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Debye–Hückel Theory for Rigid-Dipole Fluids

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The dipolar analog of classical linearized Debye–Hückel theory is formulated for a finite fluid system of arbitrary shape composed of rigid polar molecules. In contrast to the ionic case, the dipolar Debye–Hückel (DDH) theory is nonunique due to an inherent arbitrariness in the choice of a local field E^*. This nonuniqueness is expressed in terms of a parameter θ related to the ellipticity of the spheroidal cavity used to define E^*. The theory then leads to an expression for the direct correlation function $c(\theta)$ as a function of θ. Only the short-range part of $c(\theta)$ depends upon θ; the long-range part equals $-\phi_d/kT$ for all θ, where ϕ_d is the bare dipole–dipole potential. This result for $c(\theta)$ implies the existence of the dielectric constant ϵ for all θ and leads to a formula for $\epsilon(\theta)$. The DDH results for $c(\theta)$ and $\epsilon(\theta)$ are formally identical to the "mean-field" results of Høye and Stell (obtained for an infinite system by a $\gamma \to 0$ limiting procedure) in which θ represents a "core parameter."

I. INTRODUCTION

Mean-field theories have proven very useful in providing simple and tractable approximations to the behavior of strongly interacting many-particle systems. Examples from statistical thermodynamics are the van der Waals theory of simple fluids,[1] the Weiss molecular-field theory of ferromagnetism,[2] the Debye–Hückel theory of ionic fluids,[3] and the Lorentz and Onsager local-field dielectric theories.[4,5] The basic idea of the mean-field theories is very simple and intuitively appealing. One focuses attention on a particular representative particle in the system, and assumes that its net interaction with the other particles may be represented by an appropriate "mean" (the terms "self-consistent," "local," and "effective" are also used) force field due to them. The statistical problem then reduces to that of a single particle interacting with a force field and may be solved trivially. Of course, to obtain useful information one must choose a situation where the mean field is nonzero. Such a situation may be realized either by holding some other particle fixed, or by imposing an external field on the system. In the former case one obtains information about pair correlations in the system, while in the latter case one obtains information about the response of the system to an external field. Mean-field theories seldom yield satisfactory quantitative results, but they usually lead to a substantially correct qualitative understanding of the physical phenomenon in question.

The principal disadvantage of the mean-field theories as originally formulated is that it is unclear how to obtain systematic improvements or corrections to them. During recent years, this disadvantage has been largely overcome, at least in principle, by the development of systematic expansion procedures[6] which exploit the fact that the mean-field theories typically become exact in the limit of infinitely weak and infinitely long-range intermolecular interactions. This limit is conveniently taken by introducing the Kac inverse-range parameter γ into the interaction potential and sending γ to zero. The correspondence of the $\gamma \to 0$ limit to the classical mean-field results has been established for simple nonpolar fluids,[6,7] simple lattice systems,[8] ionic fluids,[9] and polar dielectric fluids.[10,11] For $\gamma > 0$, systematic corrections to the mean-field results can be generated by

means of γ-ordering theory.[6]

The classical mean-field theory for ionic fluids is the Debye–Hückel (DH) theory, in which one particle is held fixed and the average density of particles around it is evaluated, thereby determining the pair distribution function. The classical mean-field theories for polar dielectrics are the Lorentz and Onsager local-field theories, in which the response of the system to an external electric field is considered, thereby determining the dielectric constant. Because of this difference in emphasis, the local-field dielectric theories have little in common with the DH theory. Fundamentally, however, one would expect the ionic and polar cases to be closely analogous, since in both cases the dominant effect is that of long-range electrostatic interactions. In this paper we develop and confirm this analogy by formulating a generalized mean-field theory for the pair distribution function of a rigid-dipole fluid[12] in zero applied field. This theory may be regarded as the dipolar analog of the classical linearized DH theory, to which it is procedurally and conceptually isomorphic. It will therefore be referred to as the dipolar Debye–Hückel (DDH) theory.

In order to develop the DDH theory it is necessary to assume a form for the local electric field E^* in a polarized medium. It is natural to define $E^*(r)$ to be the field inside an infinitesimal cavity at the point r. In the ionic case this E^* is unique and is simply equal to the Maxwell electric field E. In the polar case, however, E^* depends upon the shape of the cavity[13] and hence is not uniquely defined. This shape dependence unfortunately cannot be removed; it is inherent in the description of a polarized medium in terms of a dipole moment density. Therefore, we carry the shape dependence along by defining E^* in terms of a spheroidal cavity of arbitrary ellipticity. The cavity ellipticity is specified by a parameter θ which becomes an adjustable parameter of the theory.

