

Continuum and Dipole-Lattice Models of Solvation

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Dipole-lattice and continuum-dielectric models, which are two important “simplified” models of solvation, are analyzed and compared. The conceptual basis of each approach is briefly examined, and the relationship between the two methodologies is explored. The importance of dipole lattices in the development of dielectric theory is stressed. The Clausius–Mossotti equation, which is the result of early attempts at relating the dielectric constant to “microscopic” quantities, also applies to cubic lattices of Langevin dipoles or point polarizabilities. The presence of thermal fluctuations, rather than inter-dipolar or specific short range interactions is found to be the fundamental reason for the deviation of dipolar materials from the Clausius–Mossotti equation. The fact that the continuum dielectric is the infinite dipole density limit of a more general dipole-lattice description is shown by recovering the continuum results with dipole lattices of high number density. The linearity of a continuum model is shown to be a direct consequence of being the infinite density limit of a dipole lattice. Finally, it is shown that the discreteness involved in the numerical solution of the Poisson equation cannot capture the effect of the physical discreteness in dipole lattices.

1. Introduction

Understanding and predicting solvation effects is a fundamental prerequisite for predicting and modeling chemistry properly in any environment other than gas phase.¹ A particularly important aspect of solvation is the electrostatic interaction of a solute system with its surroundings. Over the years, various theoretical approaches have been developed to represent the solvent.^{2–5} Before the advent and widespread availability of computers, “modeling” essentially meant analytical equations, such as the continuum theories of solvation, which usually came at the price of overidealizing the nature of the solvent and oversimplified system geometries, although the latter limitation rarely had a qualitative impact on the conclusions. Nevertheless, those early works provided valuable insight into some of the more general aspects of solvation and provided a useful reference point for further development. As computers became increasingly accessible and fast, “modeling” became essentially synonymous with numerical simulations with various degrees of realism.⁶ One avenue of computational studies has been to model a system as realistically as possible and attempt to obtain detailed “experimental” information otherwise not available from “laboratory” experiments. Another approach has been to explicitly represent only the “interesting” part of a system and focus on modeling that part of a system in greater detail while the details of the rest of the system are absorbed into a simplified model.^{7,8} Simplified representations of a solvent (such as dielectric continuum or a lattice of dipoles) with a relatively realistic description of a solute is an example of the latter approach. In this article we address the relationship between two important methods used to simplify the solvent and solvation: lattice of dipoles^{3,9–11} and continuum dielectric.^{12–14}

2. Models and Methods

A. Dipole Lattices. Dielectric theory^{15,16} has always used dipoles for conceptualizing polarization in matter and connecting macroscopic and microscopic descriptions. A dipole-lattice (DL) approach explicitly retains the dipolar nature of electric

polarization, and in that sense is a truly microscopic representation even though it has no pretense of capturing the molecular geometry.

In analogy with the calculations of Langevin on magnetic moments, Debye used the polarization of a dipole in an electric field to construct a theory for describing the dielectric behavior of polar gases.¹⁷ The success of his theory was due to the fact that the assumption of noninteracting dipoles is a good one in the case of dilute gases. However, in condensed phase, neither dielectric nor solvation behavior can be done justice without taking interdipolar interactions into account. As a matter of fact, lattices of interacting dipoles (at least with their nearest neighbors) have been used for studying collective electrostatics in condensed matter for a long time, dating as far back as 1937.^{9–11,18–32} In 1976, Warshel and Levitt³ presented a “practical” use of a dipolar lattice by representing the solvation behavior of water by a simple cubic lattice of Langevin dipoles—a model that proved to be useful and robust for modeling solvation in solution^{1,33–35} and proteins.^{33,36–38} DLs have recently been utilized in studies of solvation dynamics to obtain insight into the fundamentals of polar solvation, as well as a direct test of various theories of solvation dynamics.^{5,10,31} The dielectric behavior of a DL is a function of its geometry (such as simple cubic or face-centered cubic) and its dimensionless “polarity”

$$\eta = \frac{\rho \mu_0^2}{3k_B T} \quad (1)$$

where ρ is the number density of dipoles in the lattice, μ_0 is the permanent moment of individual dipoles, k_B is the Boltzmann constant, and T is the temperature. This dependence on a single, dimensionless quantity provides a rigorous way to construct “equidielectric” DLs of different grid spacing (or “lattice parameter” as it is sometimes called) by adjusting μ_0 and ρ at constant η .³⁹

A theoretically appealing prototype of dipolar solvents is provided by the Brownian dipole lattice (BDL)¹⁰ model, composed of point dipoles at fixed lattice sites, undergoing rotational diffusion while interacting with each other and a

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solute. Such a model captures the explicit thermal fluctuations in the system while retaining the simple framework of DL models.

A further simplification of a BDL is possible through replacing each individual permanent dipole (of magnitude μ_0) with its equivalent "Langevin dipole" whose polarization in response to an imposed electric field is rigorously described by

$$\mu = \left[\coth(y) - \frac{1}{y} \right] \mu_0 \mathbf{E}, \quad y = E \frac{\mu_0^2}{3k_B T} \quad (2)$$

which is the well-known Langevin function. Equation 2 captures the net response of a thermally fluctuating (reorienting) permanent dipole in an external electric field. Explicit thermal fluctuations in interdipolar fields are not preserved. The resulting model is a lattice of Langevin dipoles (LDL). Langevin dipoles have been used successfully to represent the solvation provided by water in biological systems.¹

A natural extension of a lattice of permanent dipoles is a lattice of point polarizabilities (PPL), which can actually be regarded as Langevin dipoles in the linear limit (small \mathbf{E}) of eq 2. The linear polarizability of a Langevin dipole is given by

$$\alpha = \frac{\mu_0^2}{3k_B T} \quad (3)$$

and the polarity η of a PPL is thus given by $\rho\alpha$. A PPL can therefore be regarded as a linear version of the LDL because its constituent dipoles, as well as the totality of the system, polarize linearly at all field strengths.

As a useful reference point we also consider noninteracting DLs (NIDL) where the dipoles do not interact with each other. In an NIDL there is no difference between the polarization behavior of Langevin dipoles and Brownian dipoles except for the presence of explicit fluctuations in the BDL model.

To summarize, a DL approach assumes that the response of the environment of a solute can be represented by that of a lattice of dipoles with the proper polarity. Number density or the lattice geometry of a DL need not resemble that of the solvent it represents. However, matching the number density of the material a DL claims to represent may have the advantage of being consistent with the actual level of "discreteness" near the solute.⁵⁴

B. Continuum Dielectric via Solving the Extended Poisson Equation. The concept of "continuum dielectric" is simply a limiting case of a dipolar representation where the number density ρ of the dipoles is taken to be infinite.⁴⁰ To understand why this is the case, one only needs to observe that polarization, a fundamental quantity in dielectric theory and continuum formalism, is nothing but dipole per unit volume. The fact that one *integrates* this quantity in the continuum formalism rather than summing it is enough to deduce that the continuum limit corresponds to infinitesimally separated dipoles, i.e., infinite number density of dipoles. Alternatively, in practical terms, the continuum dielectric can also be regarded as the limit of a dipolar representation where the number of dipoles (or dipole polarizabilities) in a volume element relevant to the process of interest (such as solvation or macroscopic dielectric phenomena) is very large. For solvation, such a volume element would involve a microscopic volume around the solute. For a macroscopic dielectric constant measurement, the volume would be macroscopic and would contain $\sim 10^{23}$ dipoles. Discretized continuum (DC) approach assumes that the solvent can be represented as a homogeneous dielectric continuum and obtains the electrostatic potential over the system by solving the

extension of the Poisson equation to a continuum dielectric

$$-\nabla \cdot \epsilon \nabla \phi = 4\pi \rho_q \text{ (atomic units)} \quad (4)$$

numerically over a cubic grid, where ϵ is the dielectric constant, ϕ is position-dependent electric potential, and ρ_q is the position-dependent charge density. In the present study, we employed a finite-difference algorithm¹²⁻¹⁴ to solve eq 4. Although ϵ can be defined as a function of spatial coordinates, there are practical and theoretical drawbacks in doing so even in a "homogeneous" yet real material. Since ϵ is a fundamentally nonlocal quantity, its variation in a system (even if it is a "homogeneous" liquid) cannot be rigorously represented merely by a dependence on spatial coordinates. In a microscopic process such as solvation, the microscopic structure of a real material becomes important through the non-negligible contribution from the dielectric function at nonzero wave vectors.⁴¹ Although the validity of a continuum representation at atomic length scales is clearly questionable, this method has been used with some success to handle solvation in liquids,⁷ supercritical fluids,⁴² and macromolecules.⁴³ It is important not to equate the terms "dielectric" and "continuum dielectric" since the latter is an idealized limiting case of the former that encompasses virtually all matter, albeit from the perspective of electrical properties. While the continuum dielectric is a widely known limit and leads to illuminating analytical equations for simple cases, it offers no obvious reason for being a more rigorous or adequate representation of a solvent than a DL in the "discrete" regime (where ρ is finite, as in any real material with distinguishable dipoles or polarizabilities), particularly because it is basically a simplification of the dipolar representation.

