Algebraic perturbation theory for polar fluids: A model for the dielectric constant

V. I. Kalikmanov
Department of Applied Physics, Computational Physics Section, University of Delft, Lorentzweg 1, 2628 CJ Delft, The Netherlands
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An alternative microscopic theory of the dielectric constant is proposed based on the algebraic technique due to Ruelle and the statistical mechanical perturbation approach. The resulting analytical expression is third order in the interaction energy and fifth order in the density. A comparison with other theoretical models and computer simulations for dipolar hard spheres and Stockmayer fluids is presented. The theory is equally applicable for describing the initial magnetic susceptibility of ferrofluids, in which case it is in good agreement with experimental data. [S1063-651X(99)01804-8]

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I. INTRODUCTION

The theory of the dielectric constant \(\varepsilon\) pioneered in 1912 by Debye [1] still remains an intensively developing area. Its fundamental and practical importance has motivated a lot of theoretical work and computer simulation studies (for reviews see, e.g., [2] and [3]). However, agreement between various models and simulations remains rather poor, especially for condensed systems at relatively low temperatures when interparticle interactions play an increasingly important role. In a seminal paper [1], Debye obtained \(\varepsilon\) by studying the response of a dilute gas of particles to an applied external electrical field \(E_{\text{ext}}\) (in the same fashion as Langevin’s work on a paramagnetic gas in an external magnetic field). Subsequent models mainly used an approach which relates \(\varepsilon\) to the properties of the system in the absence of \(E_{\text{ext}}\). In these theories each particle is regarded as a source of a field acting on its neighbors and \(\varepsilon\) describes the response of the system to this field.

In the present paper we propose a theory of the dielectric constant for a polar nonpolarizable fluid in the spirit of the original Debye-Langevin approach: we study the response of a dielectric system to a weak external field, taking into account dipole-dipole interactions. These are long ranged and anisotropic and represent the main source of difficulties arising in theoretical descriptions and simulation studies. Our model is based on a statistical mechanical perturbation theory and a powerful “algebraic technique” due to Ruelle [4]. In view of the similarity between electrical and magnetic quantities, this model is straightforwardly applicable for the description of the static initial magnetic susceptibility of ferrofluids.

II. MODEL

We consider a polar fluid, in which polarizability effects are neglected, as a system of \(N\) hard spheres with point dipoles at their centers. The fluid is contained in a volume \(V\) at temperature \(T\) and placed into a weak external homogeneous electric field \(E_{\text{ext}}\). Each particle \(i\) is characterized by a five-dimensional vector \(\mathbf{r}_i = (r_i, \mathbf{\omega}_i)\), where \(r_i\) is its radius vector and \(\mathbf{\omega}_i = (\theta_i, \varphi_i)\) denotes the orientation of its dipole moment \(s_i\). We assume that particles are identical, so that \(d\) is the hard-sphere diameter and \(|s_i| = s\) (extension to mixtures is straightforward). The potential energy for an arbitrary configuration consists of an interparticle interaction energy and an external field contribution, \(U(\mathbf{r}_i^N) = U_0(\mathbf{r}_i^N) + U_1(s^N)\),

\[
U_0 = \sum_{\{ij\}} [u_{d,ij} + u_{ij}^{(dd)}],
\]

\[
U_1 = -sE_{\text{ext}} \sum_i \cos \theta_i.
\]

Here \(u_{d,ij} = u_d(r_{ij})\) is the hard-sphere interaction, \(r_{ij}\) the particle separation, \(\theta_i\) the angle between \(s_i\) and \(E_{\text{ext}}\), and

\[
u_{ij}^{(dd)} = \frac{s^2}{r_{ij}^3} D(i,j)
\]

the dipole-dipole potential in which the angular part is given by

\[
D(i,j) = \hat{s}_i \hat{s}_j - 3(\hat{s}_i \hat{r}_{ij})(\hat{s}_j \hat{r}_{ij}),
\]

where \(\hat{x}\) denotes a unit vector \(x\). The formulation of any perturbation theory starts with decomposing the system into a reference and perturbative parts. Since we are aiming at a detailed description of the influence of interparticle interactions on the dielectric constant, it is reasonable to include them in a reference model. The latter is characterized by the energy \(U_0\) and represents the system of dipolar hard spheres in a zero field. The interaction with an external field is treated as a perturbation. Introducing the Mayer function

