Debye–Hückel Theory for Particles of Arbitrary Electrical Structure

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Classical linearized Debye-Hückel theory is formulated for a finite fluid system, of arbitrary shape, composed of rigid particles with arbitrary internal electrical structure. The multipole description is eschewed in favor of the more basic description of a particle in terms of its charge density function. This function is left arbitrary, so the particles may be charged or neutral, polar or nonpolar, etc. The theory implies that the direct correlation function $c(12) = - v(12)/kT$, where $v(12)$ is the Coulomb interaction energy between the charge densities of particles 1 and 2. In the case of uncharged polar molecules, the dielectric constant may be evaluated in closed form from $c(12)$; the result is the Langevin–Debye equation. This development removes the nonuniqueness in the original formulation of dipolar Debye–Hückel theory [J. Chem. Phys. 64, 3666 (1976)], and demonstrates that this nonuniqueness was an artifact of the multipole description rather than the mean-field approximation. Specialization to the case of simple finite dipoles shows that the nonuniqueness is associated with premature passage to the point dipole limit.

I. INTRODUCTION

The Debye–Hückel (DH) mean-field theory\textsuperscript{1} was the first major advance in our understanding of ionic systems. An analogous theory for dipolar fluids was recently formulated.\textsuperscript{4} A curious and unsatisfactory feature of the dipolar Debye Hückel (DDH) theory is its nonuniqueness, which resulted from an ambiguity in the choice of a local electric field. The ambiguity arises because the local field is defined as the field inside an infinitesimal cavity, and this field depends on the cavity shape in a medium described by a dipole moment density.\textsuperscript{3,4}

Attempts to define a local field in the presence of higher multipole densities meet with even more serious difficulties.\textsuperscript{4} However, use of the multipole description is not compulsory: A polarized medium may alternatively be described in terms of an induced charge density. The cavity field in a continuous charge distribution is well defined and independent of the cavity shape; it is just the macroscopic Maxwell electric field.\textsuperscript{3,4} These considerations suggest that the nonuniqueness of the DDH theory may be an artifact of the multipole description rather than the mean-field approximation, and that it may be possible to remove the nonuniqueness by using the charge-density description instead.

In order to pursue these questions, we formulate the linearized DH theory for particles of arbitrary internal electrical structure. The multipole description of this structure is eschewed in favor of a particle charge density function $f(\mathbf{r})$, which represents the charge density at the point $\mathbf{r}$ of a particle whose affixed coordinate frame coincides with the laboratory frame. Since $f(\mathbf{r})$ is left arbitrary, the theory encompasses charged particles, uncharged particles with dipole moments, etc. (In the case of charged particles, a uniform neutralizing background is included to ensure neutrality of the system as a whole.) A synthesis of ionic and dipolar DH theory is thereby effected within a framework more general than either.

The present theory, like the original DH and DDH theories, is based on the familiar DH mean-field approximation, in which the potential of mean force is replaced by the interaction energy of a particle with the local electrostatic field that results from holding another particle fixed. Since this field is now unique, the theory leads to unique results for any $f(\mathbf{r})$, including the dipolar case. Linearization of the Boltzmann weighting factor then yields an integral equation of the Ornstein–Zernike form, enabling the direct correlation function $c(12)$ to be identified. It is found that $c(12) = - \beta v(12)$, where $\beta = (kT)^{-1}$ is the reciprocal temperature in units of energy, and $v(12)$ is the Coulomb interaction energy between the charge densities of particles 1 and 2.

The nonuniqueness of the original DDH theory\textsuperscript{2} led to a nonunique value for the dielectric constant $\epsilon$. Since the present theory removes this nonuniqueness, it is of interest to specialize the theory to the case of uncharged polar molecules to see what unique value of $\epsilon$ now results. This value may be determined by the known expression\textsuperscript{5,6} for $\epsilon$ in terms of $c(12)$. It is found that $\epsilon$ depends on $f(\mathbf{r})$ only through the molecular dipole moment $\mu$, and that the resulting expression for $\epsilon$ in terms of $\mu$ is simply the Langevin–Debye equation. This equation is obtained in the original DDH theory\textsuperscript{2} by setting the nonuniqueness parameter $\theta = 1$, which corresponds to identifying the local electric field with the macroscopic Maxwell electric field. Since this identification is unique and unambiguous in the present theory, it is not surprising that we obtain the corresponding result for $\epsilon$.