C. Measurement of the Macroscopic Dielectric Constant: Continuum Dielectric Formulations. The most obvious way of comparing microscopic models to continuum dielectric models is the calculation of their dielectric constants.

In continuum dielectric formalism, calculating the dielectric constant ϵ involves placing a spherical sample of the model molecules in a continuum dielectric with ϵ_s (which can also be vacuum, with $\epsilon_s = 1$). ϵ is then calculated⁴⁴ either from the average total dipole moment fluctuation $\delta M^2 = \langle M^2 \rangle - \langle M \rangle^2$ (where M is the total dipole moment) of the sample and using

$$\frac{(\epsilon - 1)(2\epsilon_s + 1)}{(\epsilon + 2\epsilon_s)} = \frac{4\pi}{3k_B T} \frac{\delta M^2}{V} \quad (5)$$

or by applying a homogeneous external electric field \mathbf{E}_0 and measuring the induced polarization \mathbf{P} of the sample and using⁴⁴

$$\frac{(\epsilon - 1)(2\epsilon_s + 1)}{(2\epsilon_s + \epsilon)} = 4\pi \frac{|\langle \mathbf{P} \rangle|}{|\mathbf{E}_0|} \quad (6)$$

Equation 6 for $\epsilon_s = 1$ can be obtained in an intuitively simple manner by recognizing that the electric field \mathbf{E} inside a sphere⁴⁵ of isotropic continuum dielectric in vacuum is given by

$$\mathbf{E} = \frac{3}{\epsilon + 2} \mathbf{E}_0 \quad (7)$$

Substituting eq 7 into the fundamental relationship

$$(\epsilon - 1)\mathbf{E} = 4\pi \langle \mathbf{P} \rangle \quad (8)$$

yields eq 6 with $\epsilon_s = 1$.

D. Measurement of the Microscopic Dielectric Constant: Solvation Formulations. A somewhat unorthodox yet potentially useful method of calculating the dielectric constant of a substance involves a comparison of the microscopic

solvation behavior with the continuum predictions. This approach would probe a “microscopic” region around the solute. If a continuum description of solvation is valid, the dielectric constant obtained by continuum dielectric (i.e., macroscopic) and solvation (i.e., microscopic) formulations should be consistent.⁴⁶ Therefore, in order to judge the extent to which the solvation behavior of a solvent model resembles that of a dielectric continuum, we can place a charge in a cavity at the center of a spherical sample and measure, across the whole system, the polarization and the resulting electric potential generated by the spherical solvent shell. For such a simple geometry, there exist analytical predictions, serving as useful reference points. However, one should keep in mind that the usual analytic formulas do not take “edge effects” near the solute cavity and the outer surface of the solvent system into account. A more general and probably more consistent approach would be to solve the continuum problem via a DC calculation (by solving the extended Poisson equation) and deduce the dielectric constant that gives the best agreement with the microscopic model. We can also address the question of whether the discreteness of the finite-difference DC method possesses any *physical* significance related to the discreteness of a dipolar model by performing DC calculations using the same grid spacing as in DL calculations.

Polarization Inside the Solvent Caused by a Solvated Charge. The radial polarization in a homogeneous dielectric solvating a point charge is given by⁴⁷

$$P(r) = \frac{q}{4\pi r^2} \left(1 - \frac{1}{\epsilon}\right) \quad (9)$$

where r is the distance from the charge to the point where the polarization is measured. The first step for making the connection to microscopic models is converting P to induced dipole magnitudes μ by using the number density ρ of the molecules (or dipoles), obtaining

$$\mu(r) = \frac{q}{\rho 4\pi r^2} \left(1 - \frac{1}{\epsilon}\right) \quad (10)$$

leading to a “distance-dependent” microscopic dielectric function

$$\epsilon_P(r) = \left(1 - \mu(r) \frac{4\pi \rho r^2}{q}\right)^{-1} \quad (11)$$

and its average over the solvent

$$\epsilon_P = \left(1 - \langle \mu(r)r^2 \rangle \frac{4\pi \rho}{q}\right)^{-1} \quad (12)$$

It is important to note that one has to average $\mu(r)r^2$ in eq 12 rather than $\epsilon_P(r)$ directly by using an average such as $N^{-1}\sum \epsilon_i$. In order to be consistent with the fundamental relationship given by eq 8, the calculation of a dielectric constant must involve averaging a quantity that is proportional to polarization P . In the case of microscopic dielectric constant of ionic solvation, P is proportional to $1 - 1/\epsilon$. Equation 12 reflects this requirement.

Reaction Potential in the Solvent in Response to a Solvated Charge. The term “reaction potential” refers to the electric potential generated by the solvent in the solvation process. The reaction potential *at the solute* is usually the focus of solvation studies. This is reasonable since the solute–solvent interaction energy of a solvated charge is given by qV , where V is the reaction potential at the solvated charge. However, V is a relatively imprecise measure of the dielectric constant of a solvent since it is sensitive to the size and geometry of the

“cavity” in which the solute resides, as well as to the microscopic structure of the solvent right near the “cavity”. Being an artificial construct, neither the size nor the physical meaning of a “cavity” is an independently defined concept, rendering the dielectric constant corresponding to a given solvation energy ill-defined. This can be understood better by inspecting the equation for the solute–solvent interaction energy W_{qV} of a charge q imbedded in a continuum dielectric sphere of radius R

$$V = -q \left(1 - \frac{1}{\epsilon}\right) \left(\frac{1}{r_c} - \frac{1}{R}\right) \quad (13a)$$

$$W_{qV} = qV \quad (13b)$$

where the cavity radius r_c and dielectric constant can be simultaneously “adjusted” to give the same solute–solvent energy. However, in a dielectric continuum representation of the solvent, the reaction potential away from the solute and the cavity is independent of the cavity size and is determined entirely by the dielectric constant of the solvent. Since potential at r (in a given dielectric) is determined only by the charge contained in the inner sphere of radius r , it follows from eq 13 that the reaction potential inside a spherical, *macroscopic* sample of a continuum dielectric at a distance r from a charge q is given by

$$V(r) = -q \left(1 - \frac{1}{\epsilon}\right) \left(\frac{1}{r} - \frac{1}{R}\right) \quad (14)$$

neglecting the “edge effects” near the dielectric discontinuity at the outer surface of the sphere. Equation 14 can be solved for ϵ , giving

$$\epsilon_V(r) = \left[\frac{V(r)}{q} \left(\frac{1}{r} - \frac{1}{R}\right)^{-1} + 1 \right] \quad (15)$$

and

$$\epsilon_V = \left[\frac{1}{q} \left\langle V(r) \left(\frac{1}{r} - \frac{1}{R}\right)^{-1} \right\rangle + 1 \right]^{-1} \quad (16)$$

As in the case of calculating ϵ_P , the calculation the microscopic dielectric constant ϵ_V is best done in a manner consistent with the fundamental relationship given by eq 8; the averaged quantity must be proportional to polarization P . Averaging $V(r) - (1/r - 1/R)^{-1}$ (instead of $\epsilon_V(r)$) in eq 16 reflects this.

The edge effects ignored in eqs 9–16 can be important due to the microscopic size of the sample. We attempt to remedy this deficiency by comparing $P(r)$ and $V(r)$ in the DL with DC results for a series of ϵ values. A pointwise comparison across the solvent leads to $\epsilon_P(r)$, $\epsilon_V(r)$, ϵ_P , and ϵ_V . Of course, if a solvent can truly be described as a dielectric continuum, all of the above methods for calculating ϵ should give the same value. In reality, we can only hope for similarity among the values of ϵ calculated by different methods.