\[
f_i = e^{\alpha \cos \theta_i - 1},
\]

where

\[
\alpha = \frac{sE_{\text{ext}}}{k_B T},
\]

we write the configuration integral as

\[
Q = \int d\mathbf{r}_i^N e^{-\beta U} \left[ 1 + \sum_{n=1}^{N} \left( \sum_{1 \leq i_1 < \cdots < i_n \leq N} f_{i_1} \cdots f_{i_n} \right) \right].
\]
\[ \beta = \frac{1}{k_B T} \]

The same quantity for the reference model reads
\[ Q_0 = \int d\mathbf{R}^N e^{-\beta U_0}. \]

Then Eq. (3) becomes
\[ \frac{Q}{Q_0} = 1 + \sum_{n=1}^{N} \frac{1}{n!} \left( \int d\mathbf{R}^n \frac{e^{-\beta U_0}}{Q_0} \left[ \sum_{i_1 < i_2 < \cdots < i_n} f_{i_1} \cdots f_{i_n} \right] \right). \]

Each term of the sum is a thermal average over the reference model of the quantity in the round brackets. This implies that introducing the \( n \)-body reference correlation function \( g_0^n(\mathbf{r}^n) \), we can rewrite this expression as
\[ \frac{Q}{Q_0} = 1 + \sum_{n=1}^{N} \frac{1}{n!} \left( \int d\mathbf{R}^n \frac{e^{-\beta U_0}}{Q_0} \left[ \sum_{i_1 < i_2 < \cdots < i_n} f_{i_1} \cdots f_{i_n} \right] \right). \]

where \( \rho = N/V \) is the number density of the fluid. The standard scheme of the perturbation approach (see, e.g., [5]) is based on the expansion of \( Q \) in terms of the Mayer functions. However, in our case, this is not appropriate, since \( f_i \) is purely orientational and therefore does not compensate for the long-range behavior of \( g_0^n(\mathbf{r}^n) \) when mutual separations between particles become large.

Instead of the standard route, we use an approach based on the algebraic technique proposed by Ruelle [4] (see also [6]). Not entering into the way in which this technique is established, we merely formulate here its main result and outline the way it can be applied to our problem. Consider a series
\[ a(z) = \sum_{n=0}^{\infty} \frac{z^n}{n!} a_n, \]

where \( z \) is a formal parameter and the coefficients \( a_n \) are given by
\[ a_0 = 1, \quad a_n = \int d\mathbf{R}^n q_n^a(\mathbf{r}^n), \quad n \geq 1, \]

\( q_n^a(\mathbf{r}^n) \) being arbitrary real functions. It is rigorously proved in [4] that \( a(z) \) can be rewritten in the form of an exponential of some other series
\[ a(z) = \exp[b(z)] = \exp \left[ \sum_{n=0}^{\infty} \frac{z^n}{n!} b_n \right], \]

where
\[ b_0 = 0, \quad b_n = \int d\mathbf{R}^n q_n^b(\mathbf{r}^n), \quad n \geq 1, \]

and the functions \( q_n^b \) are unambiguously constructed algebraic combinations of \( q_n^a(\mathbf{r}^n) \). It is worth emphasizing that this method is a rigorous mathematical procedure based on a homomorphism of the algebra of infinite-dimensional vectors
\[ q_n = (\text{const} \cdot q_1^a(\mathbf{r}_1), q_2^a(\mathbf{r}_1, \mathbf{r}_2), \ldots, q_n^a(\mathbf{r}_1, \ldots, \mathbf{r}_n), \ldots) \]

into the algebra of power series \( a(z) \).

