Onsager model for a variable dielectric permittivity near an interface

Reimar Finken, Vincent Ballenegger, and Jean-Pierre Hansen

Department of Chemistry
University of Cambridge
Cambridge CB2 1EW (UK)

(Dated: November 11, 2018)

Abstract

Using a generalisation of an Onsager type approach, we are able to predict a dielectric permittivity profile of an inhomogeneous dipolar fluid in the presence of a dielectric interface. The reaction and cavity fields are calculated semi-analytically using bispherical coordinates. An asymptotic expression for the local permittivity is derived as a function of distance from the interface.
I. INTRODUCTION

Since Onsager [1] and Kirkwood [2] it is well known that the macroscopic dielectric constant (or permittivity) $\epsilon$ of a material of polar, polarizable molecules is related to the fluctuations of the total dipole moment of a spatially homogeneous sample [3]. While the relation is well understood for infinite or periodic [4] bulk materials, much less is known about the static dielectric properties of confined polar fluids, or polar fluids near interfaces. The generally accepted view is that near interfaces, the dipole moment fluctuations are restricted, e.g. when dipole moments of individual molecules tend to orient themselves preferentially parallel or perpendicular to an interface, and that the resulting local permittivity is reduced relative to its bulk value. This is particularly important when considering water molecules near electrodes, biological macromolecules (e.g. proteins or DNA) or membranes in electrochemical and biophysical applications. On purely phenomenological grounds it is often assumed that the dielectric response of a polar solvent in such situations may be described by a distance-dependent permittivity, which is then incorporated in expressions for the Coulomb interaction energy between ions in solution [5].

The present paper attempts a first step beyond such purely *ad hoc* procedures, in terms of a simplified molecular picture of a polar fluid near an interface, by generalising Onsager’s well-known cavity model for bulk dielectric properties to an inhomogeneous situation. The objective is to determine a permittivity “profile” which varies with the distance from a planar interface separating a continuous medium of given permittivity $\epsilon_1$ from the medium made up of dipolar molecules.

The paper is organised as follows: The generalised Onsager cavity model is described in section II. A self-consistent set of equations determining the permittivity profile is derived in section III. In section IV the asymptotic behaviour of the dielectric permittivity far away from the interface is examined. The solution to the full electrostatic problem leading to a locally self-consistent permittivity profile is sketched in section V. The results will be discussed in the final section.
II. ONSAGER MODEL NEAR A PLANAR INTERFACE

Consider two dielectric media separated by a planar interface, as shown in figure 1. The horizontal interface is placed at \( z = 0 \). Below it (\( z < 0 \)) extends a dielectric medium considered to be a homogeneous continuum of constant permittivity \( \epsilon_1 \). Above the interface (\( z > 0 \)) extends a polar fluid made up of identical spherical molecules carrying a dipole moment \( \mu \) of fixed magnitude \( |\mu| \). The interface breaks the rotational invariance of the fluid, so that its dielectric response is \textit{a priori} described by a permittivity tensor \( \epsilon_2 \) which, by symmetry, is diagonal and of the form

\[
\epsilon_2 = \begin{pmatrix}
\epsilon_2^\parallel & 0 & 0 \\
0 & \epsilon_2^\parallel & 0 \\
0 & 0 & \epsilon_2^\perp
\end{pmatrix},
\]

where \( \epsilon_2^\parallel \) denotes the identical \( xx \) and \( yy \) components parallel to the interface, while \( \epsilon_2^\perp \) denotes the vertical \( zz \) component.

In view of an approximate calculation of \( \epsilon_2^\parallel \) and \( \epsilon_2^\perp \), one assumes, following Onsager [1], that a test molecule is placed at the centre of a spherical cavity of radius \( R = (3v/4\pi)^{1/3} \), where \( v = V/N \) is the volume per molecule. Since we are interested in permittivity profiles, the centre of the cavity is placed at a vertical distance \( z \) from the planar interface, and the dielectric response will be determined as a function of \( z \). The cavity is surrounded by a dielectric continuum characterised by the dielectric tensor \( \epsilon_2 \), of yet unknown components \( \epsilon_2^\parallel \) and \( \epsilon_2^\perp \). Following Onsager’s mean field approach [1], the dipole \( \mu \) inside the cavity is subjected to a cavity field \( \mathbf{E}_C \), induced by some external field taking the value \( \mathbf{E}^{\text{ext}} \) far above the planar interface (i.e. at \( z \to +\infty \)). In addition, the dipole polarises the surrounding dielectric media I and II, giving rise to polarisation charges on the surface of the cavity and on the planar interface. These polarisation charges generate a reaction field \( \mathbf{E}_R \) acting on the dipole inside the cavity. Both fields \( \mathbf{E}_C \) and \( \mathbf{E}_R \) are calculated from the laws of macroscopic electrostatics. The mean dipole moment inside the cavity is then calculated by averaging over orientations with the appropriate Boltzmann weight determined by the coupling of the dipole to the total electric field \( \mathbf{E} = \mathbf{E}_C + \mathbf{E}_R \) inside the cavity. The dielectric tensor components \( \epsilon_2^\parallel \) and \( \epsilon_2^\perp \) are finally determined by identifying the calculated mean dipole with the predictions of macroscopic electrostatics for parallel and orthogonal orientations of the external field.
FIG. 1: Geometry of the Onsager model. The test dipole $\mu$ is in a spherical cavity with centre a distance $z$ above the dielectric interface, below which extends a continuum of permittivity $\epsilon_1$. The fluid in region II has a local permittivity tensor $\epsilon_2$. Far above the wall the electric field is the external field $E^\text{ext}$. The polar angle of dipole with respect to the $z$ axis is denoted by $\vartheta$.

The calculation sketched above is quite straightforward in the case of isotropic, bulk dielectrics, but, as will become clear below, it is technically much more involved in the presence of an interface between two different dielectric media.