3. Dielectric Constants of DLs as a Function of Polarity

A. Macroscopic Dielectric Constants. We first analyze the *macroscopic* dielectric behavior as measured by the methods of section 2C. Note, however, that the fluctuating total dipole moment method cannot be used for calculating ϵ for LDLs since they lack explicit thermal fluctuations. Therefore, in order to keep the methodology for obtaining ϵ consistent, we used eq 6 for all systems. An interesting feature of the dipolar lattices is the significantly different dielectric behavior of Brownian and Langevin DLs. Even though individual dipoles are rigorously

TABLE 1: Macroscopic ϵ of LDL and PPL as a Function of Polarity^a

η	ϵ_{CM}	$\epsilon_{\text{fcc,LDL}}$	$\epsilon_{\text{sc,LDL}}$	$\epsilon_{\text{fcc,PPL}}$	$\epsilon_{\text{sc,PPL}}$
0.05	1.795	1.796	1.794	1.796	1.794
0.10	3.162	3.175	3.172	3.175	3.172
0.15	6.07	6.18	6.18	6.18	6.18
0.18	10.2	10.5	10.7	10.6	10.4
0.19	12.7	13.2	12.8	13.5	
0.20	16.5	17.4	9.7	18.0	
0.21	22.9	24.8	8.5	26.3	

^a ϵ is calculated from eq 6 with $E_0 = 10^{-5}$ au. CM = Clausius–Mossotti result.

equivalent in terms of their average polarization behavior, the presence or absence of *explicit* thermal fluctuations in the interdipolar fields seems to have important consequences for the *collective* polarization behavior. As Table 1 illustrates, both LDL and PPL follow the Debye equation¹⁵

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \rho \left(\alpha + \frac{\mu_0^2}{3k_B T} \right) \quad (17)$$

which can be regarded as a generalization of the Clausius–Mossotti (CM) equation¹⁵

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \rho \alpha \quad (18)$$

to include orientational polarizability $\mu_0^2/3k_B T$. LDL and PPL follow eq 18 almost up to the so-called Curie point of a CM dielectric where the system undergoes a ferroelectric transition (in the case of fcc lattices) with a divergent ϵ or an antiferroelectric transition (in the case of sc lattices) with a “saturating” ϵ . At low to moderate polarities there is good agreement between the dielectric constants of DL and PPL. For $\eta > 0.18$, sc PPL does not converge to a self-consistent polarization, marking an antiferroelectric transition. As the Curie point is approached, sample size dependence of ϵ (for fcc lattices) becomes stronger and recovering the CM result requires increasingly large systems (Table 2), with ϵ showing positive deviations. At polarities past the Curie point, the measured ϵ of the “ferroelectric” fcc LDL goes to infinity while that of “antiferroelectric” sc LDL depends strongly on E_0 employed. Overall, the agreement of the CM equation with LDL and PPL systems is essentially exact, the only limitation being the size of the system being used to extract ϵ . The reason for the applicability of the CM equation to LDL and PPL can be

understood if one acknowledges the fact that, even at high polarities, the total field exerted on each dipole by other dipoles vanishes^{15,16} in lattices of cubic symmetry. Therefore, the actual field E_i polarizing individual dipoles is equal to the external field E_0 .⁴⁸ This has the interesting consequence of leading to a dielectric material that follows the Debye equation *at finite polarities* with large dielectric constants, rather than following the Kirkwood–Fröhlich (KF) equation given by

$$g_K \mu_0^2 = \frac{k_B T (\epsilon - 1)(2\epsilon + 1)}{4\pi \rho \epsilon} \quad (19)$$

where g_K is the Kirkwood correlation factor.¹⁶ It appears that the domain of applicability for the CM equation extends to systems that can have large dielectric constants but do not exhibit explicit fluctuations in interparticle electric fields. Although this extended range of validity might appear to be limited only to cubic lattice systems such as LDLs and PPLs from symmetry arguments,¹⁵ CM must also apply to macroscopically homogeneous, isotropic fluid systems that have little or no fluctuations in interparticle electric fields. As could be surmised from the fact that the Debye equation was derived for dilute polar gases with the assumption of negligible interdipolar interactions, the macroscopic dielectric constant of an NIDL follows eq 18 as well. It is important to note that the particular functional dependence of ϵ on the microscopic parameters (such as CM or KF equations) is irrelevant to the dielectric behavior (including nonspecific solvation effects) of a material with a given ϵ . In contrast to LDL and PPL, BDL deviates measurably from the CM equation even for polarities as low as $\eta \approx 0.05$ where the dielectric constant of a CM dielectric is 1.79 (in perfect agreement with LDL and PPL) whereas that of BDL is 1.76 (Table 3).⁴⁹ While such a small difference can easily be overlooked when discussing the experimental dielectric constants of real materials, the fact that there is a measurable difference at all reveals that CM equation is not meant for describing the polarity dependence of ϵ for materials with permanent dipoles.^{50,51}

The difference between LDL and BDL can be understood by recognizing that the cancellation of the fields from the rest of the lattice is precise in LDLs because of the absence of explicit thermal fluctuations in interdipolar interactions, while in a BDL the rotational diffusion seems to break the symmetry of the fields (and the resulting precise cancellation at any instant) even though the translational symmetry is the same as in LDL. Therefore, the reason why the CM equation is limited to

TABLE 2: Macroscopic ϵ as a Function of Sample Size^a

R^c (Å)	$\eta = 0.05$	$\eta = 0.10$	$\eta = 0.15$	$\eta = 0.18$	$\eta = 0.19$	$\eta = 0.20^b$	$\eta = 0.21^b$
sc LDL							
7.96	1.801	3.261	7.07	16.1	27.6	114	−39
12.34	1.801	3.254	6.90	14.5	22.2	54	13.8
15.78	1.798	3.212	6.52	12.2	16.5	14.3	14.1
24.18	1.797	3.201	6.40	11.6	14.5	2.8	1.7
36.07	1.797	3.188	6.29	11.2	14.4	10.4	13.9
44.00	1.783	3.135	6.07	10.4	13.2	6.7	3.4
60.01	1.794	3.172	6.18	10.7	12.8	9.7	8.5
fcc LDL							
8.34	1.798	3.205	6.45	11.9	15.9	23.2	41.5
12.10	1.798	3.205	6.44	11.8	15.7	22.7	39.3
15.96	1.798	3.209	6.47	12.0	16.0	23.4	42.3
23.99	1.797	3.199	6.38	11.6	15.2	21.6	36.3
35.74	1.796	3.187	6.28	11.1	14.3	19.6	30.4
44.05	1.796	3.180	6.22	10.8	13.8	18.7	28.0
60.06	1.796	3.175	6.18	10.6	13.5	18.0	26.3

^a ϵ is calculated from eq 6 with $E_0 = 10^{-5}$ au. ^b The system is antiferroelectric at this polarity for sc LDL. ^c R is the radius of the sphere that corresponds to the number of dipoles (N) in the system with number density ρ , and is equal to $[(N/\rho)/(4\pi/3)]^{1/3}$.

TABLE 3: Macroscopic ϵ of BDL as a Function of Polarity^a

η	ϵ_{CM}	ϵ_{fcc}	ϵ_{sc}
0.05	1.795	1.76	1.76
0.10	3.162	2.85	2.82
0.20	16.49	6.71	5.73
0.25		10.0	7.5
0.33		21.5	10.7
0.50		∞	13.6

^a ϵ is calculated from eq 6 with $E_0 = 10^{-3}$ au, then corrected⁴⁹ for dielectric saturation using eq 2.

nonpolar materials can be traced to the fluctuations⁵² in interdipolar fields rather than the absence of such interactions. However, since the LDLs can be quite polar (and for fcc LDLs ϵ can have arbitrarily large values) and have successfully been used in modeling polar liquids, the range of validity of the CM equation has to be revised. If we include numerical models into a generalized definition of a “material”, the domain of applicability for the CM equation has to be rephrased as follows: *The CM equation is valid for materials in which the interdipolar fields have negligible fluctuations.*

Before we conclude this section, we would like to reflect on the traditional dielectric concepts by using the above observations. For this purpose, we choose to focus on Fröhlich’s classic book.¹⁵ Note that a PPL (which is simply the linearized version of an LDL) is identical to the model dielectric considered by Fröhlich, who showed the cancellation of the dipole fields analytically using symmetry arguments. One essential ingredient in that model is the absence of “short range forces” ($f_i = 0$ in Fröhlich’s notation). While PPL model lacks these forces *physically* by design, LDL lacks them *mathematically* because a Langevin dipole (despite its Brownian origins) responds in much the same way as a point polarizability. However, a BDL explicitly retains the stochastic nonelectrostatic forces, therefore making the so called “short range forces” nonzero at any given instant. Since the only difference between LDL and BDL is the presence of explicit thermal fluctuations, the inability of the CM equation to describe the relationship between polarity and dielectric constant for polar dielectrics can plausibly be traced to thermal fluctuations, rather than *specific* short range interactions per se or interactions between the dipoles of molecules. While the derivation of the CM formula is rigorous for a lattice of polarizabilities, it is not so for a material with permanent dipoles in thermal agitation. However, it is important to remember that whatever the relationship between polarity and dielectric constant, the dielectric and solvation behaviors are determined by the macroscopic and microscopic dielectric constants of the material, respectively (although solvation can be parametrized in terms of polarity as well, and the solute cavity size and shape can be used to capture the specifics of a particular solute–solvent combination). In other words, even though the relationship between the microscopic variables (such as dipole density and magnitude) and macroscopic parameters (such as dielectric constant) is different for a CM dielectric and a dipolar fluid, a CM dielectric can capture the solvation (or dielectric) behavior of a dipolar solvent if the appropriate values for the microscopic variables are chosen.

