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Generic density functional for electric double layers in a molecular solvent

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A simple, generic density functional for a statistical description of electric double layers in a molecular solvent is presented. The functional, which may be adapted to any geometry, is applied to the case of planar geometry, to pinpoint the limitations of the usual continuum description of the solvent.
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Electric double layers of microscopic co- and counterions, distributed around mesoscopic polyions, play a key role in determining the stability and structure of aqueous solutions or suspensions of macromolecules (polyelectrolytes), membranes and colloids. Since the pioneering work of Gouy [1] and Chapman [2], statistical theories of isolated or interacting double layers almost invariably neglect the molecular nature of the solvent, which is generally replaced by a continuum of dielectric constant ϵ. Such a ''primitive model'' may be a reasonable approximation on scales much larger than the diameter of the solvent molecules, but it is clearly inadequate on nanometric scales, where surface force measurements detect oscillatory solvation forces due to molecular layering [3]. Efforts to incorporate the molecular nature of the solvent are mostly restricted to double layers near infinite, uniformly charged planes. Excluded volume effects may be modeled via a lattice gas approach [4], which cannot reproduce layering. More realistically, the solvent may be modeled by bare [5–7] or dipolar [8,9] hard spheres. The former can only capture packing or layering effects, while the latter pose the notoriously difficult problem of an accurate statistical description of the dielectric properties. Qualitative results may be obtained from the mean-spherical approximation (MSA) [10,11,8], which is known to grossly underestimate the dielectric constant ϵ. More elaborate theories, based, e.g., on the hypernetted chain (HNC) closure [9], are technically very demanding.

In this Rapid Communication we present a simple, generic free energy functional suitable for the description of electric double layers in any geometry. The functional will be written down for a mixture of spheres with embedded point charges (for the electrolyte) or dipoles (for the solvent), but may easily be generalized to account for higher multipoles and other refinements. For comparative purposes, the functional is put to work to obtain density profiles and related properties in the much studied planar geometry.

Consider a three-component mixture of spheres of diameter σ_i carrying point charges Q_i or point dipoles $\mathbf{p}_i$ ($1 \leqslant i \leqslant 3$), and adopt the convention $Q_1 = Q_+$, $\mathbf{p}_1 = 0$: cations; $Q_2 = Q_-$, $\mathbf{p}_2 = 0$: anions; $Q_3 = 0$, $\mathbf{p}_3 = \mathbf{p}$: dipolar solvent. The electrostatic interaction between two spheres i and j is

$$V_{ij}(\underline{q}_i,\underline{q}_j') = \frac{Q_iQ_j}{r_{ij}} - (Q_i\mathbf{p}_j' - Q_j\mathbf{p}_i)\cdot\boldsymbol{\nabla}_{\mathbf{r}_i}\left(\frac{1}{r_{ij}}\right) - \mathbf{p}_i\cdot\boldsymbol{\nabla}_{\mathbf{r}_i}\boldsymbol{\nabla}_{\mathbf{r}_i}\left(\frac{1}{r_{ij}}\right)\cdot\mathbf{p}_j', \quad r_{ij}>\sigma_{ij}, \tag{1}$$

where $\underline{q}_i = (\mathbf{r}_i, \hat{\mathbf{p}}_i)$, $\mathbf{p}_i = p_i\hat{\mathbf{p}}_i$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j'|$ is the center-to-center distance between particles of species i (at $\mathbf{r}_i$) and j (at $\mathbf{r}_j'$) and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. The free energy of the inhomogeneous mixture is a functional of the three local densities $n_i(\mathbf{r},\hat{\mathbf{p}})$, which satisfy the normalization conditions,

$$\int n_i(\mathbf{r},\hat{\mathbf{p}})d\mathbf{r}\, d\hat{\mathbf{p}} = \int n_i(\mathbf{r})d\mathbf{r} = N_i, \tag{2}$$

where N_i is the total number of particles of species i and $n_i(\mathbf{r})$ is the spatial density profile of species i.