Finally, to obtain further insight into the underlying cause of the original DDH nonuniqueness, we consider the special case of a finite dipole composed of point charges $\pm q$ separated by a length $2d$. It is of interest to examine the behavior of this case in the point dipole limit, namely $q \rightarrow \infty$, $d \rightarrow 0$, $2qd = \mu = \text{constant}$. In this case the expression for $c(12)$ is of the form (12)
limit $c(12)$ becomes nonunique and assumes the form it had in the original DDH theory. If $\epsilon$ is evaluated using this form for $c(12)$, the nonunique DDH result is obtained. However, the unique $\epsilon$ of the present theory remains unchanged in the point dipole limit, since it depends only on $q_1d$ to begin with. The nonuniqueness in $\epsilon$ therefore appears to be an artificial consequence of taking the point dipole limit prematurely. This was implicitly done in the original DDH theory by assuming that only dipole moments produce and interact with the mean field.

II. THE DEBYE–HÜCKEL DIRECT CORRELATION FUNCTION

We consider a finite volume $V$, of arbitrary shape, containing $N$ identical rigid particles of arbitrary internal electrical structure. The number density $N/V$ is denoted by $n$. The position and orientation of particle $k$ are denoted by $r_k$ and $\omega_k$, respectively, and are collectively represented by the shorthand notation $(k)$. The angular measure $\int d\omega$ is denoted by $\Omega$.

To each particle is rigidly affixed a coordinate frame that translates and rotates with the particle. These coordinate frames are defined in the same way for all the particles, so that two particles coincide if their coordinate frames coincide. The internal electrical structure of a representative particle is described by a charge density function $\rho(r)$, which represents the charge density at the point $r$ of a particle whose affixed coordinate frame coincides with the laboratory frame. The charge density of particle $k$ is denoted by $\rho(r; k)$, which is related to $\rho(r)$ by

$$\rho(r; k) = f(A(\omega) \cdot (r - r_k)),$$

(1)

where $A(\omega)$ is the rotation tensor. If orientations are specified by the Euler angles, then $\omega = (\theta, \phi, \psi)$, $\Omega = S^2$, and $A(\omega)$ is the tensor whose components in the laboratory frame are just the matrix elements in Eq. (4-46) of Ref. 7.

The net charge carried by each particle is $Q = \int d\omega f(r)$, which may or may not be zero. To allow for the latter possibility, we endow the system with a uniform background charge density of $-nQ$, so that the system as a whole is neutral. This global neutrality is necessary to prevent pathological behavior.

Suppose that particle 1 is held fixed at $(r_1, \omega_1)$. The resulting mean charge density at the point $r$ is then

$$\overline{\rho}(r | 1) = \rho(r; 1) + (n/Q) \int d(r; 2) \rho(r; 2) n_2(12) - nQ,$$

(2)

where $n_2(12)$ is the two-particle generic distribution function. Since $f d(r; 2) \rho(r; 2) = \Omega Q$, Eq. (2) may be rewritten as

$$\overline{\rho}(r | 1) = \rho(r; 1) + (n/Q) \int d(r; 2) \rho(r; 2) h(12),$$

(3)

where $h(12) = (n/Q)^2 n_2(12) - 1$ is the total correlation function. The electrostatic potential field produced by $\overline{\rho}(r | 1)$ is

$$\phi(r | 1) = \int d(r') |r - r'|^{-1} \overline{\rho}(r | 1).$$

(4)

The interaction energy of a representative particle, say particle 2, with $\phi(r | 1)$ is

$$U(2 | 1) = \int d(r; 2) \rho(r; 2) \phi(r; 1).$$

(5)

We now adopt the fundamental DH approximation of replacing the potential of mean force by $U(2 | 1)$, so that $h(12) = \exp[- \beta U(2 | 1)] - 1$. Linearization of the Boltzmann factor then yields the linearized DH approximation to $h(12)$:

$$h(12) = - \beta U(2 | 1).$$

(6)