Now that we clarified that the CM equation was derived for a system of point polarizabilities that do not display explicit thermal fluctuations, we examine an alternative derivation (due to Onsager) of that equation presented in pages 25–26 of ref 15. Without going into the details, we notice that it utilizes “...in the absence of a macroscopic field, a spherical region which is polarized homogeneously, thus having a dipole moment \mathbf{M} ...”. The inconsistency is that a region containing only polarizabilities, without permanent dipoles at a finite temper-

ature, is incapable of spontaneously developing a polarization or a dipole moment in the absence of an applied field. Furthermore, the Onsager derivation involving a reaction field \mathbf{R} “...produced inside the spherical region by the surroundings if polarized by the former” suffers not only from the absence of a spontaneous polarization to cause a reaction field but also from the fact that the field on a *solvent* dipole (produced via a *polarizability*; and this is a crucial point) from the surroundings is identically zero for a CM dielectric (and to the extent that it is different from zero, the material deviates from the target equation being derived). Therefore, in the Onsager derivation of the CM equation both the reaction field \mathbf{R} and the so-called internal field are fictitious quantities since the CM equation rigorously applies only to systems where there are no fluctuations in interparticle fields. It thus seems that the CM result can be derived in a way that is inconsistent with the physics of the system to which it applies, providing an example where the assumptions in a particular derivation do not provide guidance on the nature of even the idealized system being described.

B. Microscopic Dielectric Constants. The “microscopic” dielectric constants as measured by solvation of a point charge, described in section 2D, reveal that the dielectric or solvation behavior of DLs is much richer than suggested by a continuum description. Before we address the issue of calculating the microscopic dielectric constant, it is useful to understand the polarization process associated with solvating a charge. Equation 10 implies that, in the continuum limit where $\rho \rightarrow \infty$, the induced dipoles associated with the induced polarization \mathbf{P} become vanishingly small. In this limit both overall system response and the response of the hypothetical individual dipoles are perfectly linear, consistent with the linearity of continuum dielectric descriptions of solvation. Therefore, linear response is clearly an inherent property of a *continuum* description of matter, rather than an extra assumption that can be relaxed if desired. In other words, *continuum* implies *linearity*. For instance, a “nonlinear continuum” model that attempted to account for “dielectric saturation” would have a fundamental inconsistency.⁵³ At finite ρ , the polarization of individual dipoles as well as that of the overall system response can deviate from linearity. The extent of the nonlinearity in the solvent polarization for a given solute charge depends not only on the distance from the charge but also on the particular position of a dipole relative to its neighbors (i.e., lattice structure). Figure 1 shows the distance-dependent polarization induced by $q = 0.05$, $q = 1$, and $q = 3$, properly scaled for comparison. For small to moderate charges, polarization oscillates around the continuum prediction, and there is no obvious sign of “dielectric saturation”. Strongly nonmonotonous r -dependence observed at small solute charge is largely washed out at $q = 1$ and almost entirely subdued at $q = 3$ where we also observe extensive “dielectric saturation”. Although at first sight it might seem counter-intuitive that $P(r)$ for a small charge (weak field) is much more nonmonotonic and deviates from the continuum prediction much more strongly than that for a large charge, it is an expected result. At weak ionic field strengths the interdipolar fields compete with the applied field more readily and lead to more “structure” in the polarization. This change in the radial profile of polarization as a function of solute charge implies that the polarization response to increasing solute charge is different at each point in the solvent. It also implies that the total solvent response to a charge and its degree of nonlinearity need not resemble those of the individual dipoles. The solvation of a charge can be fairly linear while the contributions from individual dipoles in the solvent are much more nonlinear. This nonlinearity of individual dipoles is not simply due to being in

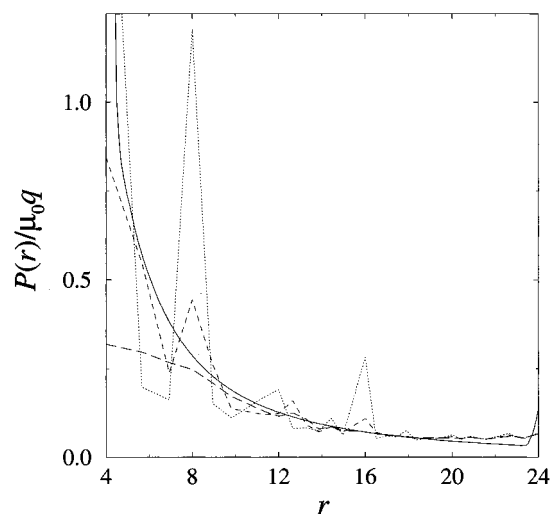


Figure 1. Polarization induced into a spherical (of radius $R = 24$ Å) sample of sc LDL ($a = 4$ Å, $\eta = 0.19$) by a point charge that displaces one solvent dipole (i.e., a nominal cavity radius of 4 Å). The solid line is the DC result for $\epsilon = 12.7$; dotted, short-dashed and long-dashed curves correspond to $q = 0.1, 1$, and 3 au, respectively. $P(r)$ is in 10^{-3} atomic units (au), μ_0 is in au, and r is in angstroms.

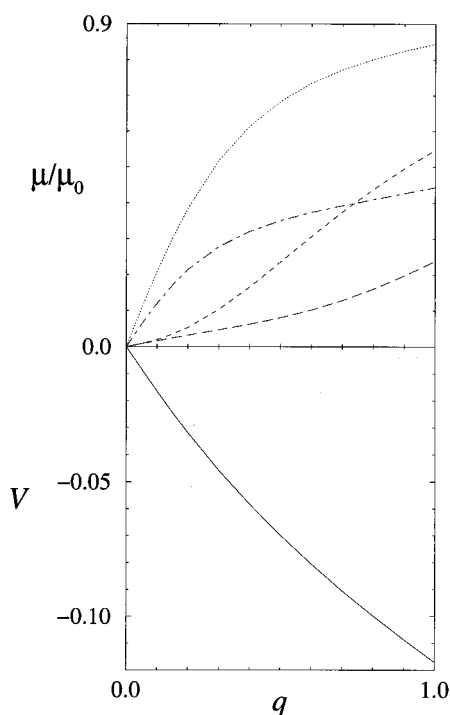


Figure 2. Normalized polarization μ/μ_0 of individual dipoles and the total response (represented by the electric potential V_0 at the solute, in atomic units au) of a dipole lattice (sc LDL, $a = 4$ Å, $\eta = 0.19$) as a function of solute charge (in au). μ/μ_0 is equivalent to $\langle \cos \theta \rangle$ for thermally fluctuating dipoles (as in BDL) where θ would be the angle between the dipole and the radial vector connecting the solute charge and the solvent dipole. The total response V is markedly more linear than the response of individual dipoles, reflecting the compensating behavior of individual polarizations. Dotted, short-dashed, long-dashed, and dot-dashed curves represent the polarization of dipoles at 4, $4\sqrt{2}$, $4\sqrt{3}$, and 8 Å, respectively.

the nonlinear regime of the Langevin function (although that does become a source of nonlinearity for dipoles near a highly charged solute) but primarily due to the complex interplay of fields from neighboring dipoles. These points are demonstrated in Figure 2 which shows that while dipoles at $r = 4$ Å and 8 Å show signs of “saturation” in the Langevin function sense by curving down, the dipolar polarization in between (at $r =$