The intrinsic part of the free energy functional separates into ideal (noninteracting) and excess parts, and the latter in turn naturally splits into hard sphere (excluded volume) (HS) and Coulombic (C) parts,

$$F[\{n_k\}] = F^{\mathrm{id}}[\{n_k\}] + F^{\mathrm{ex}}_{\mathrm{HS}}[\{n_k\}] + F^{\mathrm{ex}}_{C}[\{n_k\}], \tag{3}$$

where F^{id} is of the usual form ($\beta = 1/k_BT$)

$$\beta F^{\mathrm{id}}[\{n_k\}] = \sum_{i=1}^{3}\int n_i(\mathbf{r},\hat{\mathbf{p}})\{\ln[\Lambda_i^3 n_i(\mathbf{r},\hat{\mathbf{p}})] - 1\}d\mathbf{r}\, d\hat{\mathbf{p}}. \tag{4}$$

For the HS part we adopt the best available non-local functional based on ''fundamental measure'' weight functions [12,13]. The remaining Coulombic part is expanded around a homogeneous charge-neutral reference system with bulk densities $\{n_i^o\}$, and all terms beyond second order are neglected [13],

$$\beta F^{\mathrm{ex}}_C[\{n_k\}] = \beta F^{\mathrm{ex}}_C(\{n_k^o\}) - \sum_i \int C_i^{(1)C}(\{n_k^o\},\underline{q})\Delta n_i(\underline{q})d\underline{q} - \frac{1}{2}\sum_{i<j}\int \Delta n_i(\underline{q})C_{ij}^{(2)C}(\{n_k^o\};\underline{q},\underline{q}')\times\Delta n_j(\underline{q}')d\underline{q}d\underline{q}', \tag{5}$$

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where $\Delta n_i(\underline{q})=n_i(\underline{q})-n_i^o/4\pi$. The one and two point direct correlation functions (DCF) appearing in Eq. (5) are (minus) the first and second functional derivatives of $\beta F_C^{\rm ex}[\{n_k\}]$, taken at the homogeneous densities n_i^o [15]. Note that these DCF's are not the actual, full DCF's of the homogeneous mixture, since the HS contribution already contained in $\beta F_{\rm HS}^{\rm ex}$ has been substracted.

The ions and dipoles are subjected to the external potentials $V_i^{\rm ext}(\underline{q})$ due to the polyions; this contributes a term

$$F^{\rm ext}=\sum_i \int V_i^{\rm ext}(\underline{q})n_i(\underline{q})d\underline{q} \tag{6}$$

to the total free energy. Minimization of the latter with respect to the $\{n_i(\underline{q})\}$, subject to the constraints (2), leads to the following generic expression for the local densities:

$$\begin{aligned} n_i(\underline{q})=n_i^o \exp\Bigg\{ & -\beta V_i^{\rm ext}(\underline{q})-\beta[\mu_i^{HS}[\{n_k(\underline{q})\}]-\mu_i^{HS}(\{n_k^o\})] \\ & +\sum_j \int C_{ij}^{(2)C}(\{n_k^o\};\underline{q},\underline{q}')\Delta n_j(\underline{q}')d\underline{q}'\Bigg\}, \end{aligned} \tag{7}$$

where the local hard sphere chemical potentials are defined by

$$\mu_i^{HS}[\{n_k(\underline{q})\}]=\frac{\delta F_{\rm HS}^{\rm ex}}{\delta n_i(\underline{q})} \tag{8}$$

In arriving at Eq. (7) the three components of the inhomogeneous mixture in the external field are assumed to be at the same chemical potential μ_i as the homogeneous reference system characterized by the bulk densities n_i^o. The $C_{ij}^{(2)C}$ have an asymptotic, long-range contribution equal to $-\beta V_{ij}$ and it is customary to introduce the short range parts defined by:

$$\overline{C}_{ij}(\underline{q},\underline{q}')=C_{ij}^{(2)C}(\underline{q},\underline{q}')+\beta V_{ij}(\underline{q},\underline{q}'). \tag{9}$$

Substitution of Eq. (9) into Eq. (7) leads to the following operational expression for the local densities:

$$\begin{aligned} n_i(\underline{q})=n_i^o \exp\Bigg\{ & -\beta V_i^{\rm ext}(\underline{q})-\beta[\mu_i^{HS}[\{n_k(\underline{q})\}]-\mu_i^{HS}(\{n_k^o\})] \\ & +\sum_j \int \overline{C}_{ij}(\underline{q},\underline{q}')\Delta n_j(\underline{q}')d\underline{q}'-\beta Q_i\psi(\mathbf{r}) \\ & -\beta\mathbf{p}_i\cdot\boldsymbol{\nabla}\psi(\mathbf{r})\Bigg\}, \end{aligned} \tag{10}$$

where $\psi(\mathbf{r})$ is the total electrostatic potential of the ion-dipole distribution which satisfies Poisson's equation,

$$\Delta\psi(\mathbf{r})=-4\pi\sum_i Q_i n_i(\mathbf{r})+4\pi\sum_i \int \mathbf{p}_i\cdot\boldsymbol{\nabla}n_i(\mathbf{r},\hat{\mathbf{p}}_i)d\hat{\mathbf{p}}_i. \tag{11}$$