Combining Eqs. (3)-(6), we obtain the following closed equation for $h(12)$:

$$h(12) = - \beta v(12) + (n/Q) \int d(r; 2) h(13)[ - \beta v(32) ] + \ldots,$$

(7)

where

$$v(12) = \int dr dr' |r - r'|^{-1} \rho(r; 2) \rho(r'; 1)$$

(8)

is just the Coulomb energy of interaction between the charge densities of particles 1 and 2. Equation (7) is of the Ornstein-Zernike form, and shows that the direct correlation function $c(12)$ is given by

$$c(12) = - \beta v(12).$$

(9)

Equation (9) is the DH result for $c(12)$. Since $f(r)$ has been left arbitrary, this result applies to charged particles, to uncharged particles with dipole moments, and so on. Of course, $c(12)$ is a functional of $f(r)$; this functional is determined by Eqs. (1), (3), and (9). The DH result for $h(12)$ is implicitly determined by the integral equation (7), in which the spatial integral extends only over the sample volume $V$.

III. THE DIELECTRIC CONSTANT FOR UNCHARGED POLAR MOLECULES

In this section we specialize to the case of uncharged particles with dipole moments. Our objective is to evaluate the dielectric constant $\epsilon$, which was nonunique in the original DDH theory but which will now be uniquely determined by our unique result for $c(12)$.

Since the particles are uncharged, the interparticle potential $v(12)$ clearly becomes asymptotic to the dipole-dipole potential at large $|r_1 - r_2|$. Therefore $\epsilon$ exists and is given by

$$\epsilon = \frac{1}{\epsilon + 2} = \gamma \sum_{a, b=1} (\mu_a \mu_b / \mu^2)^2 (\hat{r} - n \hat{c})^{\perp} \delta_{ab},$$

(10)

where $\gamma = (4\pi/9)\beta \mu^3$, $\mu$ is the magnitude of the molecular dipole moment, $\hat{c}$ is its component along the $a$ axis of the molecular frame, $\hat{r}$ is the $3 \times 3$ unit matrix with elements $\delta_{ab}$, $\hat{c}$ is the $3 \times 3$ matrix with elements

$$c_{ab} = \alpha^{2} \int d\omega_2 d\omega_1 c(12) e_{a1} \cdot e_{b2},$$

(11)

and $e_{a1}$ is the unit vector along the $a$ axis of molecule $k$.

The dipole moment of molecule $k$ is given by

$$\mu_k = \sum_{a} \mu_a e_{a1} = \int d\omega_1 \rho(r; k).$$

(12)
However, Eq. (1) shows that
\[ \rho(r; k) = \rho(r; r_s, \omega_e) = \rho(r - r_s; 0, \omega_e). \]

Therefore, \( \mu_s \) may also be written as
\[ \mu_s = \int ds s \rho(s; 0, \omega_e), \]
which is the form we shall need below.

We now proceed to evaluate \( c_{ab} \). Combining Eqs. (8), (9), and (11), we obtain
\[ c_{ab} = -\beta \alpha^2 \int dr_0 \omega_0 \omega_2 e_{a1} \cdot e_{b2} \times \int dr dr' |r - r'|^{-1} \rho(r; 2) \rho(r'; 1). \]

The easiest way to evaluate them is to restrict the integrals over \( r_0, s, \) and \( s' \) extend over all space. The easiest way to evaluate them is to restrict the range of the \( r_0 \) integral to the spherical region \( |r_0| < R \), with the understanding that the limit \( R \to \infty \) is ultimately to be taken. It is then easy to show that
\[ \int dr_0 |r_0 + s - s'|^{-1} = 2\pi(R^2 - |s - s'|^2), \]
so that Eq. (16) becomes
\[ c_{ab} = (2\pi \beta/3G^2) \int \omega_1 \omega_2 e_{a1} \cdot e_{b2} \int ds ds' \rho(s; 0, \omega_e) \times \rho(s'; 0, \omega_e) |s|^2 + |s'|^2 - 2s \cdot s' - 3R^2). \]

Since the variables are uncharged, \( \int ds \rho(s; k) = 0 \) and the terms involving \( |s|^2, |s'|^2, \) and \( R^2 \) do not contribute to \( c_{ab} \). Equation (18) therefore reduces to
\[ c_{ab} = (-4\pi \beta/3G^2) \int \omega_1 \omega_2 e_{a1} \cdot e_{b2} \frac{\delta_{a1} \cdot \mu_1 \cdot \mu_2}{}, \]
where use has been made of Eq. (14). By virtue of Eqs. (1) and (6) of Ref. 6, this expression further reduces to
\[ c_{ab} = (-4\pi/9) \beta \mu_a \mu_b. \]