In the isotropic bulk, where $\epsilon_2^\parallel = \epsilon_2^\perp = \epsilon_2$, the Onsager mean field theory leads to the classic result $[1]$

$$\frac{(\epsilon_2 - 1)(2\epsilon_2 + 1)}{\epsilon_2} = \frac{\rho \mu^2}{\epsilon_0 k_B T},$$

valid for non-polarizable, polar molecules, $\rho = 1/v$ being the number density of these molecules and $k_B T$ the thermal energy; $\epsilon_0$ is the vacuum permittivity. The predictions
of [2], which does not account for correlations between the orientations of neighbouring dipoles (as embodied in the Kirkwood $g_K$-factor, see eq. [A2]), considerably underestimate the value of $\varepsilon_2$ for dense, highly polar liquids, and the same is hence to be expected for the results near the planar interface.

III. SELF-CONSISTENT EQUATION FOR THE PERMITTIVITY PROFILE

In the presence of the planar interface (cf. Fig. 1), the polarisation vector $\mathbf{P}$ in region II depends on the vertical coordinate $z$. If $\mathbf{E}(z)$ is the local electric field, the local susceptibility and dielectric tensors $\chi_2$ and $\varepsilon_2$ can be defined as usual by the linear relation

$$\mathbf{P}(z) = \varepsilon_0 \chi_2(z) \cdot \mathbf{E}(z) = \varepsilon_0 (\varepsilon_2(z) - \mathbf{I}) \cdot \mathbf{E}(z),$$

assuming a purely local response.

As explained in the previous section, the local field acting on the dipole $\mu$ inside the cavity is the sum of the cavity and reaction fields. Due to the linear nature of electrostatics, the reaction field depends linearly on the dipole moment

$$\mathbf{E}_R = \mathbf{M}_R \cdot \mu.$$  

The tensor $\mathbf{M}_R$ depends on $\varepsilon_1$ and $\varepsilon_2$ and on the geometric parameters $R$ and $z$. Due to the cylindrical symmetry of the problem, it is clear that $\mathbf{M}_R$ must be diagonal. A vertical dipole (parallel to the symmetry axis $Oz$) can only induce a vertical reaction field. For an arbitrary orientation of $\mu$, the reaction field must change sign under the inversion of the dipole $\mu \rightarrow -\mu$. In the case of a horizontal dipole, this inversion is equivalent to a rotation by $\pi$ around the vertical symmetry axis, implying that the reaction field has no vertical component. The horizontal component must moreover be parallel to the dipole, since the system is invariant under reflections by the plane containing $\mu$ and the vertical symmetry axis. The tensor $\mathbf{M}_R$ is hence of the same diagonal form as the permittivity tensor, with one vertical component $M_R^\perp = M_{Rzz}$, and two horizontal components $M_R^\parallel = M_{Rxx} = M_{Roy}$.

Similarly, the cavity field is proportional to the external field

$$\mathbf{E}_C = \mathbf{M}_C \cdot \mathbf{E}^{\text{ext}},$$

where the tensor $\mathbf{M}_C$ can only depend on $\varepsilon_1$, $\varepsilon_2$, and on the geometric parameters $R$ and $z$. The same symmetry arguments as above show that the tensor $\mathbf{M}_C$ is diagonal.
If the dipole interact with the cavity field via the energy $-\mu \cdot E_C$, the interaction energy with the reaction field is given by $-\mu \cdot E_R/2$. Indeed, increasing gradually the dipole moment from zero to its final value, we obtain a factor $1/2$ when we integrate the infinitesimal interaction energy increment $-E_R \cdot d\mu$ because of the linear relation (4).

The induced dipole moment per unit volume (or polarisation) is, within the cavity model,

$$P = \rho \langle \mu \rangle = \rho \int \frac{\mu \exp{\beta E_C \cdot \mu} \exp{\beta E_R \cdot \mu/2} d\Omega}{\exp{\beta E_C \cdot \mu} \exp{\beta E_R \cdot \mu/2} d\Omega}$$  \hspace{1cm} (6)

where the integrations are over all orientations of the test dipole. For small external field, the polarisation will be proportional to the field, and we can expand the exponential to first order in the reaction field. Taking into account the diagonal nature of the cavity field tensor $M_C$, we obtain in linear response

$$P = \rho \frac{\int \mu \exp{\beta E_R \cdot \mu/2} (1 + \beta E_C \cdot \mu) d\Omega}{\int \exp{\beta E_R \cdot \mu/2} (1 + \beta E_C \cdot \mu) d\Omega}$$

$$= \rho \int \frac{\mu \exp{\beta E_R \cdot \mu/2}}{\exp{\beta E_C \cdot \mu} \exp{\beta E_R \cdot \mu/2} d\Omega}$$

$$= \beta \rho \int \frac{\mu \exp{\beta \mu \cdot M_R / 2} d\Omega}{\exp{\beta \mu \cdot M_R / 2} d\Omega} \cdot M_C \cdot E_{\text{ext}}$$

$$= \epsilon_0 \chi_2^{\text{ext}} \cdot E_{\text{ext}}.$$  \hspace{1cm} (7)

In going from the first to the second line of (7), integrals involving an odd function of $\mu$ vanish. In the last expression we have defined the dielectric susceptibility with respect to the external field

$$\chi_2^{\text{ext}} = \frac{\beta \rho \mu^2}{\epsilon_0} \int \frac{\mu \mu \exp{\beta \mu \cdot M_R / 2} d\Omega}{\exp{\beta \mu \cdot M_R / 2} d\Omega} \cdot M_C.$$  \hspace{1cm} (8)