The remaining unknowns are the $\overline{C}_{ij}$, for which we adopt the MSA, in the strong coupling limit, whereby $\overline{C}_{ij}=0$ if $r_{ij}>\sigma_{ij}$, while for $r_{ij}<\sigma_{ij}$, $\overline{C}_{ij}$ reduces to the interaction energy between the corresponding point charges or dipoles, minus the interaction energy between pairs of effective particles of diameters σ_i and σ_j carrying suitably smeared surface charge densities; the latter are the constant $q_i=Q_i/(\pi\sigma_i^2)$ for ions and $q_i(\mathbf{r})=\mathbf{p}\cdot\mathbf{r}/(\pi\sigma_i^3/6)$ for dipoles, where $\mathbf{r}$ is the position of a point on the surface of the sphere, relative to its center [13,14].

Together with the above prescriptions for $\mu_i^{\rm HS}$ and $\overline{C}_{ij}$, Eqs. (10) and (11) form a closed set, which has the structure of the usual mean-field Poisson-Boltzmann theory of electrolytes, except that short-range correlations due both to excluded volume (HS) and electrostatics are explicitly taken into account at all levels (ion-ion, ion-solvent, and solvent-solvent).

Before considering an application of the above formalism to a specific double-layer geometry, we specialize it to the case of the pure dipolar solvent polarized by a uniform applied field. The geometry is that of a condenser, i.e., the solvent is confined between two infinite parallel planes, carrying opposite surface charge densities $\pm\Sigma$, and is in equilibrium with a reservoir of unpolarized solvent of bulk density n^o, which fixes the chemical potential μ. The local density now depends only on z (the coordinate along the normal to the plates) and $\hat{p}_z$. Specializing the general expression (10) to the present situation leads to the following local density of the dipolar solvent:

$$\begin{aligned} n(z,\hat{p}_z)=n^o \exp\Bigg\{ & 4\pi\beta\Sigma p_z-\beta[\mu^{HS}[n(z)]-\mu^{HS}(n^o)] \\ & -\beta(2\pi)^2\int g\left(\frac{|z-z'|}{\sigma}\right)p_z p_z'[n(z',\hat{p}_z')-n^o] \\ & \times\frac{dz'}{\sigma}d\hat{p}_z'\Bigg\} \end{aligned} \tag{12}$$

where $g(\xi)=12(1/5-\xi^2+\xi^3-\frac{1}{5}\xi^5)\theta(1-\xi)$ (θ denoting the Heaviside step function). The resulting local polarization per unit volume is

$$\mathcal{P}(z)=p\int_{-1}^{+1}\hat{p}_z n(z,\hat{p}_z)d\hat{p}_z. \tag{13}$$

Far from the macroscopically distant condenser plates, $\mathcal{P}(z\to\infty)$ reduces to the macroscopic (bulk) polarization $\mathcal{P}$. For low plate charge Σ, a simple linear response calculation based on the $z\to\infty$ limit of the profile (12) leads to Debye's result for the dielectric constant, $\epsilon-1=4\pi\beta p^2 n^{o\prime}/3$, where $n^{o\prime}=n(z\to\infty)$ differs from the reservoir value n^o due to electrostriction. This seemingly disappointing result may be traced back to the asymptotic MSA form for $\overline{C}(\mathbf{r}-\mathbf{r}';\mathbf{p},\mathbf{p}')$, leading to a $g(\xi)$ function which integrates up to exactly 2. An alternative $g(\xi)$ function, like that resulting from the full solution of the MSA, integrating up to a value 2α, would yield the following expression for the bulk dielectric constant:

$$\epsilon=\frac{\epsilon_D+(\alpha-1)(\epsilon_D-1)}{1+(\alpha-1)(\epsilon_D-1)}, \tag{14}$$