Comparing Eq. (4) with Eqs. (5) and (6) we identify
\[ z = \frac{\rho}{4\pi}, \quad a(z) = \frac{Q}{Q_0}, \quad q_n^a = \left( \prod_{i=1}^{n} f_i \right) g_n^0, \quad n = 1, 2, \ldots. \]

Thus,
\[ \frac{Q}{Q_0} = \exp \left[ \sum_{n=0}^{\infty} \frac{(\rho/4\pi)^n}{n!} b_n \right]. \]

The first terms of the sequence \( \{q_n^a\} \) read
\[ q_1^a = f_1 g_1^0, \quad (10) \]
\[ q_2^a = \left( \prod_{i=1}^{2} f_i \right) g_2^0 - 1 \]
\[ q_3^a = \left( \prod_{i=1}^{3} f_i \right) g_3^0 - 1 \]
(12)

We stress that taking into account each term in Eq. (9) is equivalent to taking into account an infinite number of terms in Eq. (4). The configurational free energy reads
\[ \beta \mathcal{F} = \beta \mathcal{F}_0 - \sum_{n=1}^{\infty} \frac{(\rho/4\pi)^n}{n!} b_n, \]

where \( \mathcal{F}_0 \) is the reference free energy. Equation (13) is exact: no approximations have been imposed so far.

For the derivation of the dielectric constant we need to find the linear response of the system to a weak external field which corresponds to keeping only the leading term in the expansion of the free energy in powers of \( \alpha \). Since \( \mathcal{F} \) is an even function of the field, we should cut off this series, keeping the term \( O(\alpha^2) \) and neglecting all the rest. The cutoff is only possible if the \( b_n \) contain converging integrals. This is really the case since \( g_0^n \) in Eq. (4) are replaced by \( h_n^0 = g_0^n - 1 \) in Eqs. (11) and (12), vanishing at large separations, thus ensuring convergence of Eq. (13) for \( n \geq 2 \). Substituting Eqs. (10)–(12) into Eq. (8) and expanding the Mayer functions to second order in \( \alpha \) we obtain, for the free energy,
\[ \beta \mathcal{F} = \beta \mathcal{F}_0 - N \frac{\alpha^2}{6} - \frac{1}{2} \left( \frac{\rho}{4\pi} \right)^2 b_2 + o(\alpha^4). \]

The second term gives the energy of independent dipoles in an external field \( E_{\text{ext}} \) (cf. paramagnetic Langevin gas) while the third one accounts for interparticle interactions in the presence of \( E_{\text{ext}} \). The pair correlation function of dipolar hard spheres reads [5]
\[ g_n^0(r_{12}, \omega_1, \omega_2) = g_0(r_{12}) + \sum_{m=1}^{\infty} (\beta s^2)^m g_m(r_{12}, \omega_1, \omega_2), \]

where
\[ g_1 = -\frac{g_d(r_{12})}{r_{12}^3} D(1,2), \]  
(16)  
\[ g_2 = \frac{1}{2} \frac{g_d(r_{12})}{r_{12}^6} D^2(1,2) \]  
(17)  
\[ + \frac{1}{6} \rho D(1,2) \int dr_3 \frac{1 + 3 \cos \alpha_1 \cos \alpha_2 \cos \alpha_3}{(r_{13} r_{23})^3} g_d(123) \]  
(18)  
\[ + \frac{1}{3} \rho \Delta(1,2) \int dr_3 3 \cos^2 \alpha_3 - 1 \frac{(r_{13} r_{23})^3}{(r_{13} r_{23})^3} g_d(123). \]  
(19)  

Here \( \Delta(1,2) = \hat{s}_1 \cdot \hat{s}_2 \cdot g_d(r) \) and \( g_d(123) \) are the two- and three-body hard-sphere correlation functions and \( \alpha_1, \alpha_2, \alpha_3 \) are the angles of the triangle formed by the three particles [7]. A cutoff of Eq. (15) at \( m = 2 \) implies

\[ b_2 = \alpha^2 V \sum_{m=0}^2 b_2^{(m)}, \]

where

\[ b_2^{(0)} = \int dr_{12} \int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 [g_d(r_{12}) - 1], \]
\[ b_2^{(1)} = (\beta s^2) \int dr_{12} \int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 g_1, \]
\[ b_2^{(2)} = (\beta s^2)^2 \int dr_{12} \int d\omega_1 d\omega_2 \cos \theta_1 \cos \theta_2 g_2. \]

Integration over \( \omega_1, \omega_2 \) yields \( b_2^{(0)} = 0 \) and

\[ b_2^{(1)} = -\beta s^2 \left( \frac{4\pi}{3} \right)^2 \int_{r_{12} > d} dr_{12} \frac{1}{r_{12}^2} (1 - 3 \cos^2 \theta_{12}), \]