$4\sqrt{2}$ Å and $r = 4\sqrt{3}$ Å) actually curve up due to the fields from neighboring dipoles. From the discussion above, it must also be clear that the weak-field limit is unrelated to the continuum limit, even though both would yield linear behavior for polarization. At very small solute charges, both the overall solvation response and the polarization at any point within the solvent is linear. However, these linear responses have different slopes, and these slopes in general do not follow the continuum prediction. It appears that even if a dielectric material follows the Debye equation, its detailed microscopic polarization does not follow the monotonous behavior that would be predicted by the assumptions used in deriving the Debye equation. This complex, compensatory polarization behavior in a “coarse” lattice ($a = 4$ Å), leads to ϵ_P and ϵ_V that deviate significantly from the dielectric constant ϵ_{CM} predicted by the CM equation. Table 4 presents an extensive compilation of the microscopic dielectric constants. The finiteness of the sample and the resulting distortion of polarization causes deviations from eqs 12 and 16 even within a continuum dielectric description and leads to very large or negative dielectric constants which clearly are not physically sensible. Thus, although eqs 12 and 16 are the most fundamental *analytical* equations one can devise (without resorting to a wave vector dependent dielectric function, which would cease to be a *continuum* treatment) for calculating the microscopic dielectric constants of ionic solvation, their usefulness is limited to either weakly polar systems or to large (or infinite) systems where one could extend the averaging to large distances without encountering “edge effects”. Therefore, ϵ_P and ϵ_V values calculated by a pointwise comparison to DC calculations (columns labeled DC in Table 4) are much more reliable than those calculated by eqs 12 and 16 (columns labeled “Anl” in Table 4). The terms “microscopic dielectric constant”, ϵ_P and ϵ_V in the remainder of this article refer to ϵ_P and ϵ_V values calculated by a pointwise comparison to DC calculations. Even with sample finiteness taken into account, microscopic dielectric constants differ from the macroscopic ϵ because the lattice geometry and interdipolar interactions interplay in a way that cannot be captured by a continuum description. That is, the dielectric constant extracted from solvation energetics is different from the macroscopic dielectric constant, and reflects a degree of physical inconsistency in the continuum description of systems with microscopic structure. It is both interesting and instructive to realize that even a continuum description of solvation requires that interdipolar interactions not vanish even for a CM dielectric.⁵⁴ The solute–solvent interaction is attenuated by a shielding constant^{54,55} whose source is inevitably the interdipolar interactions. Therefore, the differences between microscopic and macroscopic dielectric constants is due to the part of dipole–dipole interactions that reflects the individuality of the solute–solvent system (largely determined by the lattice geometry) rather than non-vanishing interdipolar fields (in the case of solvation) per se. The microscopic dielectric constants converge to the macroscopic ϵ as the number density of dipoles is increased, again supporting the conclusion that a continuum description of a solvent is the infinite dipole density limit of a dipolar representation. At finer lattice resolutions (such as $a = 2$ Å or $a = 1$ Å for sc, and $a = 3.17$ Å or $a = 1.59$ Å for fcc) which are closer to the continuum limit, ϵ_P and ϵ_V (Table 4) agree reasonably well with the CM equation (Table 1). This is expected because the microscopic and macroscopic dielectric constants of a physically consistent dielectric converges as the distance between solvent particles becomes small compared with the size of the solute, i.e., $\rho^{-1/3}/r_c \rightarrow 0$ and the system starts looking like a true continuum. At this juncture, it may be useful to remember that this limiting process is valid only when the

TABLE 4: Microscopic Dielectric Constants ϵ_P and ϵ_V As Measured by Radial Polarization in a Spherical Sample of a LDL Lattice ($a = 1, 2$, and 4 \AA for sc and the Corresponding $a = 1.59, 3.17$, and 6.35 \AA for fcc) with a Concentric Spherical Cavity of Radius r_c Containing at Its Center a Point Charge of 0.1 au^a

	$a = 1 \text{ \AA}$				$a = 2 \text{ \AA}$				$a = 4 \text{ \AA}$			
	DC (A)	DC (B)	Anl (A)	Anl (B)	DC (A)	DC (B)	Anl (A)	Anl (B)	DC (A)	DC (B)	Anl (A)	Anl (B)
$\eta = 0.05^b$	1.78	1.79	1.83	1.79	1.83	1.79	1.87	1.79	1.92	1.94	1.94	1.94
$\eta = 0.10^b$	2.98	3.16	3.47	3.17	3.35	3.07	3.85	3.08	4.35	4.75	4.88	4.79
$\eta = 0.15^b$	4.95	6.04	8.52	6.13	6.41	5.27	14.2	5.34	24.7	95	-76	1300
$\eta = 0.18^b$	6.7	10.1	26.3	10.7	9.6	7.3	-46.7	7.6	-25.6	-13.2	-8.5	-10.7
$\eta = 0.19^b$	7.4	12.8	70.5	14.1	10.8	8.0	-20.2	8.5	-16.2	-10.0	-6.7	-8.3
$\eta = 0.05^c$	1.83	1.79	2.07	1.82	1.71	1.68	1.74	1.70	2.27	1.84	3.13	1.87
$\eta = 0.10^c$	3.21	3.14	5.49	3.41	2.81	2.74	3.11	2.92	5.43	3.67	-13.9	4.27
$\eta = 0.15^c$	5.83	5.82	-65	7.98	4.76	4.66	6.65	5.83	17.7	9.30	-3.18	46
$\eta = 0.18^c$	8.9	9.1	-9.5	20.8	6.9	6.8	14.4	11.2	110	25.8	-2.42	-12.3
$\eta = 0.19^c$	10.5	10.8	-7.4	40.2	7.9	7.8	22.3	15.7	-305	52.4	-2.27	-8.8

	$a = 1 \text{ \AA}$				$a = 2 \text{ \AA}$				$a = 4 \text{ \AA}$			
	DC (C)	DC (D)	Anl (C)	Anl (D)	DC (C)	DC (D)	Anl (C)	Anl (D)	DC (C)	DC (D)	Anl (C)	Anl (D)
$\eta = 0.05^d$	1.78	1.79	1.81	1.80	1.81	1.80	1.82	1.80	1.82	1.79	1.84	1.79
$\eta = 0.10^d$	3.07	3.16	3.29	3.16	3.27	3.17	3.41	3.17	3.32	3.10	3.60	3.10
$\eta = 0.15^d$	5.46	6.05	6.95	6.07	6.51	6.21	7.97	6.22	6.51	6.31	9.46	6.51
$\eta = 0.18^d$	8.1	10.3	14.0	10.4	11.2	11.1	21.0	11.3	9.9	20.6	31.8	31.4
$\eta = 0.19^d$	9.4	12.0	19.7	12.2	13.7	16.0	44.5	16.6	10.9	-400	93	-36.9
$\eta = 0.05^e$	1.83	1.80	2.00	1.81	1.74	1.75	1.76	1.76	2.02	1.85	2.49	1.87
$\eta = 0.10^e$	3.20	3.16	4.42	3.26	2.93	3.01	3.17	3.10	3.68	3.57	25.23	3.78
$\eta = 0.15^e$	5.98	5.99	24	6.72	5.22	5.55	6.82	6.14	5.88	8.33	-4.91	11.1
$\eta = 0.18^e$	10.0	10.0	-17.9	13.3	8.1	8.9	15.3	11.2	7.61	16.9	-3.22	55
$\eta = 0.19^e$	12.1	12.3	-12.4	18.4	9.8	10.9	25.7	15.2	8.43	22.7	-2.95	35000

	$a = 1.59 \text{ \AA}$				$a = 3.17 \text{ \AA}$				$a = 6.35 \text{ \AA}$			
	DC (A)	DC (B)	Anl (A)	Anl (B)	DC (A)	DC (B)	Anl (A)	Anl (B)	DC (A)	DC (B)	Anl (A)	Anl (B)
$\eta = 0.05^f$	1.78	1.79	1.83	1.79	1.78	1.78	1.86	1.78	1.88	1.90	1.94	1.90
$\eta = 0.10^f$	2.98	3.16	3.47	3.17	2.97	2.99	3.76	3.00	3.81	4.05	4.69	4.05
$\eta = 0.15^f$	4.95	6.04	8.52	6.13	4.73	4.96	12.1	5.03	10.2	13.0	280	13.3
$\eta = 0.18^f$	6.75	10.2	26	10.7	6.10	6.74	-340	6.98	35.0	95	-10.6	150
$\eta = 0.19^f$	7.47	15.8	50	17.4	6.60	7.47	-35	7.81	115	-140	-8.1	-86
$\eta = 0.05^g$	1.83	1.79	2.07	1.82	2.15	1.89	4.12	1.93	2.72	1.81	-15.81	1.83
$\eta = 0.10^g$	3.21	3.14	5.49	3.41	4.47	3.75	-4.59	4.26	3.39	3.60	-1.40	3.87
$\eta = 0.15^g$	5.83	5.82	-65	7.98	9.98	9.21	-1.92	23	2.48	10.0	-0.87	17.6
$\eta = 0.18^g$	8.91	9.1	-9.49	21	17.5	22	-1.51	-21	2.05	37	-0.74	-26.4
$\eta = 0.19^g$	10.9	11.1	-5.52	47	21	35	-1.42	-13.5	1.94	135	-0.71	-15.1

