation of \( \alpha_\omega \) can be avoided at the expense of introducing the high-frequency dielectric constant \( \epsilon_\omega \) into the theory as a macroscopic parameter. It is important to realize that this procedure (which has been followed by a number of authors) depends critically upon the frequency independence of \( \alpha(\omega) \) over the range \( 0 < \omega < \omega_c \).

### III. THE ONSAGER MODEL

We now address the problem of how to specialize our previous expressions to the Onsager model of a polar fluid.\(^1\) In this model all molecules except molecule 1 are replaced by a continuum of dielectric constant \( \epsilon \). Since the polarization \( P \) and the Maxwell electric field \( E_\omega \) are uniform within the spherical sample, all possible locations of molecule 1 are equivalent. We may therefore restrict molecule 1 to the center of the sample sphere.

In the Onsager model, molecule 1 is considered to be located at the center of a spherical cavity in the surrounding continuum. If the density of the material inside the cavity is to be the same as that of the bulk dielectric, the cavity radius \( \alpha \) must be chosen so that

\[
(4\pi/3)\alpha^3 = 1.
\]

The electrostatic properties attributed to molecule 1 are a permanent dipole moment \( \mu_\alpha \) and an isotropic harmonic polarizability \( \alpha \).

The Onsager model implies the following basic expression for the dipole moment of molecule 1 in the presence of the field\(^2\):\(^15\):

\[
p_1 = (1 - \alpha \tau)|\mu_1 \theta + 3(\epsilon + 2)^{-1} \alpha_\omega E| \]

where

\[
g = \frac{3\epsilon}{2(\epsilon + 1)}; \quad f = \frac{(2/a)^3(\epsilon - 1)}{(\epsilon + 1)} = \frac{(8\pi/3)(\epsilon - 1)}{(2\epsilon + 1)}. \]

We now come to perhaps the most crucial point in this article. The central question is the following: To what quantity in the statistical theory does \( p_1 \) correspond? At first one may be tempted to regard \( \omega_1 \) as the only molecular degree of freedom, and therefore to identify \( \omega_1 \) with \( \tau \) and \( p_1 \) with \( \mu_1(\tau, E) \). This would be wrong, however, for the other \( (N-1) \) molecules are not absent—they are being represented by a continuum, which means that they must be regarded as having already been averaged over, for fixed \( \omega_1 \). Once this point is appreciated, it becomes clear that the proper identification is that of \( p_1 \) with \( m_0(\omega_1, E) \); thus

\[
m_0(\omega_1, E) = (1 - \alpha \tau)|\mu_1 \theta + 3(\epsilon + 2)^{-1} \alpha_\omega E| \]

is the correct specialization of the statistical theory to the Onsager model.

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The incorrect identification of \( p_1 \) with \( \mu_1(\tau, E) \) would lead to erroneous values for \( \bar{\alpha}_e \) and \( \Delta \). In particular, one would incorrectly find \( \Delta \) to be identically zero for the Onsager model, which in turn would lead one wrongly to conclude that the RSVD expression reduces to the Onsager equation. However, the value of \( A = \bar{\alpha}_e + \Delta \) would fortuitously be correct in spite of the error. The values of \( \mu_a \) and \( (e_1 \cdot \mathbf{M})_0 \) would also be unaffected by the error.

It is now a simple matter to evaluate \( \mu_a \) and \( A \) by means of Eq. (24). Combining Eqs. (7) and (24), we find that

\[
\mu_a = (1 - \alpha)/3 \mu_0 ,
\]

while from Eqs. (10) and (24) we obtain

\[
A = 3 \alpha g/(\epsilon + 2)(1 - \alpha/\epsilon) .
\]

All that remains is to evaluate \( \langle e_1 \cdot \mathbf{M} \rangle_0 \); this will be done by means of Eq. (17). We first write, with complete generality,

\[
\langle e_1 \cdot \mathbf{M} \rangle_0 = \int d\omega_1 f_0(\omega_1)e_1 \cdot \mathbf{M}(\omega_1) ,
\]

where

\[
\mathbf{M}(\omega_1) = \int d\sigma f_0(\sigma) \mathbf{M}(\sigma) ,
\]

In order the evaluate \( \mathbf{M}(\omega_1) \) for the Onsager model, we will make use of the following well-known result from macroscopic electrodynamics: The total dipole moment of a dielectric continuum which fills the region between two concentric spheres of radii \( R_1 \) and \( R_2 \) is equal, in the limit \( R_2 \rightarrow R_1 \), to the dipole moment of the material within the smaller sphere multiplied by the factor \( c(\epsilon) = 9\epsilon/[2(\epsilon + 1)(\epsilon + 2)] - 1 \). Applying this theorem to the present situation (with \( R_1 = \sigma \) and \( R_2 = (3V/4\pi)^{1/3} \)), we obtain

\[
\mathbf{M}(\omega_1) = m_1(\omega_1, 0) + c(\epsilon)m_1(\omega_1, 0) = 9\epsilon m_1(\omega_1, 0)/[2(\epsilon + 1)(\epsilon + 2)] .
\]