(21)  

where we replaced \( g_d(r_{12}) \) with the step function

\[ \Theta(r_{12} > d) = \Theta_{12} = \begin{cases} 1 & \text{for } r_{12} > d, \\ 0 & \text{for } r_{12} < d. \end{cases} \]

(22)  

We assume that the container is an (infinitely) long cylinder with an axis parallel to the external field. This ensures the absence of a depolarization field inside the sample (the depolarization factor of a long cylinder is zero) and therefore the macroscopic electric field in it is just \( E_{\text{ext}} \). Integration of Eq. (21) over a long cylinder gives

\[ b_2^{(1)} = \beta s^2 \left( \frac{4\pi}{3} \right)^3. \]

This is a direct manifestation of the long-range nature of dipole-dipole interactions. The last contribution to \( b_2 \) given by Eq. (20) contains in turn three terms originating from \( g_2(r_{12}, \omega_1, \omega_2) \) in Eqs. (17)–(19); in all of those the radial dependence is short ranged \((\sim 1/r^6)\) which makes it possible to replace integration over a cylinder by integration over a sphere. Only the contribution from Eq. (19) survives:

\[ b_2^{(2)} = \left( \frac{4\pi}{3} \right)^2 \rho (\beta s^2)^2 \gamma_0, \]

where the dimensionless quantity \( \gamma_0 \) is

\[ \gamma_0 = \int dr_{12} \int dr_3 \frac{3 \cos^2 \alpha_3 - 1}{(r_{13} r_{23})^3} g_d(123). \]

(23)  

For \( g_d(123) \) Kirkwood’s superposition approximation gives

\[ g_d(123) \approx g_d(12) g_d(13) g_d(23) \approx \prod_{1 \leq i < j \leq 3} \Theta_{ij}. \]

Equation (23) can then be integrated analytically to give

\[ \gamma_0 = \frac{5}{3} \frac{\pi^2}{2}. \]

(24)  

Summarizing, we can write the free energy (14) in a closed form,

\[ \beta F = \beta F_0 - N \frac{\alpha^2}{6} - \frac{\alpha^2}{54} \rho^2 V (4 \pi \lambda + \frac{5}{3} \pi^2 \rho \lambda^2), \]

(25)  

where

\[ \lambda = \beta s^2 / d^3 \]

is a coupling constant characterizing the strength of the dipole-dipole interaction. The macroscopic polarization \( P \) is related to the free energy via [8]

\[ P = -\frac{1}{V} \frac{\partial F}{\partial E_{\text{ext}}}, \]

yielding

\[ P = \frac{\alpha}{3} \rho s \left[ 1 + \frac{4\pi}{9} \rho d \lambda + \frac{5}{27} \pi^2 (\rho d \lambda)^2 \right]. \]

Finally, the dielectric constant is obtained from the thermodynamic relationship

\[ (\epsilon - 1) E_{\text{ext}} = 4\pi P, \]

which results in

\[ \epsilon - 1 = 3 y \left( 1 + y + \frac{15}{16} y^2 \right), \]

(26)  

where

\[ y = \frac{4\pi}{9} \beta \rho s^2. \]

As in other theoretical models, \( \epsilon \) in Eq. (26) is a function of only one parameter—\( y \). Physically, one can expect, how-
ever, a dependence on two parameters, $\lambda$ and the volume fraction $\phi = (\pi/6) \rho d^3$. The $\phi$ dependence can be introduced if we go beyond the van der Waals step-function approximation for $g_d(r)$ in the perturbative terms of the free energy and set

$$
 h_d(r_{12}; \rho) = \begin{cases} 
 \rho \int dr_{3} c(r_{13}; \rho = 0) h(r_{23}; \rho = 0) + o(\rho^2) & \text{for } r_{12} > d, \\
 -1 & \text{for } r_{12} < d.
\end{cases}
$$

Here $c_d(r; \rho)$ is a direct pair correlation function and $h_d(r; \rho) = g_d(r; \rho) - 1$. Routine integration gives

$$
 G_1(r) = \Phi(r) = 8 - 6 \left( \frac{r}{d} \right) + \frac{1}{2} \left( \frac{r}{d} \right)^3, \quad d < r < 2d.
$$