	$a = 1.59 \text{ \AA}$				$a = 3.17 \text{ \AA}$				$a = 6.35 \text{ \AA}$			
	DC (C)	DC (D)	Anl (C)	Anl (D)	DC (C)	DC (D)	Anl (C)	Anl (D)	DC (C)	DC (D)	Anl (C)	Anl (D)
$\eta = 0.05^h$	1.79	1.79	1.81	1.79	1.79	1.80	1.83	1.80	1.82	1.78	1.86	1.78
$\eta = 0.10^h$	3.07	3.16	3.29	3.16	3.10	3.21	3.43	3.21	3.34	2.97	3.82	2.98
$\eta = 0.15^h$	5.45	6.08	6.89	6.08	5.55	6.47	8.09	6.51	6.77	4.68	13.85	4.73
$\eta = 0.18^h$	8.2	10.2	13.5	10.2	8.3	12.1	21	12.3	11.7	5.77	-50	5.88
$\eta = 0.19^h$	9.5	12.8	18.8	12.8	9.7	16.3	41	16.7	14.6	6.04	-20	6.18
$\eta = 0.05^i$	1.83	1.80	1.95	1.81	2.04	1.84	3.01	1.85	2.44	1.89	5.01	1.90
$\eta = 0.10^i$	3.22	3.16	4.26	3.27	4.01	3.40	-16.70	3.54	4.93	3.85	-3.70	4.04
$\eta = 0.15^i$	6.02	6.00	19.26	6.75	8.44	7.29	-3.09	8.69	7.65	11.5	-1.71	16.7
$\eta = 0.18^i$	9.5	9.8	-32	12.8	14.4	14.3	-2.25	25	9.21	73	-1.38	-34
$\eta = 0.19^i$	11.3	11.9	-18.2	17.4	17.4	19.5	-2.08	59	9.80	-130	-1.30	-18

^a "DC" indicates that ϵ_P or ϵ_V is evaluated from a comparison to a DC calculation. "Anl" stands for "analytical" and indicates that ϵ_P is evaluated from a comparison to eq 12, and ϵ_V from a comparison to eq 16. Results obtained by averaging over the entire solvent and over a "middle" region away from the surfaces are presented. (A), (B), (C), and (D) refer to sampling ranges of $r = 10\text{--}14 \text{ \AA}$, $11\text{--}13 \text{ \AA}$, $4\text{--}14 \text{ \AA}$, and $6\text{--}12 \text{ \AA}$, respectively.

^b ϵ_P of sc LDL, $r_c = 10 \text{ \AA}$. ^c ϵ_V of sc LDL, $r_c = 10 \text{ \AA}$. ^d ϵ_P of sc LDL, $r_c = 4 \text{ \AA}$. ^e ϵ_V of sc LDL, $r_c = 4 \text{ \AA}$. ^f ϵ_P of fcc LDL, $r_c = 10 \text{ \AA}$. ^g ϵ_V of fcc LDL, $r_c = 10 \text{ \AA}$. ^h ϵ_P of fcc LDL, $r_c = 4 \text{ \AA}$; ϵ_V of fcc LDL, $r_c = 4 \text{ \AA}$.

solvent (or the microscopic model) has a convergent, well-defined dielectric constant. A simple continuum representation with a single macroscopic dielectric constant is incapable of describing states of matter that are ferromagnetic or antiferromagnetic. Interestingly, the macroscopic dielectric constant of NIDL, which is a model that is *constructed* to obey the assumptions of the Debye equation turns out to be completely different than its microscopic dielectric constants at any lattice resolution, reflecting the fundamental inconsistency of requiring polar molecules at condensed-phase density not to interact (Table 5). The NIDL example offers an extreme case highlight-

ing the potential utility of calculating microscopic dielectric constants ϵ_P and ϵ_V . An NIDL can be viewed as an extreme case of applying a "cut-off" radius to electrostatic interactions, and the microscopic dielectric calculation reveals the inconsistent behavior of such a model. In a similar and more general way, ϵ_P and ϵ_V can be used to detect dielectric inconsistencies introduced into computational models by numerical "tricks". It appears that LDL and PPL follow eq 17 not simply because there are no interdipolar interactions (as is the case in a NIDL), but because the interdipolar interactions lead to a configuration that results in the eventual cancellation of the dipolar fields.

TABLE 5: Microscopic Dielectric Constants ϵ_P and ϵ_V of NIDL, Calculated from Eqs 12 and 16, Respectively^a

η	ϵ_{CM}	ϵ_P (fcc)	ϵ_V (fcc)	ϵ_P (sc)	ϵ_V (sc)
0.020	1.274	1.336	1.336	1.336	1.336
0.030	1.431	1.605	1.604	1.605	1.606
0.050	1.795	2.69	2.69	2.69	2.70
0.060	2.007	4.06	4.06	4.06	4.08
0.065	2.122	5.46	5.45	5.46	5.49
0.070	2.245	8.31	8.28	8.31	8.38
0.075	2.374	17.4	17.3	17.4	17.7
0.078	2.456	50.4	49.4	50.4	53.5

^a ϵ_{CM} is the Clausius–Mossotti (eq 18) prediction, which is identical to the macroscopic ϵ of NIDL.

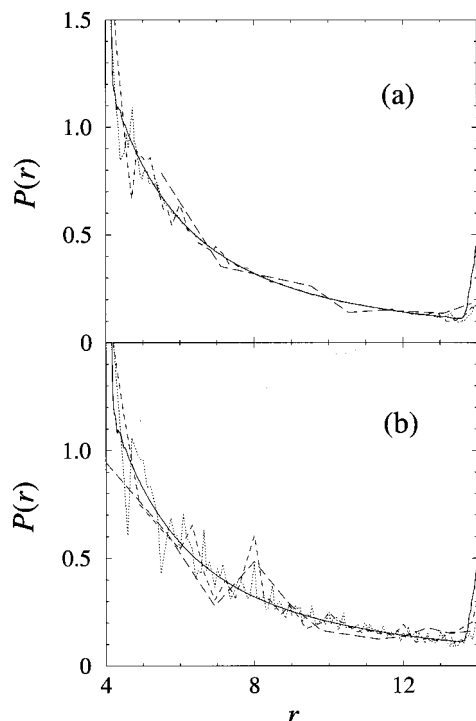


Figure 3. Distance-dependent polarization profile $P(r)$ in LDLs of various coarseness. The solute is a unit charge at the center of a spherical sample ($R = 14$ Å) of the lattice. A “cavity” is formed by excluding dipoles at $r < 4$ Å, where r is the distance from the solute. $P(r)$ is in 10^{-3} au and r is in angstroms. (a) fcc LDL with $\eta = 0.19$; the solid line is the DC result for $\epsilon = 12.7$; dotted, short-dashed, and long-dashed curves correspond to a values of 1.59, 3.17, and 6.35 Å (i.e., $(4)^{1/3}$, $2(4)^{1/3}$, $4(4)^{1/3}$, corresponding to the same ρ as an sc lattice with a values of 1, 2, and 4 Å). (b) sc LDL with $\eta = 0.19$; the solid line is the DC result for $\epsilon = 12.7$; dotted, short-dashed, and long-dashed curves correspond to a values of 1, 2, and 4 Å.

Figure 3 shows the polarization in sc and fcc LDLs of varying coarseness solvating a point charge. At lattice parameters comparable to the cavity radius (e.g., $a = r_c = 4$ Å for the sc lattice) the continuum prediction for polarization captures only a very coarse, average trend of the actual solvent polarization which oscillates wildly. As the lattice parameter a gets smaller, the system behavior increasingly resembles that of a continuum dielectric. However, even for $a = 1$ Å, $P(r)$ in sc LDL exhibits significant structure, suggesting that a continuum description may not capture the detailed microscopic behavior of a dielectric no matter how hard we try to make the model resemble a continuum. It appears that, as the density of the dipoles is increased, the polarization of individual dipoles may actually converge to continuum behavior (as is the case for fcc LDLs) or may persist in noncontinuum behavior (as in sc LDLs). However, the volume over which one has to average the polarization to obtain continuum-like polarization shrinks with increased ρ (as a visual inspection of Figure 3 clearly suggests)

and vanishes as $\rho \rightarrow \infty$. It is worthwhile to note that the LDL results are obtained by averaging over a number of starting configurations. For a coarse lattice (e.g., $a = 4$ Å sc) $P(r)$ converges to its ultimate profile in a single run, regardless of the starting configuration, while obtaining a converged average $P(r)$ in a fine lattice (e.g., $a = 1$ Å sc) requires dozens of independent starting configurations.⁵⁶ In contrast, $V(r)$ and the solvation energy of the solute do converge to the average in a single run even in the fine lattices regardless of the starting configuration. This suggests that essentially the same electric potential distribution in a given system can be accomplished by different polarization distributions, and the flexibility to achieve the same solvation by different microscopic polarization schemes increases as the number density of dipoles around the solute increases. This leads to the apparent paradox that as we construct our dielectric in an increasingly fine-grained manner, its *average* microscopic behavior starts resembling that of a continuum while any given snapshot of the polarization in the system is increasingly different from the continuum prediction. This is not a true paradox however, since the continuum model inherently involves an *average* and contains no knowledge or ability to produce “snapshots” of a microscopic system. At best, it aims that the average it predicts is close to the one produced by the real substance or a good microscopic model. The fact that (for sc LDL) individual configurations in an average that converges to the continuum result show increased deviations from the same continuum prediction is interesting but in no way physically inconsistent. Some dielectrics, however, can be less intriguing than others: while the polarization in a sc lattice does not show a natural tendency to conform to a continuum description, even a relatively coarse ($a = 3.17$ Å, equivalent to $a = 2$ Å for sc) fcc LDL polarizes in much the same way as the continuum prediction, with significantly less averaging than required for the sc lattice.