The components of this tensor are

$$\chi_\parallel^{\text{ext}} = \frac{9y}{2} (1 - \Delta_R) M_\parallel,$$

$$\chi_\perp^{\text{ext}} = \frac{9y}{2} \Delta_R M_\perp,$$  \hspace{1cm} (9)

with $y = \beta \rho \mu^2/\epsilon_0$ and

$$\Delta_R = \frac{1}{2\alpha^2} - \frac{e^{-\alpha^2}}{\sqrt{\pi} \alpha \text{Erf}(\alpha)}, \quad \alpha = \sqrt{\mu^2 (M_\parallel - M_\perp)/2}. \hspace{1cm} (10)$$

(Erf denotes the error function). The external susceptibility (8) must now be related to the local susceptibility $\chi_2$ defined in (3).
In the present case of a planar interface, it is easy to find the macroscopic relation between the polarisation \( \mathbf{P}(z) \) and the external field. For a given field far away from the wall and a given permittivity profile, the electric field at every point is known from the macroscopic equations. When the external field is horizontal, it will stay constant throughout space, since the permittivity is only varying perpendicularly to the field. Therefore the field felt by the test dipole in the macroscopic picture is simply \( \mathbf{E}^{\text{ext}} \), leading to the polarisation \( \mathbf{P} = \epsilon_0(\epsilon_2^\parallel(z) - 1)\mathbf{E}^{\text{ext}} \). In the case of a vertical field, however, the displacement field

\[
\mathbf{D}(z) \equiv \epsilon_0 \mathbf{E}(z) + \mathbf{P}(z) = \epsilon_0 \mathbf{e}_2 \cdot \mathbf{E}(z)
\]  

will remain constant. Therefore, at distance \( z \) from the interface, the electric field is \( \mathbf{E}^{\text{ext}} \epsilon_2^\perp(\infty)/\epsilon_2^\perp(z) \), leading to the polarisation \( \mathbf{P} = \epsilon_0(\epsilon_2^\perp(\infty) - \epsilon_2^\perp(z))\mathbf{E}^{\text{ext}} \). The permittivity far away from the wall is simply the bulk permittivity.

Comparing the above expression of the polarisation with the result (9) obtained from Onsager’s model gives

\[
\chi_{2,\parallel}^{\text{ext}} = \epsilon_2^\parallel(z) - 1 = \frac{9y}{2} (1 - \Delta_R) M_2^\parallel \\
\chi_{2,\perp}^{\text{ext}} = \epsilon_2^\perp(\infty) - \epsilon_2^\perp(z) = \frac{9y}{2} \Delta_R M_2^\perp.
\]  

(12a, 12b)

The tensors \( M_C \) and \( M_R \) [which determine \( \Delta_R \) via (10)] are to be obtained by solving the associated electrostatic problems. Since the permittivity tensor \( \epsilon_2(z) \) itself enters these problems, equations (12a) and (12b) are self-consistent equations for this permittivity profile.

Before determining the cavity and reaction field tensors in section V, we obtain first the asymptotic behaviour of the permittivity.

IV. ASYMPTOTIC BEHAVIOUR OF THE DIELECTRIC PERMITTIVITY

It is instructive to obtain an approximate estimate of the corrections to the reaction and cavity fields, valid for a test dipole far away from the interface, such that \( z \gg R \). The dielectric tensor will then practically reduce to the bulk value \( \epsilon_2 \mathbf{I} \). The polarisation of the cavity surface by the test dipole in the absence of an external field is such that the latter acts outside the cavity as an effective dipole moment of strength \( \frac{3}{2\epsilon_2 + \Pi} \mu \). The cavity model only yields an approximate estimate of the effective dipole moment. An exact calculation, sketched in Appendix A yields a general expression for the screened (effective)
dipole moment which reduces to the prediction of the cavity model if the Onsager value for $\varepsilon_2$ is substituted in equation (A6).

The additional electric field generated by the polarisation of the planar interface at $z = 0$ by this effective dipole may be described as being due to an image dipole of strength $\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \frac{3}{2\varepsilon_2 + 1} \mu$ situated at $-z$ below the interface. Since $z/R \gg 1$, the resulting field may be regarded as homogeneous over a distance equal to the diameter $2R$ of the cavity. The reaction field inside the cavity will be that outside the cavity, amplified by a factor $3\varepsilon_2/(2\varepsilon_2 + 1)$. The field depends of course on the orientation of the image dipole which itself is determined by the orientation of the test dipole. If the test dipole has both vertical and horizontal components, $\mu^\perp$ and $\mu^\parallel$, the reaction field is therefore

$$E_R = \frac{1}{4\pi \varepsilon_0} \left[ 2\frac{\varepsilon_2 - 1}{2\varepsilon_2 + 1} \frac{\mu}{R^3} - \left( \frac{3}{2\varepsilon_2 + 1} \right)^2 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \frac{1}{8z^3} [\mu^\parallel + 2\mu^\perp] \right],$$

and hence is no longer collinear with $\mu$. The electrostatic interaction energy of the dipole with the reaction field $-\mu \cdot E_R$ therefore depends on the orientation of the molecule. In figure 2 it can be seen that the orientation dependence of the energy is negligible even in the immediate vicinity of the wall.

In the presence of an external field two parts are contributing to the effective dipole moment. The test molecule aligns on average with the cavity field, leading to a permanent dipole, which appears screened outside the cavity. A second contribution originates from the polarisation of the cavity surface by the external field. Both terms lead to an electric field outside the cavity as due to an effective dipole moment

$$\mu^\text{eff} = \left[ \frac{3}{2\varepsilon_2 + 1} \frac{\mu^2}{3k_B T} \frac{3\varepsilon_2}{2\varepsilon_2 + 1} - 4\pi \varepsilon_0 \frac{\varepsilon_2 - 1}{2\varepsilon_2 + 1} R^3 \right] E^\text{ext}. \quad (14)$$