For $r > 2d$, $\Phi(r) = 0$. The second-order term can be estimated using the “kinetic theoretical considerations” of [9], yielding

$$
 G_2(r) = \frac{1}{2} \Phi^2(r).
$$

Thus, both $G_1$ and $G_2$ are nonzero at $d < r < 2d$ and zero outside this interval. The only contribution to $b_2$ affected by this correction is $g_0$ given by Eq. (23). The product of step functions in the Kirkwood approximation for $g_d(r, 123)$ is replaced by

$$
 \prod_{1 \leq i < j < k \leq 3} \Theta_{ij} + \Phi W_1 + \Phi^2 W_2 + \cdots,
$$

where $W_1$ is a sum of products $\Phi_{ij} H_{ij} \Theta_{ik} \Theta_{im}$ with

$$
 \Phi_{ij} = \Phi(r_{ij}), \quad H_{ij} = \Theta(r_{ij} > d) \Theta(r_{ij} < 2d)
$$

and $W_2$ contains terms of the type $\Phi_{ij} H_{ij} \Phi_{kl} H_{kl} \Theta_{mn}$. Hence, $g_0$ is replaced by

$$
 g = g_0(1 + a_1 \phi + a_2 \phi^2).
$$

All the integrations can be performed analytically. Both coefficients prove to be positive and small:

$$
 a_1 = 0.036, \quad a_2 = 0.372,
$$

implying that $\epsilon$ is slightly sensitive to the density dependence of $\gamma$; the correction to $\gamma_0$ does not exceed 2–5%. Equation (26) now becomes

$$
 g_d(r) = \Theta(r > d) + \phi G_1(r) + \phi^2 G_2(r) + \cdots,
$$

where the functions $G_1(r)$ vanish at $r$ exceeding several particle diameters. $G_1(r)$ can be found by linearizing in density the Ornstein-Zernike equation for hard spheres in the Percus-Yevick approximation

$$
 \epsilon - 1 = \frac{3 \gamma}{1 - \gamma}.
$$

which is third order in the coupling constant $\lambda$ and fifth order in the density.

### III. RESULTS AND DISCUSSION

Figure 1 shows the dielectric constant as a function of $\lambda$ for $\rho = \rho^* d^3 = 0.8$ predicted by various theoretical models—Debye [1], Onsager [10], mean-spherical approximation (MSA) [11], linearized hypernetted-chain approximation (LHNC) [12], and the present, algebraic perturbation theory (APT)—and that found in simulation studies [13]. The Debye theory

$$
 \epsilon - 1 = \frac{3 \gamma}{1 - \gamma}
$$

has a singular behavior at $\gamma = 1$ which is known to be incorrect [5]. In the Onsager theory

![Graph of dielectric constant vs. lambda](image.png)

**FIG. 1.** Dielectric constant as a function of $\lambda$ for $\rho d^3 = \rho^* = 0.8$. Labels correspond to various theoretical models: Deb, Debye theory; Ons, Onsager theory; MSA, mean-spherical approximation; LHNC, linearized hypernetted-chain approximation; APT, algebraic perturbation theory, Eq. (28). Squares: simulation results [13] for dipolar hard spheres and Stockmayer fluid.
\[ \epsilon - 1 = \frac{3}{4} (3y - 1 + \sqrt{1 + 2y + 9y^2}), \] (30)

the singularity is avoided but \( \epsilon \) is underestimated. In the MSA \( \epsilon \) is written in a parametric form

\[ \epsilon - 1 = \frac{q(2\xi) - q(-\xi)}{q(-\xi)}, \] (31)

where \( \xi \) is a real root of the equation

\[ q(2\xi) - q(-\xi) = 3y, \] (32)

with the function \( q(x) \) given by

\[ q(x) = \frac{(1 + 2x)^2}{(1 - x)^4}. \]

In all likelihood MSA also underestimates \( \epsilon \) [2]. If in the APT orientational correlation is completely ignored, then the reference pair correlation function reduces to that of hard spheres, \( b_2 = g_d \), providing that \( b_2 = 0 \). Thus, the APT expression (28) becomes \( \epsilon - 1 = 3y \), which is the dielectric constant of the Langevin gas. Exactly the same result follows from all the other above mentioned theories (29)–(31) in the limit of small \( y \).