Having thus defined the local field, we proceed to approximate the potential of mean force by the interaction energy between one molecule and the local field which results from holding another molecule fixed. This approximation is precisely in the spirit of the original DH theory. The usual linearization then leads to an inte-

gral equation of Ornstein–Zernike form for the pair distribution function, and hence determines the form of the direct correlation function c. Only the short-range part of c depends upon θ; the long-range part equals $-\phi_d/kT$ for all θ, where ϕ_d is the bare dipole–dipole potential. This result for c implies the existence of the dielectric constant ϵ for all θ and leads to a formula for ϵ as a function of θ.

The same formula for $\epsilon(\theta)$, and the result that ϵ exists for all θ, are obtained by using $\mathbf{E}^*(\theta)$ in the conventional manner to calculate the polarization produced by an external electric field. This agreement serves as a check on the internal consistency of the theory.

Recently Høye and Stell (HS)[10,11] have shown how to generate a one-parameter family of mean-field results for the pair distribution function and the dielectric constant of a rigid-dipole fluid, by sending γ to zero within the framework of γ-ordering theory. The parameter in their theory is a "core parameter" related to the way in which the pair potential is decomposed into a reference term and a perturbing term. The general theory of HS is invariant to the value of the core parameter, but this invariance no longer holds in the $\gamma \to 0$ limit. Upon comparison, it is found that the DDH results for $c(\theta)$ and $\epsilon(\theta)$ are *formally identical* to the corresponding $\gamma \to 0$ results of HS, in which θ represents their core parameter. Although a correspondence between the results of the "classical" DDH mean-field theory and those of the modern $\gamma \to 0$ limiting procedure would certainly have been expected, it is remarkable that in both approaches one is led to introduce a parameter of nonuniqueness, in two quite different ways, and that the detailed functional dependences of the results upon their respective parameters are identical. Thus, the core parameter of HS is shown to have, in addition to its original significance, a second and purely geometrical interpretation in terms of a cavity ellipticity. In addition, one gains a new insight into the fact that the HS theory becomes nonunique in the "mean-field" $\gamma \to 0$ limit: the non-uniqueness arises because the mean field itself is non-unique in a polarized medium.

II. DERIVATION OF THE DDH THEORY

Consider a rigid-dipole fluid[12] which occupies a volume V of arbitrary shape suspended in vacuum in zero applied field. Hold one of the molecules fixed at position $\mathbf{r}_0$ with orientation $\boldsymbol{\omega}_0$. Then the probability of there being another molecule in the interval $d^3r\,d\omega$ about position $\mathbf{r}$ and orientation $\boldsymbol{\omega}$ is $d^3r\,d\omega$ times

$$p(\mathbf{r}, \boldsymbol{\omega} \mid \mathbf{r}_0, \boldsymbol{\omega}_0) = (4\pi/\rho)\rho^{(2)}(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_0, \boldsymbol{\omega}_0) , \quad (1)$$

where ρ is the number density and $\rho^{(2)}$ is the two-molecule generic distribution function. The polarization which exists at the point $\mathbf{r}$ in the system is given by

$$\mathbf{P}(\mathbf{r} \mid \mathbf{r}_0, \boldsymbol{\omega}_0) = \mu_0 \left[\mathbf{e}(\boldsymbol{\omega}_0)\delta(\mathbf{r} - \mathbf{r}_0) \right.$$
$$\left. + \int d\omega\, \mathbf{e}(\boldsymbol{\omega})p(\mathbf{r}, \boldsymbol{\omega} \mid \mathbf{r}_0, \boldsymbol{\omega}_0) \right], \quad (2)$$

where μ_0 is the magnitude of the molecular dipole moment and $\mathbf{e}(\boldsymbol{\omega})$ is the unit vector with orientation $\boldsymbol{\omega}$. We

define the local electric field produced by this polarization to be

$$\mathbf{E}^*(\mathbf{r} \mid \mathbf{r}_0, \boldsymbol{\omega}_0) = -(4\pi\theta/3)\mathbf{P}(\mathbf{r} \mid \mathbf{r}_0, \boldsymbol{\omega}_0)$$
$$+ \lim_{\delta \to 0} \int_V d^3r'\, \mathbf{T}_\delta(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}' \mid \mathbf{r}_0, \boldsymbol{\omega}_0) , \quad (3)$$