We next eliminate \( m_1(\omega_1, 0) \) by means of Eq. (24) and combine the result with Eq. (27) to obtain

\[
\langle e_1 \cdot \mathbf{M} \rangle_0 = 9\epsilon \mu_0/[(2\epsilon + 1)(\epsilon + 2)] .
\]

Equation (9) can now be specialized to the Onsager model by using Eqs. (17), (25), (26), and (30). The result is

\[
\langle e_1 \cdot \mathbf{M} \rangle_0 = \frac{\epsilon - 1)(2\epsilon + 1)}{4\pi \epsilon} = \frac{\rho}{1 - \alpha} - \frac{\beta \mu_0^2}{1 - \alpha} + \frac{3\alpha}{1 - \alpha} ,
\]

which is just the Onsager equation in the equivalent from given by Brown.\(^{15}\) Thus the rigorous theory of the previous section does reduce to the Onsager equation when properly specialized to the Onsager model.

Occasionally the question has been raised as to whether Onsager used the proper expression for the orienting torque on molecule 1 in his derivation of Eq. (31). Most authors have concluded that Onsager's treatment was correct; our results provide an independent confirmation of this conclusion, since we obtain the Onsager equation by a method in which the question of the proper orienting torque does not arise. This question is avoided by using the obviously correct expression (17), which is derived by considering the interaction energy between the entire sample and the external field.

Our next objective is to investigate the behavior of the RSVD expression \( [1, \varepsilon] \), Eq. (16) with the term \( \Delta \) omitted] in the Onsager model. As we have seen, the Onsager model provides an expression for \( m_1(\omega, E) \) but not for \( \mu_1(\tau, E) \); thus \( A \) can be directly evaluated, but \( \bar{\alpha}_e \) and \( \Delta \), taken separately, cannot. However, it is possible to evaluate \( \bar{\alpha}_e \) by generalizing the Onsager model to the case of an external electric field which is sinusoidal with angular frequency \( \omega \). The generalization of Eq. (24) is straightforward; the result is

\[
m_1(\omega, E) = \frac{\mu_0 \mu}{1 - \alpha} + \frac{3\alpha g(\omega)E}{[\epsilon(\omega) + 2][1 - \alpha(\omega)]} ,
\]

where \( f(\omega) \) and \( g(\omega) \) are the same functions of \( \epsilon(\omega) \) as \( f \) and \( g \) are of \( \epsilon \) [see Eqs. (22) and (23)]. Equation (32) immediately implies that

\[
A(\omega) = 3\alpha g(\omega)/[\epsilon(\omega) + 2][1 - \alpha(\omega)] .
\]

We now set \( \omega = \omega_0 \), where \( \omega_0 \) is the lowest frequency at which molecular orientation may be considered negligible. But \( A(\omega_0) = \bar{\alpha}_e(\omega_0) + \bar{\alpha}_e(\omega_0) \), and in connection with Eqs. (18) and (19) we saw that \( \Delta(\omega_0) = 0 \) and that \( \bar{\alpha}_e(\omega_0) = \bar{\alpha}_e(0) = \bar{\alpha}_e \). Thus \( A(\omega_0) = \bar{\alpha}_e \), which together with Eq. (33) implies that

\[
\bar{\alpha}_e = 3\alpha g_e /([\epsilon_e + 1] - \alpha) .
\]

Thus, for the Onsager model, \( \bar{\alpha}_e \) reduces to the polarizability \( \alpha \) of an isolated molecule. This implies, via Eq. (19), that the high-frequency dielectric constant in the Onsager model obeys the Clausius–Mossotti equation;

\[
(\epsilon_e - 1)/(\epsilon_e + 2) = 4\pi \alpha/3 .
\]

We are now in a position to specialize the RSVD expression for \( \epsilon \) to the Onsager model. If Eqs. (17), (25), (30), and (35) are substituted into the RSVD expression, there results

\[
\frac{(\epsilon - 1)(2\epsilon + 1)}{4\pi \epsilon} = \frac{\rho}{1 - \alpha} - \frac{\beta \mu_0^2}{1 - \alpha} + 3\alpha ,
\]

where

\[
F = (1 - \alpha)E(2\epsilon + 1)\rho/9\epsilon .
\]

Equation (37) differs from the Onsager equation (31) by the presence of the factor \( F \), which cannot be reduced to unity (unless \( \epsilon = \epsilon_e \) or \( \epsilon = 1 \)). Thus the RSVD expression does not reduce to the Onsager equation when specialized to the Onsager model. The reason is that RSVD effectively approximate \( A \) by \( \bar{\alpha}_e \); but according to Eqs. (26) and (35) these two quantities are not equal in the Onsager model. This in turn implies that \( \alpha \) is nonzero for the Onsager model. To some approximation, therefore, the Onsager model does represent the effect of fluctuations, in spite of the fact that the model
at first appears to be one in which fluctuations are neglected from the beginning.