The corresponding image dipole $\mu^\text{img} = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \mu^\text{eff}$ induces an approximately homogeneous field $E^\text{img}$ near the cavity, which is the first order correction of the local electric field $E^\text{loc} = E^\text{img} + E^\text{ext}$ over the external field. From the local field the local polarization can be determined to first order in $z^{-3}$

$$P = \rho \langle \mu \rangle = \frac{\rho \beta \mu^2 \varepsilon_2}{2\varepsilon_2 + 1} E^\text{loc}$$

$$= 9 \varepsilon_0 \varepsilon_2 \left\{ E^\text{ext} + 2E^\text{ext}_\perp \frac{\varepsilon_2 - 1}{\varepsilon_2 + \varepsilon_1} \frac{3\varepsilon_2 \beta \mu^2}{32 \pi \varepsilon_0 z^3} \left[ \frac{3\varepsilon_2 \beta \mu^2}{(2\varepsilon_2 + 1)^2} - 4\pi \varepsilon_0 R^3 \frac{\varepsilon_2 - 1}{2\varepsilon_2 + 1} \right] \right\}. \quad (16)$$
FIG. 2: Potential energy $-\mu \cdot E_R/2$ divided by the thermal energy $k_BT$ as a function of the azimuthal angle $\vartheta$ due to the interaction of the dipole with the reaction field as predicted by the Onsager model (solid line) and as given by the asymptotic expansion (dashed line). The dipole is located in a distance $2R$ above the wall. Dipole moment $\mu = 1.86D = 6.2 \cdot 10^{-30}$Cm and number density $\rho = 3.346 \cdot 10^{28}$m$^{-3}$ are the experimental values measured for water at $T = 293$K. This leads in the bulk to an Onsager value of $\epsilon_2 = 18.4$. The material below the interface is vacuum $\epsilon_1 = 1$. The constant electrostatic interaction energy which is also present in the bulk has been subtracted. The amplitude of the orientation dependent energy is less than $0.01k_BT$ even in the immediate vicinity of the wall.

After extracting $\chi_2^{\text{ext}}$ we can find the dielectric permittivities to first order in $z^{-3}$ as

$$
\epsilon_2^\parallel(z) - \epsilon_2(\infty) = -\frac{\epsilon_2 - 1}{32\pi\epsilon_0 z^3} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \left[ \frac{3\epsilon_2^2 \beta \mu^2}{(2\epsilon_2 + 1)^2} - 4\pi\epsilon_0 R^3 \frac{\epsilon_2 - 1}{2\epsilon_2 + 1} \right],
$$

$$
\epsilon_2^\perp(z) - \epsilon_2(\infty) = -\frac{\epsilon_2(\epsilon_2 - 1)}{16\pi\epsilon_0 z^3} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \left[ \frac{3\epsilon_2^2 \beta \mu^2}{(2\epsilon_2 + 1)^2} - 4\pi\epsilon_0 R^3 \frac{\epsilon_2 - 1}{2\epsilon_2 + 1} \right].
$$
All quantities appearing on the r.h.s in these expressions are bulk values.

V. SOLUTION OF THE ELECTROSTATIC PROBLEM

To find the tensors $\mathbf{M}_C$ and $\mathbf{M}_R$ we have to solve two purely electrostatic problems. One involves finding the reaction field induced by the polarised material at the centre of the cavity. In this case we consider a dipole at the centre of the spherical cavity, surrounded by dielectric material of permittivity $\epsilon_2$ at a distance $z$ above a medium with isotropic permittivity $\epsilon_1$. The electric field must decay to zero as $z \to \infty$. To find the cavity field on the other hand, we consider an empty sphere, and an external field which goes to $\mathbf{E}^{\text{ext}}$ far from the cavity. In both problems the electrostatic equations are the same; they differ only in the boundary conditions: for the cavity field we require the electric field to be finite within the sphere and approach a prescribed value at infinity; for the reaction field we require a dipolar singularity at the centre of the sphere and the electric field vanishes far away from the interface.

In the geometry considered here there are two dielectric interfaces: One is a planar interface where the dielectric permittivity jumps from $\epsilon_1$ to $\epsilon_2$. The other is a sphere where the permittivity jumps from $\epsilon_2$ to 1. These interfaces divide space into three regions as shown in figure 1. Within each region the electrostatic potential satisfies the relation

$$\nabla \cdot (\mathbf{e} \cdot \nabla \psi) = 0. \quad (19)$$

With a spatially varying tensor permittivity $\mathbf{e}_2(z)$, eq. (19) cannot be solved analytically. Instead of computing a numerical solution, we shall determine the cavity and reaction fields for the simpler case of a constant and scalar permittivity $\epsilon_2$. These results will then be used to determine a permittivity profile from the Onsager equations (12a) and (12b). These equations will be solved in a locally self-consistent manner: when the cavity is at a distance $z$ from the interface, we shall use the cavity and reaction field tensors corresponding to the case of a homogeneous and isotropic medium II of dielectric constant $\overline{\epsilon}_2 \equiv \text{Tr}(\mathbf{e}_2(z))/3 = [2\epsilon_2^\parallel(z) + \epsilon_2^\perp(z)]/3$. This scheme provides a reasonnable approximation to $\mathbf{e}(z)$, since the deviations of $\mathbf{e}(z)$ from the bulk behaviour $\epsilon_2\mathbf{I}$ prove to be small for $z > 2R$ (see section VI).