We now make the connection between LDL and BDL. From the discussion presented so far, the reader may have obtained the impression that, since the relationship between polarity η and macroscopic dielectric constant ϵ is different for LDL and BDL, there is no simple way to interrelate their microscopic polarization behavior (particularly as it relates to solvation). However, the macroscopic dielectric constant provides the required pivot point for relating these two models. As presented above, the continuum dielectric prediction for $P(r)$ provides an “average” curve for the actual microscopic $P(r)$ in a solvent. The particulars of the “structure” in the $P(r)$ of a solute–solvent system then determines the exact value of the microscopic dielectric constants ϵ_V and ϵ_P . Implicit in this observation is the fact that $P(r)$ for any two solvents will be quite similar since the “average” $P(r)$ s provided by the continuum theory would be identical. For an LDL and a BDL that share the same lattice geometry (analogous with two fluids that have identical structure factors) the similarity is expected to be even more pronounced. This expectation is confirmed by Figure 4 which shows $P(r)$ for an LDL and a BDL with $\epsilon \approx 6$. While for the coarse lattice spacing of 4 Å there are slight differences between the two lattices, $P(r)$ for LDL and BDL almost completely coincide. The agreement for the finer lattice ($a = 2$ Å) is so good that the two curves are almost indistinguishable. Table 6 lists the microscopic dielectric constants corresponding to the systems considered in Figure 4. The example above reminds us that the particular relationship (CM or KF) connecting the microscopic and macroscopic properties is inconsequential for determining the fitness of a model to represent solvation in real materials, as long as the parameters of the model are chosen in

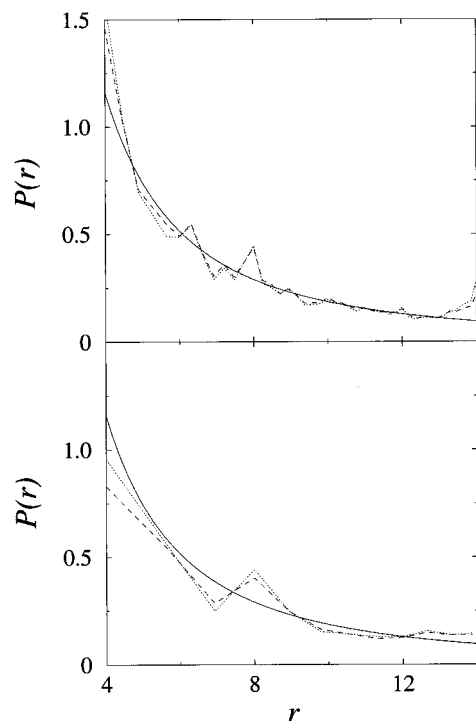


Figure 4. Comparison of polarization profiles $P(r)$ in BDL and LDL for $\epsilon \approx 6$, when solvating a unit charge in a 4 Å cavity (formed by deleting dipoles or setting $\epsilon = 1$ at $r < 4$ Å) concentric with the solvent sphere with a radius of 14 Å. $P(r)$ is in 10^{-3} au, and r is in angstroms. The solid curve is the analytical continuum dielectric prediction (eq 9). Dotted and dashed curves represent $P(r)$ in BDL and LDL, respectively. (a) Fine lattice ($a = 2$ Å). (b) Coarse lattice ($a = 4$ Å).

TABLE 6: Microscopic Dielectric Constants ϵ_P and ϵ_V of sc LDL and sc BDL for $\epsilon \approx 6$, Determined by a Pointwise Comparison with the Corresponding DC Calculation

lattice	η	ϵ_P^a	ϵ_P^b	ϵ_V^a	ϵ_V^b
sc LDL; $a = 2$ Å ^c	0.15	6.4	6.1	5.2	5.5
sc BDL; $a = 2$ Å ^c	0.20	5.8	5.4	5.2	5.3
sc LDL; $a = 4$ Å ^c	0.15	6.3	4.8	6.0	8.3
sc BDL; $a = 4$ Å ^c	0.20	6.9	4.8	6.9	9.4

^a Averaged over $r = 4$ –14 Å. ^b Averaged over $r = 6$ –12 Å. ^c Solute charge $q = 1$ au.

a self-consistent manner. The simplest way to achieve this consistency is to use an LDL polarity η_{LDL} that corresponds to the solvent's ϵ . The CM equation (eq 18) quite accurately represents the relationship between η and ϵ for LDLs. Thus we have

$$\eta_{\text{LDL}} = \frac{3}{4\pi} \frac{\epsilon - 1}{\epsilon + 2} \quad (20)$$

In order to find the η_{LDL} that produces a dielectric and solvation behavior (e.g., $P(r)$ profile) comparable to that of a KF dielectric (which is generally regarded as broadly applicable to real solvents) we solve eq 19 for ϵ to obtain

$$\epsilon = \frac{1 + 12\pi\eta_{\text{KF}}g_{\text{K}} + \sqrt{8 + (1 + 12\pi\eta_{\text{KF}}g_{\text{K}})^2}}{4} \quad (21)$$

From eqs 20 and 21 we obtain the relationship

$$\eta_{\text{LDL}} = \frac{3}{4\pi} \frac{12\pi g_{\text{K}}\eta_{\text{KF}} + \sqrt{8 + (1 + 12\pi g_{\text{K}}\eta_{\text{KF}})^2} - 3}{12\pi g_{\text{K}}\eta_{\text{KF}} + \sqrt{8 + (1 + 12\pi g_{\text{K}}\eta_{\text{KF}})^2} + 9} \quad (22)$$

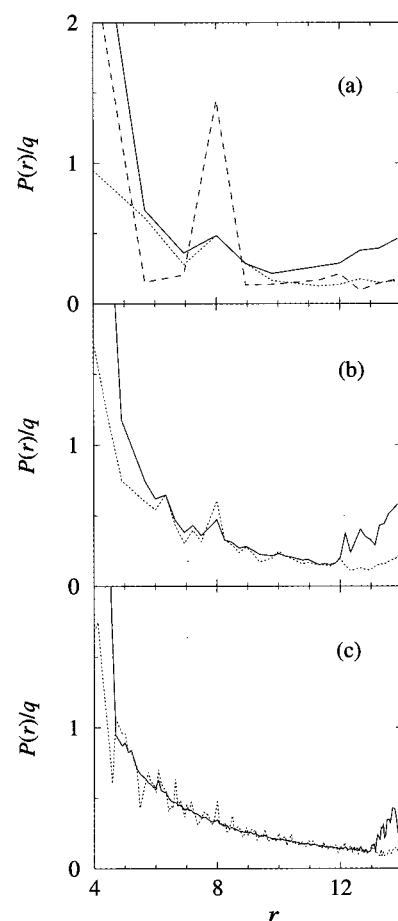


Figure 5. Comparison of the polarization $P(r)$ (in units of 10^{-3} au) scaled by solute charge q (in au) observed in sc LDL ($\eta = 0.19$) with that obtained by a DC calculation using the same “grid spacing” a when solvating a unit charge in a 4 Å cavity (formed by deleting dipoles or setting $\epsilon = 1$ at $r < 4$ Å) concentric with the solvent sphere with a radius of 14 Å. r is in angstroms. The solid curves are the DC results and the dotted curves are the sc LDL results. (a) $a = 4$ Å. (b) $a = 2$ Å. (c) $a = 1$ Å. In (a), the dashed curve is the scaled polarization for $q = 0.1$.

that connects η_{LDL} and η_{KF} . If we know the dipole number density of the particular KF dielectric and want to be consistent with its level of discreteness, ρ can be chosen to be the same as that of the KF dielectric. In that case, since $\eta = \rho\alpha$, η s in eq 22 can be expressed in terms of effective polarizabilities (α) or squares of the effective permanent dipole magnitudes (see eq 3).