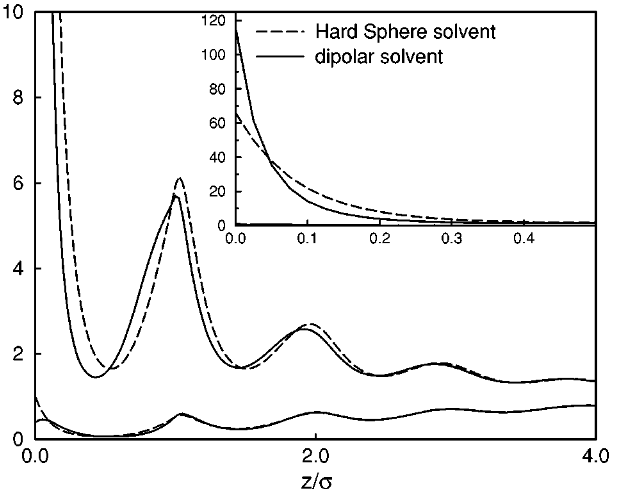

FIG. 1. Counterion (upper curves) and coion density profiles calculated from Eq. (10) for two solvent models: bare hard spheres, with a reduction of the Coulomb interactions by ϵ (dashed curves) and dipolar hard spheres (full curves). The inset shows the profiles near contact. Physical parameters: $\Sigma^* = \Sigma\sigma^2/e = 0.05$; monovalent electrolyte concentration: 0.1 M; solvent dipole: $p^{*2} = p^2/(\sigma^3 k_B T) = 2.5$; solvent density: $n_3^o = 0.8\sigma^{-3}$; $\sigma = 4$ Å; $T=298$ K; ϵ (pure solvent) $= 58.4$.

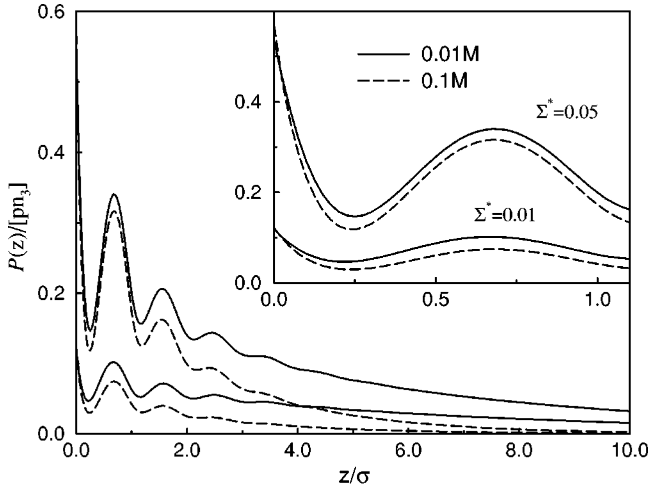

FIG. 2. Dimensionless polarization per dipole as a function of the distance z from the plate. Two electrolyte concentrations are considered: 0.01 M (full curves) and 0.1 M (dashed curves). For each value of the electrolyte concentration, the upper curve corresponds to a reduced surface density $\Sigma^* = 0.05$, and the lower curve to $\Sigma^* = 0.01$; all other physical parameters as in Fig. 1. The inset shows the polarization profiles near contact.

where $\epsilon_D = \epsilon(\alpha = 1)$ is the above quoted Debye value. We checked analytically the consistency of the MSA, whereby the value of ϵ predicted by Eq. (14) (obtained from the density profile near a charged wall) is identical to the standard expression for ϵ obtained from Wertheim's solution of the MSA for a bulk solvent of dipolar hard spheres. For physical parameters appropriate for water, $\epsilon_D \simeq 7.2$, the MSA yields $\alpha \simeq 0.87$ and $\epsilon \simeq 35$, while the experimental value $\epsilon \simeq 78$ corresponds to $\alpha \simeq 0.854$. This extreme sensitivity of ϵ to small variations of α, which contrasts with a lack of sensitivity of the density profiles (except in the asymptotic regime governed by the Debye screening length, and hence by ϵ), suggests a simple and very useful phenomenological approach. Multiplying the asymptotic MSA form of $\overline{C}$, and hence the value of g, by a constant factor α we recover Eq. (14). α is then chosen such as to make ϵ coincide with the best available estimate for the bulk dipolar HS model, based on QHNC theory [16]. The resulting α is found to be of the order of 0.8, and only slightly state dependent.