In each regions, equation (19) now reduces to Laplace’s equation

$$\Delta \psi = 0. \quad (20)$$
At the dielectric interfaces we impose the usual boundary conditions: The tangential component of the electric field $\mathbf{E} = -\nabla \psi$ must be identical on both sides of the interface:

$$\nabla \psi \bigg|_{t,I} = \nabla \psi \bigg|_{t,II}$$

This condition is automatically satisfied if the potential is continuous across the interface:

$$\psi \bigg|_{I} = \psi \bigg|_{II}$$

Likewise the normal part of the displacement field $\mathbf{D} = \epsilon_0 \epsilon_2 \mathbf{E}$ must be identical on both sides of the boundary.

$$\epsilon_1 \nabla \psi \bigg|_{n,I} = \epsilon_2 \nabla \psi \bigg|_{n,II}$$

The electrostatic problem is best solved in bispherical coordinates. Some properties of this system are summarised in Appendix B. This coordinate system is well suited for our problem because the two interfaces turn out to be surfaces of constant coordinate $\eta$. A set of these surfaces is sketched in figure 3. Furthermore Laplace’s equation is separable in these coordinates. We therefore proceed to express the yet unknown electrostatic potential in each region as a series of fundamental solutions of Laplace’s equation with unknown expansion coefficients. The latter will be determined by the boundary conditions. In bispherical coordinates the component of the displacement field normal to the surface of constant coordinate $\eta$ is given by

$$D_\eta = -\frac{\cosh \eta - \cos \vartheta}{a} \epsilon_0 \epsilon_2 \frac{\partial \psi}{\partial \eta}.$$  

We fix the parameter $a$ in the bispherical coordinates to $a = R \sqrt{z^2/R^2 - 1}$ and define $\eta_0 = \ln(z/R + \sqrt{(z/R)^2 - 1})$. With these choices the planar interface corresponds to the surface $\eta = 0$, and the spherical cavity to the surface $\eta = \eta_0$. The centre of the sphere has coordinates $\eta_1 = 2\eta_0$, $\vartheta_1 = 0$, and $\phi_1 = 0$. The solutions of Laplace’s equation in bispherical coordinates are of the form

$$\psi(\eta, \vartheta, \phi) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ A_{mn} \psi^-_{mn}(\eta, \vartheta, \phi) + B_{mn} \psi^+_{mn}(\eta, \vartheta, \phi) \right],$$

with the fundamental solutions

$$\psi_{mn}^{\pm}(\eta, \vartheta, \phi) = \sqrt{\cosh \eta - \cos \vartheta} e^{\pm(n+1/2)\eta} Y_n^m(\vartheta, \phi).$$  

11
FIG. 3: Surfaces of constant $\eta$ in bispherical coordinates. A cut through the cartesian $xz$-plane is shown. In three dimensions the surfaces are spheres. As $\eta \to \infty$, the centres of the spheres approach the point $z = a$.

Here the $Y_n^m$ are spherical harmonics and the $A_{mn}$ and $B_{mn}$ are constant expansion coefficients. The $\psi^\pm_{mn}$ diverge at $\eta \to \pm \infty$, i.e. $x = y = 0, z = \pm a$. Because the potential in region I is regular, only the $\psi^+_{mn}$ can contribute to the expansion. Likewise the expansions of the cavity and reaction field inside the cavity only contain $\psi^-_{mn}$ terms. However, the field produced by the dipole itself contains contributions from the divergent $\psi^+_{mn}$ (see Appendix B). This is due to the singularity of the potential at the centre of the sphere. We
therefore expand the potential in each of the regions in the following series:

\[ \psi_I = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} A_{mn} \psi_{mn}^+ \]  
(27)

\[ \psi_{II} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ B_{mn} \psi_{mn}^- + C_{mn} \psi_{mn}^+ \right] \]  
(28)

\[ \psi_{III} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ D_{mn} \psi_{mn}^- + E_{mn} \psi_{mn}^+ \right] \]  
(29)

bearing in mind that the \( E_{mn} \) are the known expansion coefficients of the dipolar potential given by equations (B9) and (B10). When calculating the reaction field, the \( E_{mn} \) vanish. In this case the expansion coefficients of the external field, given by equations (B11) and (B12), have to be included in the \( B_{mn} \). The expansion coefficients are determined by the boundary conditions. Condition (22), i.e. continuity of the electric potential, directly leads to

\[ \sum_{n=0}^{\infty} \sum_{m=-n}^{n} A_{mn} \psi_{mn}^+ \bigg|_{\eta=0} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ B_{mn} \psi_{mn}^- + C_{mn} \psi_{mn}^+ \right] \bigg|_{\eta=0} \]  
(30)

\[ \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ B_{mn} \psi_{mn}^- + C_{mn} \psi_{mn}^+ \right] \bigg|_{\eta=\eta_0} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ D_{mn} \psi_{mn}^- + E_{mn} \psi_{mn}^+ \right] \bigg|_{\eta=\eta_0} \]  
(31)

for all \( \vartheta \) and \( \phi \). Multiplying these equations with \( Y_M^*(\vartheta, \phi)/\sqrt{\cosh \eta - \cos \vartheta} \) and integrating over \( \sin \vartheta d\vartheta d\phi \), one is able to separate the terms in the sums, with the result:

\[ A_{MN} = B_{MN} + C_{MN} \]  
(32)

\[ B_{MN} e^{-(N+1/2)\eta_0} + C_{MN} e^{(N+1/2)\eta_0} = D_{MN} e^{-(N+1/2)\eta_0} + E_{MN} e^{(N+1/2)\eta_0}. \]  
(33)

The second condition, i.e. continuity of the normal component of the displacement field, eq. (23), leads to the equations

\[ \epsilon_1 \sum_{n=0}^{\infty} \sum_{m=-n}^{n} A_{mn} \frac{\partial \psi_{mn}^+}{\partial \eta} \bigg|_{\eta=0} = \epsilon_2 \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ B_{mn} \frac{\partial \psi_{mn}^-}{\partial \eta} + C_{mn} \frac{\partial \psi_{mn}^+}{\partial \eta} \right] \bigg|_{\eta=0} \]  
(34)

\[ \epsilon_2 \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ B_{mn} \frac{\partial \psi_{mn}^-}{\partial \eta} + C_{mn} \frac{\partial \psi_{mn}^+}{\partial \eta} \right] \bigg|_{\eta=\eta_0} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ D_{mn} \frac{\partial \psi_{mn}^-}{\partial \eta} + E_{mn} \frac{\partial \psi_{mn}^+}{\partial \eta} \right] \bigg|_{\eta=\eta_0} \]  
(35)