where $\mathbf{T}_\delta(\mathbf{r}) = H(|\mathbf{r}| - \delta)\nabla\nabla|\mathbf{r}|^{-1}$, and $H(x)$ is unity if $x \geq 0$ and zero otherwise. The field $\mathbf{E}^*(\mathbf{r} \mid \mathbf{r}_0, \boldsymbol{\omega}_0)$ is the field inside a small spheroidal cavity centered at $\mathbf{r}$ with symmetry axis along $\mathbf{P}(\mathbf{r} \mid \mathbf{r}_0, \boldsymbol{\omega}_0)$, in the limit as the cavity volume tends to zero. The parameter θ is related to the ellipticity of the cavity in the following way:

$$\theta = 1 - 3D , \quad (4)$$

where D is the depolarizing factor for the spheroid along its symmetry axis.[13] The value of θ varies from -2 in the extreme oblate limit (flat disk-shaped cavity) to $+1$ in the extreme prolate limit (thin needle-shaped cavity). For a spherical cavity, θ is zero and $\mathbf{E}^*$ reduces to the Lorentz local field.[4] The choice $\theta = 1$ makes $\mathbf{E}^*$ equal to the macroscopic Maxwell electric field.

It is convenient to define an auxiliary tensor

$$\mathbf{C}_\delta(\mathbf{r}) = \mathbf{T}_\delta(\mathbf{r}) - (4\pi\theta/3)\delta(\mathbf{r})\mathbf{U} , \quad (5)$$

where $\mathbf{U}$ is the unit tensor. Equation (3) can then be rewritten in the shorter form

$$\mathbf{E}^*(\mathbf{r} \mid \mathbf{r}_0, \boldsymbol{\omega}_0) = \lim_{\delta \to 0} \int_V d^3r'\, \mathbf{C}_\delta(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}' \mid \mathbf{r}_0, \boldsymbol{\omega}_0) . \quad (6)$$

The interaction energy of a molecule at $(\mathbf{r}, \boldsymbol{\omega})$ with $\mathbf{E}^*$ is

$$\phi(\mathbf{r}, \boldsymbol{\omega} \mid \mathbf{r}_0, \boldsymbol{\omega}_0) = -\mu_0 \mathbf{e}(\boldsymbol{\omega}) \cdot \mathbf{E}^*(\mathbf{r} \mid \mathbf{r}_0, \boldsymbol{\omega}_0) . \quad (7)$$

We now make the fundamental assumption, precisely in the spirit of the original DH theory, that

$$p(\mathbf{r}, \boldsymbol{\omega} \mid \mathbf{r}_0, \boldsymbol{\omega}_0) \cong (\rho/4\pi)\exp[-\beta\phi(\mathbf{r}, \boldsymbol{\omega} \mid \mathbf{r}_0, \boldsymbol{\omega}_0)]$$
$$\cong (\rho/4\pi)[1 - \beta\phi(\mathbf{r}, \boldsymbol{\omega} \mid \mathbf{r}_0, \boldsymbol{\omega}_0)] , \quad (8)$$

where $\beta = (kT)^{-1}$. Combining Eqs. (1), (2), (6), (7), and (8) and introducing the total correlation function

$$h(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_0, \boldsymbol{\omega}_0) = (4\pi/\rho)^2\rho^{(2)}(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_0, \boldsymbol{\omega}_0) - 1 , \quad (9)$$

we obtain

$$h(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_0, \boldsymbol{\omega}_0) = \beta\mu_0^2\mathbf{e}(\boldsymbol{\omega}) \cdot \mathbf{C}_\delta(\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{e}(\boldsymbol{\omega}_0) + (\rho/4\pi)$$
$$\times \int_V d^3r' \int d\omega'\,\beta\mu_0^2\mathbf{e}(\boldsymbol{\omega}) \cdot \mathbf{C}_\delta(\mathbf{r} - \mathbf{r}')$$
$$\cdot \mathbf{e}(\boldsymbol{\omega}')h(\mathbf{r}', \boldsymbol{\omega}'; \mathbf{r}_0, \boldsymbol{\omega}_0) \quad (\delta \to 0) , \quad (10)$$

where the notation $(\delta \to 0)$ means that this limit is to be taken *after* all other manipulations in any particular calculation have been performed. Equation (10) is of Ornstein–Zernike form[14] and permits the immediate identification of the direct correlation function:

$$c(\mathbf{r}, \boldsymbol{\omega}; \mathbf{r}_0, \boldsymbol{\omega}_0) = \beta\mu_0^2\mathbf{e}(\boldsymbol{\omega}) \cdot \mathbf{C}_\delta(\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{e}(\boldsymbol{\omega}_0)$$
$$= -(4\pi\theta/3)\beta\mu_0^2\mathbf{e}(\boldsymbol{\omega}) \cdot \mathbf{e}(\boldsymbol{\omega}_0)\delta(\mathbf{r} - \mathbf{r}_0)$$
$$+ \beta\mu_0^2\mathbf{e}(\boldsymbol{\omega}) \cdot \mathbf{T}_\delta(\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{e}(\boldsymbol{\omega}_0) \quad (\delta \to 0). \quad (11)$$