It is now a simple matter to evaluate the inverse of the matrix \((I - nC)\). This task is made even easier by choosing the molecular coordinate frame so that \( \mu_a \) and \( e_{a2} \) are collinear. Then \( \mu_a = \mu_a e_{a2}, \) \( nC_{ab} = -\delta_{ab} \delta_{a3}, \) and
\[ (I - nC)_{ab} = \delta_{ab}(1 + y \delta_{a3}). \]

Since \((I - nC)\) is now a diagonal matrix, its inverse follows trivially:
\[ [(I - nC)^{-1}]_{ab} = \delta_{ab}(1 + y \delta_{a3})^{-1}. \]

Equation (10) for \( \epsilon \) now becomes
\[ \frac{\epsilon - 1}{\epsilon + 2} = \chi[(I - nC)^{-1}]_{33} = \frac{y}{1 + y}. \]

This expression for \( \epsilon \) may be obtained in the original DDH theory by setting the nonuniqueness parameter \( \theta = 1 \). This choice corresponds to the use of a needle-shaped cavity to define the local electric field, which makes the local field equal to the macroscopic Maxwell electric field. In itself this is not surprising, since the local field in the present treatment is independent of cavity shape and is unambiguously equal to the Maxwell field. However, it is somewhat remarkable that regardless of the form of \( j(r) \), \( \epsilon \) depends only on the dipole moment \( \mu_1 \); more complicated functional dependences on \( j(r) \) might easily have been imagined.

One readily verifies that Eq. (23) is equivalent to
\[ \epsilon = 1 + 3y, \]
which is just the Langemn-Debye equation. In the linearized DH approximation, therefore, \( \epsilon \) is uniquely and unambiguously given by the Langemn-Debye equation. This equation, of course, is known to be an unsatisfactory approximation for \( \epsilon \). This reflects the fact that \( \epsilon \) is determined by the short-range part of \( c(12) \), which one cannot expect to be accurately obtained in the linearized DH approximation.

IV. ORIGIN OF THE DDH NONUNIQUENESS

It is apparent from the preceding development that the nonuniqueness of the original DDH theory was an artifact of the multipole description rather than the mean-field approximation. To obtain further insight into the origin of the nonuniqueness, we consider the special case of a simple finite dipole composed of point charges \( \pm q \) separated by a length \( 2d \). Then \( \mu = 2qd \) and
\[ \rho(r; k) = q\delta(r - r_s - d_a) - q\delta(r - r_s + d_a), \]
where \( d_a = d(\omega_e) \) is the vector of length \( d \) from the point \( r_s \) to the charge \( +q \) of molecule \( k \). Clearly, \( \mu = 2qd_a \).

It is of particular interest to examine the behavior of this case in the point dipole limit \( (q = \omega_e, d = 0, 2qd = \mu = \text{constant}) \), in which all the higher multipole moments vanish. It is clear that \( \epsilon \) remains unchanged in this limit, since it depends on \( j(r) \) only through \( \mu \). We may therefore restrict our attention to the limiting behavior of \( c(12) \).

Combining Eqs. (8), (9), and (25), we obtain
\[ c(12) = -\beta q^2 |r_2 - r_1 + d_a|^{-1} - |r_2 - r_1 + d_a - d_1|^{-1} - |r_2 - r_1 - d_a - d_1|^{-1} - |r_2 - r_1 + d_a|^{-1}. \]

However,
\[ |r + a|^{-1} = |r|^{-1} + a \cdot v |r|^{-1} + \frac{1}{2} a a : v v |r|^{-1} + o(|a|^3). \]

Therefore,
\[ c(12) = -\beta q^2 [4d_1 \cdot T(r_2 - r_1) \cdot d_2] + o(q^2 d^2) \]
\[ = \beta \mu_1 \cdot T(r_2 - r_1) \cdot \mu_2 + o(q^2 d^2), \]
where \( T(r) = v v |r|^{-1} \) is the dipole tensor. In the point dipole limit, therefore, \( c(12) \) becomes simply
\[ c(12) = \beta \mu_1 \cdot T(r_2 - r_1) \cdot \mu_2. \]