Finally, we address the potential confusion that may arise from the fact that DL models and DC methods both utilize “grids”. To check whether the two kinds of discreteness are equivalent, we ask whether the polarization obtained with a coarse grid spacing (such as 4 Å, which is normally considered too large to obtain the true continuum results accurately) reproduces the polarization observed in a sc DL with the same a . As Figure 5 demonstrates, although there is a fortuitous similarity between the $a = 4$ Å sc LDL with $q = 1$ au and the corresponding DC calculation, there is no general agreement between $P(r)$ observed in the dipole lattice and calculated with the corresponding “coarse” DC calculation. While the sc LDL continues to display structure in its polarization profile, DC calculations quickly lose these oscillations as the grid spacing is reduced. The kind of microscopic discreteness that DLs have cannot be captured by a “discrete” continuum calculation. The two kinds of “discreteness” are simply different: the discreteness of a DL is physical while that of a DC model is purely numerical with no physical counterpart. However, it is worth

noting that the DC model qualitatively captures the overpolarization observed near the outer edge of the system. This overpolarization (which can also be seen in Figures 1 and 3) is perfectly physical, and can easily be explained in dipole lattices. For a dipole at the edge of the system, there are fewer nearby dipoles that compete for its "attention"; the field from the solute has less competition. For such a dipole, there is a smaller energy penalty for breaking configurations that are optimal for dipole-dipole interactions in order to polarize in the direction of the solute field, i.e., a dipole near the surface of the system is not shielded as much as it would be if it were in the bulk. Interestingly, it appears that a continuum dielectric retains enough of its dipolar origins to show similar behavior.

Finally, before we conclude this article we feel it is important to reflect on the past and future of the LDL model. As part of the protein Dipoles-Langevin dipoles (PDL) model of Warshel and Levitt,³ an LDL has been employed to represent polar solvation due to water. As such, it has performed admirably and reproduced experimentally observed values of solvation-related quantities.³³ The fact that the sc LDL could not attain very large dielectric constants⁵⁷ is inconsequential for its purpose. That is, the solvation contribution from distant parts of the solvent scales as $1 - 1/\epsilon$ (so that any moderately large ϵ gives the same result) while the solvation from microscopic distances does not follow the continuum prediction and is captured by the way the solute cavity is constructed. However, since we now know that an arbitrarily large macroscopic dielectric constant can be attained by an fcc LDL, it can be used for capturing microscopic solvation and macroscopic dielectric response simultaneously if desired.

4. Conclusions

The following are the main conclusions of this article:

1. The Clausius-Mossotti equation, which is the result of early attempts at relating the dielectric constant to "microscopic" quantities, and usually applicable to only dilute polar gases or nonpolar fluids, also applies to cubic lattices of Langevin dipoles or point polarizabilities. Thermal fluctuations in interdipolar fields, rather than the presence of interdipolar or specific short range interactions are the main cause for the deviation of dipolar materials from the Clausius-Mossotti equation. The domain of applicability for the CM equation is revised as materials in which the interdipolar fields have negligible fluctuations.

2. The presence of interdipolar interactions (even though they cancel when a homogeneous external field is applied to an LDL or PPL) are actually *required* to obtain a solvation behavior that is consistent with the conventional macroscopic dielectric constant.⁵¹ Furthermore, consistency with continuum formalism requires that the fields from the rest of the lattice dipoles exerted on a solvent dipole not cancel out when a charge is solvated, in contrast to the case with a homogeneous external field. LDL, PPL, and BDL are consistent dielectrics since they have full interdipolar interactions.

3. A novel way of obtaining microscopically relevant dielectric constants involves a point-by-point comparison of polarization and electric potential in a solute-solvent system with that obtained by a discretized continuum (extended Poisson equation) calculation. The "position-dependent" dielectric constant is then averaged to give a microscopic dielectric constant. For a physically consistent dielectric, microscopic and macroscopic dielectric constants converge as the distance between solvent particles becomes small compared with the size of the solute, i.e., $\rho^{-1/3}/r_c \rightarrow 0$.

4. The fact that the continuum dielectric is the infinite dipole density limit of a more general dipole-lattice description is

shown by recovering the continuum results with dipole lattices of high number density. The linearity of a continuum model is a direct consequence of being the infinite density limit of a dipolar model. Forcing a continuum dielectric to have a nonlinear response would be physically inconsistent.

5. Polarization produced in the solvent during the solvation process is mainly a function of the dielectric constant rather than the particular relationship (such as Clausius-Mossotti or Kirkwood-Frohlich equations) connecting the polarity and macroscopic dielectric constant of a model. A Langevin dipole lattice produces a polarization profile that is essentially identical with that of a Brownian dipole lattice of the same structure, even though the latter has explicit thermal fluctuations in its interdipolar fields and follows a different polarity-dielectric constant relationship.

6. The discreteness involved in the numerical solution of the extended Poisson equation cannot capture the effect of the physical discreteness in dipole lattices.

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(39) Equal polarity does not mean identical solvation because the arrangement of solvent dipoles around the solute, affected by r , can affect solvation energy even though it has no effect on the macroscopic dielectric constant of the pure DL.

(40) Alternatively, the system can be viewed in a coarse-grained way, and the polarization can be averaged over a large enough volume element so that the number of dipoles in the volume approaches infinity and the volume element behaves "macroscopically". However, even in this case, as soon as one goes back and uses continuum concepts at microscopic length scales the assumption of infinite dipole density is made, at least implicitly.

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(45) Note that this field inside the sample is an artificial but necessary consequence of a continuum representation and does not correspond to a microscopically meaningful field such as that on individual dipoles.

(46) In addition to providing an objective method of gauging how close a real, discrete solvent is to being a continuum dielectric in the context of solvation, the calculation of microscopic dielectric constants can measure the impact of certain numerical tricks (such as the use of cut-off radii in electrostatic forces during molecular simulations) on the solvation behavior of molecular models. For instance, even if a molecular solvent model with cut-off captures the solvation energetics of a solute, eqs 12 and 16 can, in principle, measure widely different microscopic dielectric constants for the models with and without cut-off and reveal that the solvation energy of the solute is recovered largely through changing the structure of the solvent near the solute rather than by exhibiting a globally correct solvation behavior. Such information can be used to improve existing computational models.

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(48) Note, however, that the local field in the LDL model is different from E_0 in other cases such as solvation of an ion or a dipole (or any solute charge distribution).

(49) The dielectric constant measurement for BDL was done by applying an external field of 10^{-3} au instead of 10^{-5} au that was used for LDLs and PPLs. This higher field strength had to be used in order to obtain reasonable

statistics with the thermally fluctuating BDLs and leads to a small but measurable dielectric saturation (i.e., slightly underestimates the dielectric constant). The dielectric saturation effect is corrected by calculating the average polarization of individual dipoles in the sample, calculating the corresponding γ value in eq 2, and calculating the linear polarization dipole from the linear limit of eq 2 using the linear polarizability given by eq 3. The total linear (corrected) polarization of the sample is then the total of the average individual linear polarizations.

(50) However, it clearly applies to a *model* that can represent its polarization and solvation behavior, such as an LDL or a PPL.

(51) It is important to note that the particular functional form (such as CM or KF relationships) connecting the polarity and the dielectric constant of a material is inconsequential in determining its net dielectric response for a given dielectric constant. The same argument can be made for the solvation response. In addition, the solvation energy of a solute is also influenced by the details of the solvent model in the vicinity of the solute. Since any simplified model (such as a structureless continuum or a dipolar grid) has little pretense of capturing these details, that information about the real system has to be absorbed into the way a cavity is constructed around the solute. We do not address this issue in this article.

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(53) We are not implying that such models would be useless. However, it should be recognized that a nonlinear continuum model implies a physical inconsistency. Although such models can be useful, they would nevertheless be ad hoc.

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(56) Note that the averaging is not done for obtaining a converged energy; it is for obtaining the average polarization profile corresponding to the already converged electric potential.

(57) Some versions of the PDL model did not include nearest-neighbor interactions (e.g., ref 34) and are expected to have higher dielectric constants. PDL calculations of the potential-of-mean-force between ions in water³³ repeatedly reproduced small interaction energies which correspond to large effective dielectric constants.