From Eq. (11) we see that the long-range part of the

direct correlation function in the DDH theory is simply equal to $-\beta$ times the bare dipole–dipole intermolecular potential. This result corresponds closely to that obtained for ionic systems, where the DH theory leads to a direct correlation function which is $-\beta$ times the bare Coulombic interparticle potential.[15] Since the DDH theory has been developed for a finite sample, we also see explicitly from Eq. (11) that the DDH direct correlation function is independent of the volume and shape of the sample. However, the pair distribution function $\rho^{(2)}$ is shape dependent due to the convolution in the Ornstein–Zernike equation, Eq. (10).

We now consider the dielectric implications of the DDH theory. For this purpose, it is sufficient to observe that the direct correlation function given by Eq. (11) is a special case of an assumed form for $c(\mathbf{r}, \omega; \mathbf{r}_0, \omega_0)$ which has previously been studied.[16] In this previous work it was shown that if c has the assumed form then ϵ rigorously exists and is given by

$$\frac{\epsilon - 1}{\epsilon + 2} = (4\pi/9)\beta\rho\mu_0^2[1 - (\rho/4\pi)A]^{-1} , \tag{12}$$

where

$$A = (4\pi)^{-1} \int d^3r' \int d\omega\, d\omega'\, c(\mathbf{r}, \omega; \mathbf{r}', \omega')\mathbf{e}(\omega) \cdot \mathbf{e}(\omega') . \tag{13}$$

Substitution of Eq. (11) into Eq. (13) yields

$$A = - (4\pi/3)^2 \theta\beta\mu_0^2 , \tag{14}$$

so that Eq. (12) becomes

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{y}{1 + \theta y} , \tag{15}$$

where $y = (4\pi/9)\beta\rho\mu_0^2$. For the case of a spherical cavity $\theta = 0$ and Eq. (15) reduces to the Clausius–Mossotti equation.

It is instructive to compare these results to those obtained by the direct use of the local field $\mathbf{E}^*$ in the conventional manner to calculate the polarization produced by an external electric field. Equation (3) can be applied to this situation simply by deleting the arguments $(\mathbf{r}_0, \omega_0)$ and adding an external field $\mathbf{E}_0(\mathbf{r})$ to its right-hand side:

$$\mathbf{E}^*(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) - (4\pi\theta/3)\mathbf{P}(\mathbf{r}) + \lim_{\delta \to 0} \int_V d^3r'\, \mathbf{T}_\delta(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') . \tag{16}$$

The macroscopic Maxwell electric field $\mathbf{E}(\mathbf{r})$ is obtained by setting $\theta = 1$ in Eq. (16). Therefore,

$$\mathbf{E}^*(\mathbf{r}) = \mathbf{E}(\mathbf{r}) - (4\pi/3)(\theta - 1)\mathbf{P}(\mathbf{r}) . \tag{17}$$

The interaction energy of a molecule at $(\mathbf{r}, \omega)$ with $\mathbf{E}^*$ is simply $-\mu_0\mathbf{e}(\omega) \cdot \mathbf{E}^*(\mathbf{r})$ and the corresponding Boltzmann factor is $\exp[\beta\mu_0\mathbf{e}(\omega) \cdot \mathbf{E}^*(\mathbf{r})]$. To first order in $\mathbf{E}^*$, the polarization is therefore given by

$$\mathbf{P}(\mathbf{r}) = \rho(4\pi)^{-1} \int d\omega\, \mu_0\mathbf{e}(\omega)\beta\mu_0\mathbf{e}(\omega) \cdot \mathbf{E}^*(\mathbf{r}) = \tfrac{1}{3}\beta\rho\mu_0^2\mathbf{E}^*(\mathbf{r}) , \tag{18}$$

where we have used the fact that $\int d\omega\, \mathbf{e}(\omega)\mathbf{e}(\omega) = (4\pi/3)\mathbf{U}$. Eliminating $\mathbf{E}^*(\mathbf{r})$ between Eqs. (17) and (18) results in

$$\mathbf{P}(\mathbf{r}) = (3y/4\pi)[1 + (\theta - 1)y]^{-1}\mathbf{E}(\mathbf{r}) . \tag{19}$$