In view of the long-range nature of dipolar forces, computer simulation of \( \epsilon \) proved to be a very difficult problem [2,3]. None of the simulation methods gives \( \epsilon \) for truly infinite systems described by approximate theories. Nevertheless, simulation results can give an idea about the accuracy of various models. Simulations of dipolar hard spheres appear to be technically more difficult than the simulations of a Stockmayer fluid [3], for which a larger amount of data is available. In Fig. 1 simulation results for both systems are shown. It is found in [12] that for \( \lambda < 2 \), \( \epsilon \) of a Stockmayer fluid is close to that of equivalent dipolar hard spheres; for larger \( \lambda \) the Stockmayer \( \epsilon \) is considerably lower than that of the corresponding hard-sphere system.

Real molecules usually have both dipole and quadrupole moments which makes a straightforward comparison of APT with real dielectric liquids problematic. However, by changing from the electric to magnetic language, APT can be compared with experimental data on the initial susceptibility \( \chi \) of ferrofluids in which quadrupole interactions are absent. Thus, \( s \) is now a magnetic moment of a ferroparticle, \( \epsilon - 1 \) becomes \( \mu - 1 = 4\pi\chi \), and \( y = (4\pi/3)\chi_L \), where

\[ \chi_L(T) = \frac{1}{3} \frac{\rho s^2}{k_B T} \] (33)

is the Langevin susceptibility. Figure 2 shows the temperature dependence of the initial susceptibility for a colloidal solution of magnetite in kerosene predicted by various models and the recent experimental results of [14]. To obtain

\[ \chi_L(T) \] we assume that at the highest examined temperature \( T_{\text{ref}} = 343.15 \) K, where interparticle interactions are at minimum, the experimental value \( 4\pi\chi_{\text{ref}} = 24.7 \) is described by Eq. (26). Solving this cubic equation for \( y \) we find \( 4\pi\chi_{\text{ref}} \approx 4.86 \). Then, for other temperatures using Eq. (33) we have

\[ \chi_L(T) = \frac{T_{\text{ref}}}{T} \chi_{\text{ref}} [1 - \beta_1(T - T_{\text{ref}})], \] (34)

where the term in square brackets takes into account the thermal expansion of kerosene (with the expansion coefficient \( \beta_1 \approx 0.9 \times 10^{-3} \) K\(^{-1}\)). Figure 2 shows a good agreement of APT with experimental data for the whole temperature range studied. In the same figure predictions of the Onsager theory and the MSA are also shown. To be consistent we use the same procedure for each of these models, adjusting the corresponding theoretical \( 4\pi\chi \) to the experimental value \( 4\pi\chi_{\text{ref}} = 24.7 \) at \( T_{\text{ref}} = 343.15 \) K to calculate \( \chi_L \). This implies that the reference Langevin susceptibility \( \chi_{\text{ref}} \) calculated for different models will be different. For other temperatures \( \chi_L(T) \) is found from Eq. (34). It is seen that the agreement with the Onsager theory and the MSA is poor.

In conclusion, we have proposed a microscopic model for the dielectric constant of a polar nonpolarizable fluid. The resulting analytical expression is third order in the interaction energy and fifth order in the density. The model proves to be in fair agreement with computer simulation data on the dipolar hard spheres and the Stockmayer fluids. The model has been also applied to ferrofluids: theoretical predictions of the initial magnetic susceptibility are shown to be in good agreement with experiment.

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FIG. 2. Temperature dependence of the initial magnetic susceptibility of a ferrofluid. Squares, experiment [14]; solid lines, theoretical predictions (notations are the same as in Fig. 1). Comparison with experiment is made by adjusting the corresponding theoretical \( \chi \) to the experimental value \( 4\pi\chi_{\text{ref}} = 24.7 \) at the temperature \( T_{\text{ref}} = 343.15 \) K.

\[ \chi_L(T) \]
[7] There is a misprint in Eq. (7.183) of [5]: \((r_1^3r_2^3)\) there should be raised to the power 3, not 2. I thank Professor D. Henderson for confirming this correction.