Projecting once more the sums, we find

\[ \epsilon_1 A_{MN} = \epsilon_2 (C_{MN} - B_{MN}). \]  
(36)
Equations (32), (33) and (36) can be used to express $A_{mn}$, $B_{mn}$, and $C_{mn}$ in terms of the unknown $D_{mn}$.

\[
A_{mn} = \frac{2\epsilon_2}{\epsilon_2 + \epsilon_1} \xi_n(D_{mn} + E_{mn}e^{(2n+1)\eta_0})
\]

\[
B_{mn} = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \xi_n(D_{mn} + E_{mn}e^{(2n+1)\eta_0})
\]

\[
C_{mn} = \xi_n(D_{mn} + E_{mn}e^{(2n+1)\eta_0})
\]

with

\[
\frac{1}{\xi_n} = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} + e^{(2n+1)\eta_0}.
\]

Equation (35) now reduces to

\[
\sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left\{ [\epsilon_2 B_{mn} - D_{mn}] e^{-(n+1/2)\eta_0} \left[ \frac{e^{-\eta_0}}{2} + n \cosh \eta_0 \right] + [E_{mn} - \epsilon_2 C_{mn}] e^{(n+1/2)\eta_0} \left[ \frac{e^{\eta_0}}{2} + n \cosh \eta_0 \right] - \left[ (\epsilon_2 B_{mn} - D_{mn})e^{-(n+1/2)\eta_0} + (E_{mn} - \epsilon_2 C_{mn})e^{(n+1/2)\eta_0} \right] \right\} Y_n^m(\vartheta, \phi) = 0.
\]

We multiply this equation with $Y_N^M(\vartheta, \phi)$ and integrate over $\sin \vartheta d\vartheta d\phi$. Using the product rule for spherical harmonics (see eq. (A.26) of [8]), we find

\[
\sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left[ (\epsilon_2 B_{mn} - D_{mn})e^{-(n+1/2)\eta_0} + (E_{mn} - \epsilon_2 C_{mn})e^{(n+1/2)\eta_0} \right] \times (n + 1/2) \frac{2n + 1}{2N + 1} C(n1N; 000)C(n1N; m0M),
\]

where $C(n1N; m0M)$ are Clebsch-Gordan coefficients. All terms with $m \neq M$ vanish, as well as all terms with $n \neq N, N \pm 1$. The non-zero coefficients are

\[
C(n1(n+1); m0m) = \sqrt{\frac{(n - m + 1)(n + m + 1)}{(2n+1)(n+1)}},
\]

\[
C(n1n; m0m) = \frac{m}{\sqrt{n(n+1)}},
\]

\[
C(n1(n-1); m0m) = -\sqrt{\frac{(n - m)(n + m)}{n(2n+1)}}.
\]
Equation (42) therefore reduces to a three term recursion coupling the $D_{mn}$, $D_{m(n-1)}$, and $D_{m(n+1)}$. When only a finite number of terms are taken into account, the resulting tridiagonal linear equation can be solved with standard methods. From the $D_{mn}$ the electric field inside the cavity can be obtained using equation (B5). The series $\sum_{n=0}^{\infty} \sum_{m=-n}^{n} D_{mn} \psi_{mn}(\eta, \theta, \phi)$ converges very quickly at the centre of the sphere, so that a truncation after 20 terms leads to an accurate value for the field.

After having calculated the reaction and cavity fields using a given dielectric permittivity $\epsilon_2$, equations (12a) and (12b) are employed to give new estimates for the permittivity tensor. A locally self-consistent permittivity can thus be found by an iterative procedure: We start by setting $\epsilon_2$ to the isotropic bulk permittivity as determined by the bulk Onsager relation (2). We then solve the electrostatic equations as outlined above, leading to $\chi_{2}^{\text{ext}}$. Equations (12a), (12b) are then used to obtain a new prediction of $\epsilon_2(z)$. The new isotropic permittivity $\overline{\epsilon_2} = \text{Tr}(\epsilon_2(z))/3$ is then used as a starting value of the next iteration. In practice this scheme converges very quickly. The resulting permittivity profile is shown in figure 4.

VI. DISCUSSION

By generalising Onsager's model for the dielectric permittivity in bulk fluids we were able to predict a permittivity profile of a dipolar fluid near a wall. A number of approximations have been made; some of which are of fundamental nature, and some are made to render the calculations more tractable. A fundamental weakness of the Onsager approach is the complete neglect of orientational correlations between neighbouring molecules. This leads in the bulk to a significant underestimation of the permittivity. In the vicinity of a dielectric interface the fluid becomes birefringent. In our calculations we have neglected the anisotropy of the permittivity, to simplify the calculations. It is possible to take the full tensorial nature of the permittivity into account, which would lead to a five term recurrence formula instead of the three term recursion in equation (42). However, the results (figure 4) show that the fluid stays nearly isotropic except in the immediate vicinity (i.e. a few molecular distances) of the interface. Therefore the increased effort required to treat the anisotropy exactly does not seem to be worthwhile. In order to derive a semi-analytical expression for the permittivity, an inconsistency has to be allowed for in treating the model. For each position
FIG. 4: Dielectric permittivity profile as calculated self consistently. Dipole moment and density of the fluid are the values measured for water (see caption Fig. 2). The material below the interface is vacuum. The inset shows that the dielectric permittivities approach the values predicted by the asymptotic expansion very slowly.

of the cavity the permittivity of the whole fluid is assumed to be constant. The calculated permittivities, on the other hand, depend on the distance of the cavity from the interface, leading to a permittivity profile. This inconsistency can be overcome by solving the three dimensional Laplace equation numerically starting from a given permittivity profile. Again, the results of our model show bulk behaviour nearly everywhere except in the immediate vicinity of the interface, so that the complicated fully consistent solution does not seem to be worthwhile. Far away from the wall we were able to derive a first order correction to the bulk behaviour. We are presently investigating how to incorporate the orientational correlations between neighbouring dipoles into the theory.
Acknowledgments

RF is grateful to the Oppenheimer Fund for financial support. VB acknowledges the support of the Royal Society and of the Swiss National Science foundation.