An explicit expression for \( \Delta \) in the Onsager model may be obtained from Eqs. (11), (26), and (35).

\[
\frac{\Delta}{\alpha} = -2\left[\frac{(\epsilon - 1)/(\epsilon + 2)}{(\epsilon + 3)/(\epsilon + 5)}\right],
\]

(39)

where we have used Eq. (36). We note that \( \Delta \) is a negative quantity which, for a given fixed value of \( \epsilon_o \), decreases monotonically as \( \epsilon \) is increased. The smallest physical value of \( \epsilon \) is \( \epsilon_o \), which corresponds to \( \Delta = 0 \). If \( \epsilon_o = 2 \) is taken as a typical value, we find that \( \Delta = -0.55\alpha \) for \( \epsilon = 10 \), and \( \Delta = -0.74\alpha \) for \( \epsilon = 20 \). In the limit \( \epsilon \gg \epsilon_o \), \( \Delta \) approaches the value \( -\alpha \). Since \( \Delta_o \) is the Onsager model, \( \Delta \) is seen typically to be comparable in magnitude to \( \Delta_o \) (except for very small values of \( \epsilon \)), and hence \( \Delta \) may not ordinarily be neglected. Indeed, for large \( \epsilon \) it is a better approximation to neglect both \( \Delta_o \) and \( \Delta \) (i.e., to neglect \( A \)) than it is to neglect \( \Delta \) alone. This approximation becomes exact in the limit \( \epsilon \gg \epsilon_o \), since \( A = \Delta_o + \Delta \) then approaches zero.

The above analysis, of course, applies only to the Onsager model; the degree to which real polar fluids exhibit similar behavior is not at present known. It would be of particular interest to know whether the neglect of \( A \) in Eq. (9) is generally a good approximation for real liquids with large \( \epsilon \), since the theory would then reduce to a much simpler form.

Finally, we examine the relevance of the above developments to the theory of Harris and Alder (HA). For this purpose, it is convenient to rewrite Eqs. (31) and (37) in terms of the quantities \( \mu \) and \( \epsilon_o \) given by Eqs. (25) and (36). The Onsager equation (31) then becomes

\[
\epsilon - \epsilon_o = 4\pi \rho \left( \frac{3\epsilon}{2\epsilon + 1} \right) \left[ \frac{1}{3} \beta \mu^2 \right] \left( \frac{2\epsilon + \epsilon_o}{2\epsilon + 1} \right),
\]

(40)

while the corresponding RSWD expression (37) becomes

\[
\epsilon - \epsilon_o = 4\pi \rho \left( \frac{3\epsilon}{2\epsilon + 1} \right) \left[ \frac{1}{3} \beta \mu^2 \right] \left( \frac{\epsilon_o + 2}{3} \right).
\]

(41)

Equation (41) is identical to Eq. (13c) of HA; thus the RSWD and HA theories become equivalent when specialized to the Onsager model. This is not surprising, for HA make an approximation which is equivalent to neglecting \( \beta \) when they write (in their notation) \( \langle M \rangle_o = N(\mu_o \cdot \langle M \rangle_p) \). We have shown that the neglect of \( \Delta \) is responsible for the disagreement between Eqs. (40) and (41), so we may conclude that the failure of the HA theory to reduce to the Onsager equation was due to the neglect of fluctuations in the HA theory.

The discrepancy which HA found to exist between their theory and the Onsager equation gave rise to a certain amount of controversy in the literature. Several authors analyzed the problem from various points of view\(^4,16-19\) and came to various conclusions. We shall make no attempt to summarize or compare these different treatments; we note only that our findings confirm, by a different method, Fröhlich’s conclusion\(^17\) that the basic cause of the HA discrepancy was the neglect of fluctuations.

**APPENDIX**

We take this opportunity to correct the following misprints in the RSWD paper:\(^1\)

(a) The left-hand side of Eq. (2) should be identical to the left-hand side of Eq. (3).

(b) In the second column on page 1242, \( \mu_1(\tau, E + E_o) \) should read \( \mu_1(\tau, E \cdot E_o) \).

(c) The square brackets in Eq. (14) should be deleted.

(d) In Table I, the footnote citations in the "c" column should be changed from "f" to "c", and those in the "m" column should be changed from "c" to "f".

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