Therefore the dielectric constant exists and is given by

$$\epsilon - 1 = 3y[1 + (\theta - 1)y]^{-1} , \tag{20}$$

which one readily verifies is equivalent to Eq. (15). Thus the dielectric consequences of using $\mathbf{E}^*$ to determine $\rho^{(2)}$ are identical to those of using it in the presence of an external field to determine $\mathbf{P}(\mathbf{r})$ directly. (Of course in the former case one obtains much more detailed information than in the latter.) This agreement provides a useful check on the internal consistency of the DDH theory.

It is also instructive to compare the DDH results for c and ϵ with the corresponding $\gamma \to 0$ results of HS II.[11] We first observe that our Eq. (15) is identical in form to Eq. (3.11a) of HS II, although their θ is of course defined quite differently from ours. This correspondence, while suggestive, does not of itself establish a definite relation between the two θ's (or the two theories). Such a relation is much more strongly suggested by the fact that our expression for c as a function of θ, Eq. (11), is also identical in form to the corresponding $\gamma \to 0$ expression of HS II. (HS II do not explicitly give this expression. To obtain it, one Fourier transforms their Eq. (2.19), solves for $\rho\tilde{h}(12)$, and compares the result with their Eq. (3.6). This comparison shows that $\rho\tilde{c}(12) = - 3y(D + \theta\Delta)$, which is precisely the Fourier transform of our Eq. (11).) Thus we are led to the conclusion that there is indeed an intimate relation between the two theories, and that our θ and the HS θ, although unrelated via their definitions, are for all practical purposes the same parameter. We thereby obtain new insight into the significance of the HS core parameter, which is seen to have a geometrical significance in terms of a cavity ellipticity. In addition, the fact that the HS results depend upon the core parameter in the mean-field limit becomes an understandable consequence of the inherent nonuniqueness of the mean field itself.

Equation (11) for c of course implies an expression for h or $\rho^{(2)}$ via the Ornstein–Zernike equation, Eq. (10). For a finite system this expression depends in a complicated way upon the shape of the sample. For an infinite system, however, an explicit expression for h can readily be determined by means of Fourier transforms and the angular convolution algebra of HS.[10,11] HS II have performed this calculation; the result in $\mathbf{k}$ space is their Eq. (3.8), which in $\mathbf{r}$ space becomes

$$\rho h_\infty(\mathbf{r}, \omega; \mathbf{r}_0, \omega_0)$$
$$= - 3yF(\theta, y)\{[\theta - (1 - \theta)(2 + \theta)y]\mathbf{e}(\omega) \cdot \mathbf{e}(\omega_0)\delta(\mathbf{r} - \mathbf{r}_0)$$
$$- \left(\frac{3}{4\pi}\right)\mathbf{e}(\omega) \cdot \mathbf{T}_\delta(\mathbf{r} - \mathbf{r}_0) \cdot \mathbf{e}(\omega_0)\} \quad (\delta \to 0) , \tag{21}$$

where

$$F(\theta, y) = [1 + (2 + \theta)y]^{-1}[1 - (1 - \theta)y]^{-1} , \tag{22}$$

and the subscript ∞ signifies an infinite system. According to Eq. (21), the long-range part of h_∞ is simply equal to $-\beta F(\theta, y)$ times the bare dipole–dipole potential. Thus, in contrast to the ionic base, h_∞ is not short-ranged in comparison to the pair potential; i.e., there is no dipolar analog of the Debye shielding effect.

We have seen that Eq. (15) reduces to the Clausius–Mossotti equation if the local field $\mathbf{E}^*$ is defined with

reference to a spherical cavity. The value of θ which reduces Eq. (15) to the Onsager equation does not appear to be associated with any intuitively natural choice of cavity ellipticity. This is not surprising in view of the fact that the spherical cavity used by Onsager was a *physical* cavity which was allowed to perturb the polarization around it, while the spheroidal cavity of the present development is purely mathematical. However, the fact that θ appears in our expression for c (and hence h) establishes a relation between the cavity ellipticity and the nature of the intermolecular correlations in the mean-field approximation. (A major disadvantage of the conventional dielectric local-field approach, embodied in Eqs. (16)–(20), is that it does not reveal this relation.) We are therefore free to disregard the geometrical origin of the parameter θ and simply choose it in such a way that c or h have certain desired properties. When this view is taken the Onsager equation *does* emerge naturally[11]; it results from choosing θ so that the delta-function term in Eq. (21) is zero; i.e., so that there are no short-range correlations in h_∞ except those of dipole–dipole symmetry.