APPENDIX A: EXACT EXPRESSION FOR THE EFFECTIVE DIPOLE MOMENT

Within a microscopic description of the dielectric medium modelled as a classical dipolar fluid [9], we can obtain an exact expression for the effective dipole moment $\mu^{\text{eff}}$ of a given molecule inside the fluid. We assume the non polarizable molecules to have a permanent dipole moment $\mu_i$, and we denote the position and the orientation of the $i$th molecule by $i = (r_i, \mu_i)$, $i = 1,...,N$. The molecules interact via of the dipolar pair potential

$$v_{\text{dip}}(1,2) = (\mu_1 \cdot \nabla_1)(\mu_2 \cdot \nabla_2) \frac{1}{|r_1 - r_2|}, \quad |r_1 - r_2| > 0,$$

(A1)

and a short-ranged interaction $v_{\text{sr}}(1,2)$. The short-ranged interaction (e.g. a Lennard-Jones potential) is quite arbitrary, except for the fact that it must decay faster than $|r_1 - r_2|^{-3}$ at large separations (it may thus include higher order multipole interactions between the molecules).

The dielectric constant $\epsilon$ of this fluid, at inverse temperature $\beta$ and number density $\rho = N/V$, is given by the Kirkwood formula [2]

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = yg_K, \quad y = 4\pi\beta\rho\mu^2/9,$$

(A2)

where the factor $g_K = 1 + \rho \int d^3r_1 \int d\Omega_1 \int d\Omega_2 (\hat{\mu}_1 \cdot \hat{\mu}_2)h(1,2)/(4\pi)^2$ is a measure of short-ranged angular correlations between the molecules. The Onsager approximation to $\epsilon$, equation (2), corresponds to neglecting these correlations, i.e. setting $g_K = 1$. We recall moreover that the Ursell function $h(1,2)$ of the infinite system decays asymptotically like a screened dipolar potential [9].

$$h(1,2) \sim \frac{(\epsilon - 1)^2}{9y^2\epsilon}(-\beta v_{\text{dip}}(1,2)), \quad |r_1 - r_2| \to \infty.$$  

(A3)

To evaluate $\mu^{\text{eff}}$, we introduce $\rho(1|2) = (\rho/4\pi)(1 + h(1,2))$, the density of molecules at $r_1$ with orientation $\mu_1$ when there is a dipole $\mu_2$ at $r_2$. By definition, the average polarization

$$...$$
of the fluid around the fixed molecular dipole $\mu_2$ is
\begin{equation}
\mathbf{P}(\mathbf{r}) = \int d\Omega_1 \mu_1 \rho(1|2) = \frac{\rho}{4\pi} \int d\Omega_1 \mu_1 h(1,2). \tag{A4}
\end{equation}
This polarization cloud carries a total dipole moment $\mu_{\text{cloud}} = \int \mathbf{r} \cdot (-\nabla \cdot \mathbf{P}(\mathbf{r})) d^3\mathbf{r}$. According to (A4) and (A3), $\mathbf{P}(\mathbf{r})$ decays like $|\mathbf{r}|^{-3}$ at large distances and is therefore at the borderline of integrability. The integral defining $\mu_{\text{cloud}}$ is nevertheless convergent, thanks to the harmonicity of the Coulomb potential: $-\nabla \cdot \mathbf{P}(\mathbf{r})$ decays rapidly since $\Delta(1/|\mathbf{r}|) = 0$ when $|\mathbf{r}| > 0$. An integration by parts gives
\begin{equation}
\mu_{\text{cloud}} = \lim_{V \to \infty} \left[ \int_V \mathbf{P}(\mathbf{r}) \, d^3\mathbf{r} - \int_{\partial V} \mathbf{r} (\mathbf{P}(\mathbf{r}) \cdot d\mathbf{S}) \right] \tag{A5}
\end{equation}
for any volume $V$. For a spherical volume of radius $R \to \infty$, we find using (A4) and (A2) that the volume integral of the polarization is $(g_k - 1)\mu_2$. The surface integral can be evaluated using (A3), with the result $\mu_2 (\epsilon - 1)^2 / (9\epsilon)$. This shows that the effective dipole moment is given by the simple result
\begin{equation}
\mu_{\text{eff}} = \mu + \mu_{\text{cloud}} = \frac{\epsilon - 1}{3\epsilon} \mu. \tag{A6}
\end{equation}

APPENDIX B: PROPERTIES OF THE BISPHERICAL COORDINATES

The bispherical coordinates $(\eta, \vartheta, \phi)$ are given by
\begin{align}
x &= \frac{a \sin \vartheta \cos \phi}{\cosh \eta - \cos \vartheta} \tag{B1} \\
y &= \frac{a \sin \vartheta \sin \phi}{\cosh \eta - \cos \vartheta} \tag{B2} \\
z &= \frac{a \sinh \eta}{\cosh \eta - \cos \vartheta}. \tag{B3}
\end{align}
The surfaces of constant $\eta = \eta_0$ are spheres of radius $R = a/|\sinh \eta_0|$ with centre at the Cartesian coordinates $x = 0, y = 0, z = a \coth \eta_0$. The bispherical coordinates of the centre (where the dipole is located) are $\eta_1 = 2\eta_0, \vartheta_1 = 0, \phi_1 = 0$. Given the coordinate system (B1) one can work out the unit vectors in the $\eta, \vartheta$ and
φ-direction as

\[ e_\eta = \frac{1}{\cosh \eta - \cos \vartheta} \begin{pmatrix} \sin \vartheta \sinh \eta \cos \phi \\ \sin \vartheta \sinh \eta \sin \phi \\ 1 - \cosh \eta \cos \vartheta \end{pmatrix}, \]

\[ e_\phi = \frac{1}{\cosh \eta - \cos \vartheta} \begin{pmatrix} (\cosh \eta \cos \vartheta - 1) \cos \phi \\ (\cosh \eta \cos \vartheta - 1) \sin \phi \\ \sinh \eta \sin \vartheta \end{pmatrix}, \quad e_\varphi = \begin{pmatrix} -\sin \phi \\ \cos \phi \\ 0 \end{pmatrix}. \] (B4)