Having developed a satisfactory, semiphenomenological DFT of the pure solvent, we are now in a position to make realistic predictions for electric double layers near an infinite, uniformly charged plane. For the sake of simplicity, we consider a symmetric ion-dipole mixture with $\sigma_1 = \sigma_2 = \sigma_3 = \sigma$, and $Q_1 = -Q_2 = e$ (monovalent electrolyte), neglect image forces, and restrict dipoles to six discrete orientations (parallel or antiparallel to each of the three coordinate axes). The latter assumption greatly simplifies the iterative solution of the set of Eqs. (10) and (11). Some representative results are shown in Figs. 1 to 3 under physical conditions roughly appropriate for aqueous solutions. In Fig. 1 the co- and counterion density profiles $n_1(z)$ and $n_2(z)$, obtained for a bare HS ($p=0$) and a dipolar HS ($p \neq 0$) solvent are compared. In the case of a bare HS solvent, the Coulomb interaction between ions is reduced by a dielectric constant ϵ taken equal to that derived for the pure dipolar solvent. A clear phase difference in the layering is observed, particularly in the marked oscillations of the counterion profile, which are significantly shifted towards the plate in the dipolar case, and pile up to a contact value higher by nearly a factor of 2 compared to the bare HS solvent; this in turn means a stronger depletion of the solvent. The marked discrepancies between the two models point to a strong interference between packing and electrostatic effects which are not simply superposable (a similar conclusion was reached in Ref. [7] in the case of surface forces between highly charged plates). Figure 2 shows the polarization profiles per particle, $\mathcal{P}(z)/[pn_3(z)]$ for two surface charge densities, and two electrolyte concentrations. While the profiles hardly change close to the plate, the decay of the polarization is much faster beyond a few molecular diameters in the more concentrated solution, due to the reduction of the screening length; in the latter case the local polarization vanishes beyond $z \simeq 10\sigma$.

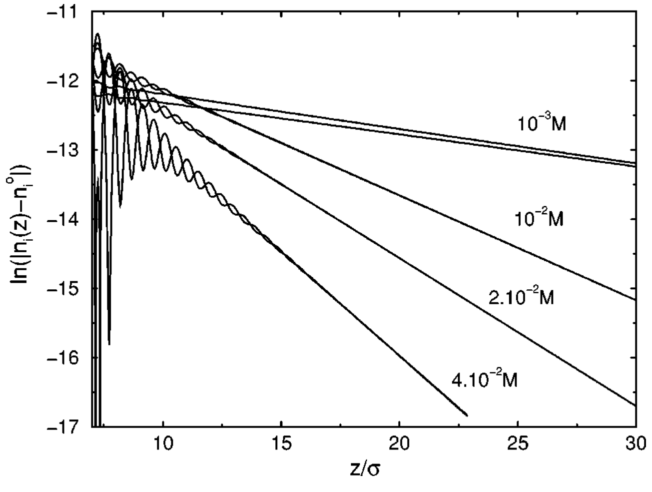

FIG. 3. Co- and counterion density profiles versus distance from plate; the curves show $\ln|n_i(z) - n_i^o|$ ($i=1,2$). $\Sigma^* = 3.2\times10^{-4}$. Electrolyte concentrations: 10^{-3}, 10^{-2}, 2×10^{-2}, and 4×10^{-2} M.

The asymptotic decay of the ionic density profiles is examined in Fig. 3, where $\ln(|n_i(z)-n_i^o|)$ is plotted versus z/σ for co- and counterions $(i=1,2)$, for several electrolyte concentrations. At the lower concentrations, the plots are straight lines beyond $z/\sigma \simeq 10$, signaling a monotonic exponential decay, as would be predicted by the ''primitive'' model. The slopes yield a Debye screening length, $\lambda_D = (8\pi n^o e^2/\epsilon k_B T)^{-1/2}$, where $n^o = n_1^o = n_2^o$, from which an effective dielectric constant ϵ can be extracted; the latter agrees very well with the bulk dielectric constant of the pure dipolar sphere solvent. We conclude that the ionic density profiles in a molecular solvent are well reproduced by the ''primitive'' model, beyond a few molecular diameters, in the low concentration (weak screening) regime. At higher concentrations, such that the Debye screening length is of the order of 15σ or less, the rapidly decaying profiles exhibit increasingly pronounced oscillations, induced by the molecular nature of the solvent; under these conditions a ''primitive'' model description of the electric double layer is found to be totally inadequate. This observation should have far-reaching consequences on the derivation of effective interactions between charge-stabilized colloids in the presence of high concentration of added salt.

The results presented in this Rapid Communication provide an illustration of the suitability of the proposed functional to cope with the molecular nature of the solvent. The flexibility of the functional will be put to use in a systematic investigation of more complex geometries, including finite membranes and platelets [17], charged rods, and curved interfaces.

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