How good are the DDH mean-field approximations for c and h? Intuitively one would expect them to be poor at short range (in part because the linearization in Eq. (8) cannot be justified there) but perhaps reasonably accurate at long range. The parameter θ is an aid in clarifying this question, since any functional dependence upon it is clearly a fictitious artifact of the mean-field approximation. (The true c and h for a rigid-dipole fluid are of course unique.) It is useful to examine the DDH expressions for c and h_∞, Eqs. (11) and (21), in this light. The short-range part of c depends upon θ and hence, as expected, represents an unsatisfactory and unrealistic approximation. Since the dielectric constant is determined by the short-range part of c,[16] the DDH theory accordingly yields only a crude (and θ-dependent) result for ϵ. The long-range part of c, however, is simply equal to $-\beta$ times the pair potential and is independent of θ. This suggests that the DDH theory may be capable of accurately representing the true long-range behavior of c. This suspicion is confirmed by the results of more rigorous theories which predict the same asymptotic behavior.[6,10,17,18] The total correlation function h_∞ depends upon θ at long range as well as at short range. This is a consequence of the fact that the long-range part of h depends upon the short-range part of c through the convolution in the Ornstein–Zernike equation. The DDH theory therefore does not provide a useful quantitative approximation to the true h_∞ at either short range or long range. The same statement clearly applies to h for a finite sample.

III. CONCLUDING REMARKS

The dipolar analog of classical linearized Debye–Hückel theory has been formulated for a finite fluid system of arbitrary shape composed of rigid polar molecules. This development demonstrates that polar and ionic fluids are susceptible to essentially the same sort of mean-field treatment, and shows clearly the similarities and differences between the two cases. The polar and ionic cases are similar in that the direct correlation function at long range is equal to the negative of the pair potential divided by kT in both cases. The two cases are different in at least two important respects: (a) the ionic (DH) theory is unique while the dipolar (DDH) theory is not, and (b) there is no dipolar analog of the Debye shielding effect which occurs in ionic systems.

The DDH theory also complements the theory of Høye and Stell in several ways. The DDH theory is the "classical" mean-field theory corresponding to the $\gamma \to 0$ mean-field theory of HS, and thus now makes possible a complete comparison between these two types of "mean-field" theory for rigid-dipole fluids. From a slightly different point of view, the DDH theory is of interest in providing a simple, direct, and intuitive derivation of the HS mean-field ($\gamma \to 0$) results. It also extends these results to the case of a finite sample, showing explicitly that in the mean-field approximation the direct correlation function is independent of the size and shape of the sample. Finally, the DDH theory lends new insight into the significance of the HS core parameter, and into the fact that a parameter of nonuniqueness enters into the results in the mean-field limit.

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[1]J. D. van der Waals, Dissertation, Leiden (1873).
[2]P. Weiss, J. Phys. Radium 6, 667 (1907).
[3]P. Debye and E. Hückel, Z. Physik 24, 185, 305 (1923).
[4]H. A. Lorentz, *The Theory of Electrons* (Dover, New York, 1952), 2nd ed.
[5]L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).
[6]J. L. Lebowitz, G. Stell, and S. Baer, J. Math. Phys. 6, 1282 (1965).
[7]P. C. Hemmer, J. Math. Phys. 5, 75 (1964).
[8]M. Kac and E. Helfand, J. Math. Phys. 4, 1078 (1963).
[9]G. Stell and J. L. Lebowitz, J. Chem. Phys. 49, 3706 (1968).
[10]J. S. Høye and G. Stell, J. Chem. Phys. 61, 562 (1974).
[11]J. S. Høye and G. Stell, J. Chem. Phys. 64, 1952 (1976).
[12]J. D. Ramshaw, J. Chem. Phys. 55, 1763 (1971).
[13]W. F. Brown, Jr., in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1956), Vol. 17, p. 1.
[14]L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam 17, 793 (1914).
[15]E. Waisman and J. L. Lebowitz, J. Chem. Phys. 56, 3086 (1972).
[16]J. D. Ramshaw, J. Chem. Phys. 57, 2684 (1972).
[17]J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 248 (1963).
[18]F. M. Kuni, Phys. Lett. A 26, 305 (1968).