The gradient is

\[ \nabla \psi = \frac{\cosh \eta - \cos \vartheta}{a} \left[ \frac{\partial \psi}{\partial \eta} e_\eta + \frac{\partial \psi}{\partial \vartheta} e_\phi + \frac{1}{\sin \vartheta} \frac{\partial \psi}{\partial \phi} e_\phi \right]. \] (B5)

The Laplace equation \( \nabla^2 \psi = 0 \) is separable in the coordinate system and its solutions are of the form given in eq. (25). Moreover, the Green’s function, i.e. the solution of the equation \( \nabla^2 G(\mathbf{r}) = -\delta(\mathbf{r} - \mathbf{r}_1) \), is

\[ G(\eta, \vartheta, \phi) = \frac{1}{a} \int \cosh \eta - \cos \vartheta \sqrt{\cosh \eta_1 - \cos \vartheta_1} \cdot \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{4\pi}{2n+1} Y_n^m(\vartheta_1, \phi_1)Y_n^m(\vartheta, \phi)e^{-(n+1/2)|\eta-\eta_1|} \]

\[ = \frac{1}{a} \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{4\pi}{2n+1} \psi_{an}^{-*}(\eta, \vartheta_1, \phi_1) \psi_{an}^+(\eta, \vartheta, \phi). \] (B6)

The last line of the expansion is only valid for \( \eta_1 > \eta \). Thus we can derive the electrostatic potential of an elementary charge located at any point. From there we obtain the potential of a dipole located at the centre of the sphere \( \eta = \eta_0 \).

The potential for a dipole pointing in z-direction is obtained by taking the derivative of the Green’s function

\[ \psi_{\text{dip}}^+(\eta, \vartheta, \phi) = \frac{\partial G}{\partial z_1} = \frac{\cosh \eta_1 - \cos \vartheta_1}{a} \frac{\partial G}{\partial \eta} \]

\[ = \frac{\sqrt{\cosh \eta_1 - 1}}{a^2} \sum_{n=0}^{\infty} \sqrt{\frac{4\pi}{2n+1}} e^{-(n+1/2)\eta_1} \left[ \frac{\sinh \eta_1}{2} - (n + 1/2)(\cosh \eta_1 - 1) \right] \psi_{on}^+(\eta, \vartheta, \phi). \] (B7)
Similarly we find for a horizontal dipole in the $x$-direction

$$\psi_{\text{dip}}^\parallel (\eta, \vartheta, \phi) = \frac{\partial G}{\partial x_1} = \cosh \eta_1 - \cos \vartheta_1 \frac{\partial G}{\partial \vartheta}$$

$$= \frac{(\cosh \eta_1 - 1)^{3/2}}{a^2} \sum_{n=1}^{\infty} \frac{4\pi}{2n+1} e^{-(n+1/2)\eta} \sqrt{n(n+1)} [\psi_{1n}^+(\eta, \vartheta, \phi) - \psi_{-1n}^+(\eta, \vartheta, \phi)].$$

(B10)

From the generating function of the Legendre Polynomials we can find the expansion of the vertical external electric field with amplitude $E_{\text{ext}}$ valid in the region $\vartheta > 0$

$$\psi_{\text{ext}}^\perp (\eta, \vartheta, \phi) = -\sqrt{8\pi a E_{\text{ext}}^\perp} \sum_{n=0}^{\infty} \sqrt{2n+1} \psi_{0n}^- (\eta, \vartheta, \phi).$$

(B11)

For the horizontal external field in $x$-direction we obtain

$$\psi_{\text{ext}}^\parallel (\eta, \vartheta, \phi) = 2\sqrt{8\pi a E_{\text{ext}}^\parallel} \sum_{n=0}^{\infty} \sqrt{\frac{n(n+1)}{2n+1}} (\psi_{1n}^- - \psi_{-1n}^-).$$

(B12)

[1] L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936)
[2] J. Kirkwood, J. Chem. Phys 7, 911 (1939)
[3] For a review, see P. A. Madden and D. Kivelson, Adv. Chem. Phys. 56, 467 (1984)
[4] M. Neumann, Molec. Phys. 50, 415 (1983)
[5] See e.g. M. Schaefer, C. Bartels and M. Karplus, Theor. Chem. Acc. 101, 194 (1999)
[6] V. S. Krylov, Elektrokhimiya 15, 90 (1979)
[7] P. M. Morse, H. Feshbach Methods of Theoretical Physics, Part II, McGraw-Hill 1953, 1298
[8] C.G. Gray, K.E. Gubbins Theory of molecular fluids, Vol. 1, Clarendon Press, Oxford 1984
[9] J.-P. Hansen, I. R. McDonald Theory of simple Liquids, 2nd ed., Academic Press 1986, 463
[10] For a tensor permittivity $\epsilon_2$, the factor $\epsilon_2$ in this equation would be replaced by $\epsilon_2^\parallel$, and there would be an additional term $-\frac{\epsilon_2^\parallel - \epsilon_2}{a} \frac{1 - \cosh \eta \cos \vartheta}{\cosh \eta - \cos \vartheta} \left[ (1 - \cosh \eta \cos \vartheta) \frac{\partial \psi}{\partial \eta} + \sinh \eta \sin \vartheta \frac{\partial \psi}{\partial \vartheta} \right]$. 

20