However, \( c(12) \) is effectively nonunique, because integrals in which it appears in the integrand are in gen-
The nonuniqueness is a consequence of the singularity at \( r_2 \neq r_1 \), which makes such integrals improper. They must therefore be evaluated by excluding from the integral a small cavity enclosing the singularity, and taking the limit as the cavity size goes to zero. This limit, however, depends on the shape of the cavity, and hence is nonunique. The nonuniqueness may be parameterized by considering the cavity to be spheroidal; the effect is to replace \( T(\mathbf{r}) \) by

\[
T_s(\mathbf{r}) = H(\mathbf{r}) - \delta \nabla \nabla \cdot \mathbf{r}^{-1} - (4\pi \theta /3) \delta(\mathbf{r}) \mathbf{U},
\]

where \( H(x) = 1 \) if \( x \geq 0 \) and is zero otherwise, \( \theta \) is related to the ellipticity of the cavity, \( \mathbf{U} \) is the unit dyadic, and it is understood that the limit \( \delta \to 0 \) is ultimately to be taken. Replacement of \( T(\mathbf{r}) \) by \( T_s(\mathbf{r}) \) in \( c_{\text{M}}(12) \) yields

\[
c_{\text{M}}(12) = -(4\pi \theta /3) \mu_1 \cdot \mu_2 \delta(r_2 - r_1)
+ \beta H(r_2 - r_1) - \mu_1 \mu_2 : \nabla_2 \nabla_2 |r_2 - r_1|^{-1},
\]

where \( \nabla_2 \) is the gradient with respect to \( r_2 \). We observe that \( c_{\text{M}}(12) \) is now precisely the same as the nonunique direct correlation function in the original DDH theory.

If \( \epsilon \) were evaluated using \( c_{\text{M}}(12) \) instead of \( c(12) \), we would obtain the original nonunique DDH result for \( \epsilon \). It is clear, however, that this nonuniqueness in \( \epsilon \) is not intrinsic in the mean-field approximation, but simply results from taking the point dipole limit prematurely. If this limit is deferred until after \( \epsilon \) has been evaluated, the unique \( \epsilon \) of the present theory results.

V. CONCLUDING REMARKS

We have formulated the linearized DH theory for particles of arbitrary internal electrical structure, and thereby have resolved the nonuniqueness in the original DDH theory. The Langevin–Debye equation now emerges as the unique expression for \( \epsilon \) in the linearized DH approximation. One may at first wonder how this uniqueness can be reconciled with the various other expressions for \( \epsilon \) (such as the Clausius–Mossotti and Onsager equations) which one thinks of as mean-field approximations. The answer is that the DH choice of the mean field is not the only possible choice. In the DH theory, the mean field is taken to be the field inside an infinitesimal mathematical cavity, which is small compared to any physical length scale in the problem (including the molecular length scale) and which is not allowed to disturb the surrounding medium. If either or both of these conditions are relaxed, other mean fields result. The Lorentz local field is the field inside a finite mathematical cavity of spherical shape, which is small macroscopically but much larger than an individual molecule. The Onsager local field is the field inside a finite physical cavity of spherical shape, which is allowed to disturb the surrounding medium in a manner consistent with macroscopic electrostatics. (The Onsager reaction field is immaterial here; it has no effect when the molecular polarizability is zero.) The superiority of the Onsager equation over the Langevin–Debye and Clausius–Mossotti equations may be regarded as a consequence of the fact that a physical cavity is more physical than a mathematical one.

Both the Lorentz and Onsager local fields would be different if a different cavity shape were chosen. In the former case, the shape dependence and its attendant nonuniqueness are again related to the point dipole limit. If this limit is taken, it is no longer possible to make the cavity small in comparison to the molecular length scale; this has the same effect as a restriction to cavities that are much larger than an individual molecule.

Finally, we recall that the nonuniqueness of the original DDH theory also appears when the mean-field approximation in a dipolar system is approached via the modern \( y \to 0 \) limiting procedure. It seems likely that the nonuniqueness of the \( y \to 0 \) limit in dipolar fluids is again associated with the multipole description, and that this limit would be unique within the framework of the charge density description.