Simple field theoretical approach of Coulomb systems. Entropic effects

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Abstract
We discuss a new simple field theory approach of Coulomb systems. Using a description in terms of fields, we introduce in a new way the statistical degrees of freedom in relation to the quantum mechanics. We show by a series of examples that these fundamental entropic effects can help account for physical phenomena in relation to Coulomb systems whether symmetric or asymmetric in valence. Overall, this gives a new understanding of these systems.

PACS numbers: 05.20.–y, 65.40.Gr, 03.50.Kk, 61.20.Qg

1. Introduction

Recently, we have developed a simple field theory (FT) approach to describe liquids [1] and more specifically electrolytes at interfaces. Adopting density fields as basic elements for the description rather than particle density distributions comes in parallel with a radically different way of accounting for the statistical degrees of freedom of the system. It is the quantum mechanics which sets the correct combinatory of the states by telling us which two states can be distinguished in the phase space. In this paper, on a series of examples related to Coulomb systems, we illustrate how within our approach the enumeration of the states can help us interpret and give an original insight into a series of phenomena related to Coulomb systems. In the first part of the paper, we discuss general aspects and consequences of the formalism. In the second part, we illustrate the entropic role of the quantum mechanics in Coulomb systems.

2. A new and simple field theory to describe liquids, exact results

The fundamental choice of our FT is to take directly the density of matter $\rho(\mathbf{r})$ as the basic real-valued field variable. As the densities fluctuate, we then fix the chemical potential

μ and set the partition function to be the grand potential. It is then a functional integral according to $-\beta P V = \ln \Xi = \ln \left[\int \mathcal{D}\rho \, e^{-\beta H[\rho]} \right]$, where β is the inverse temperature. The Hamiltonian functional H is given by a simple meaningful mean field approximation for the chemical potential $\beta\mu = \ln(\rho(\mathbf{r})\Lambda^3) + \int \rho(\mathbf{r}')v(|\mathbf{r} - \mathbf{r}'|)\,d\mathbf{r}'$ which leads to $\beta H[\rho] = \int \rho(\mathbf{r})[\ln(\rho(\mathbf{r})/\bar{\rho}_z) - 1]\,d\mathbf{r} + \int \rho(\mathbf{r})\rho(\mathbf{r}')v(|\mathbf{r} - \mathbf{r}'|)\,d\mathbf{r}\,d\mathbf{r}'$, where $\bar{\rho}_z = e^{\beta\mu}/\Lambda^3$ is the activity. In [1], we have shown through a renormalization that this theory reproduces exactly the standard statistical mechanics. The peculiarity of the approach lies in the first term which is entropic and represents the quantum mechanics enumeration of states which takes into account (i) the elementary volume in the phase space Λ^3 and (ii) the principle of indiscernibility for particles, both properties which are, for N particles, traditionally given by the $\prod_1^N d\mathbf{r}_i/(N!\Lambda^{3N})$ measure.

Dyson-like relations or equations of movement. A direct consequence of the integral functional formalism can be seen in the invariance of the functional integral with respect to a change of the dummy field variable. For any functional $A[\rho]$ we obtain for the averages $\langle \delta A[\rho]/\delta\rho \rangle = \langle A[\rho](\delta\beta H[\rho]/\delta\rho) \rangle$. Applying this relation to the partition function gives a new expression of the chemical potential: $\beta\mu = \langle \ln[\rho(\mathbf{r})\Lambda^3] \rangle + \beta \int v(|\mathbf{r} - \mathbf{r}'|)\langle \rho(\mathbf{r}') \rangle\,d\mathbf{r}'$. This relation has been discussed in view of more standard expressions [2]. These expressions generally emphasize the interaction potential, the logarithmic term being the trivial ideal system. In contrast, FT gives a simple mean interaction potential term, and the average of the entropic logarithmic term includes more intricate correlations. This displacement in the way correlations are treated naturally suggests new approximations.

New perspectives on old exact relations. We have rederived the exact Virial theorem [3] and the density contact theorem [2]. We have pointed out that our approach provides yet another point of view on this relation emphasizing the role of the logarithmic functional in the demonstration.

3. Entropic effects in Coulomb systems

Coulomb systems are peculiar mixtures: by this we mean that we have two species bound by the condition of electroneutrality. We can then consider the system in two different ways. On the one hand, we have entropic properties related to the number of each of the two indistinguishable species, the densities. On the other hand, in Coulomb systems we like to focus on the difference of the densities, the charge. Our point is to treat on the same footing the purely entropic properties and those related to the potential as they appear at the same level in our Hamiltonian. We show that this will lead to strong correlations between the different properties. Intuitively, when we change the charge, we also modify the relative number of the species, and therefore their purely entropic combinatorics contribution. We hereafter discuss simple *point ions* to focus on these entropic terms.

At a charged interface the mean field approximation gives the Gouy–Chapman theory. Discussing fluctuations beyond the mean field theory corresponds to an expansion of the entropic part of the Hamiltonian which for Coulomb systems is $H^{\text{ent}} = \int d\mathbf{r}\{\rho_+(\mathbf{r})[\ln(\rho_+(\mathbf{r})/\bar{\rho}_+) - 1] + \rho_-(\mathbf{r})[\ln(\rho_-(\mathbf{r})/\bar{\rho}_-) - 1]\}$ with separate terms corresponding to each ion. But the more natural variables for Coulombic systems are the charge $q = \rho_+ - \rho_-$ and the total density $s = \rho_+ + \rho_-$. Then the entropic Hamiltonian functional mixes these fields as we have $\rho_\pm = (s \pm q)/2$. Note, a peculiarity in FT is that linear combinations of the fluctuating fields q and s are natural and not simply combinations for the average quantities. In the expansion, the quadratic part of the Hamiltonian includes the Coulomb potential interaction. With this quadratic term, we obtain the Debye limiting law in the bulk.

The specificity of the FT lies in the higher order terms which include products of q and s fields, $\delta H^{\text{ent}} = -1/(2\bar{\rho}) \int q^2(\mathbf{r})s(\mathbf{r})\,\mathrm{d}\mathbf{r} + \cdots$, in local coupling terms.

3.1. Application to inhomogeneous systems

Ionic depletion at a neutral interface [4]. For a neutral interface and a symmetric electrolyte, there is intuitively no profile for the charge at a neutral interface. However, the loop expansion predicts a profile of the quadratic fluctuations of the charge with a simple expression in terms of the distance to the wall and of the parameter $\eta = K_D^3 / (8\pi\rho)$ which characterizes the Coulomb interaction strength, where K_D is the inverse Debye length. Physically, some fluctuations are frustrated in the vicinity of the interface due to the absence of ions in the other half space. The role of the entropic term is to imply that this Coulombic effect is coupled to the total density field, although this quantity is not directly related to the Coulomb interaction. This profile is further justified as it verifies the contact theorem which is not the case of the intuitive Gouy–Chapman or the popular analytic mean spherical approximation (MSA) approaches.

The anomalous capacitance behaviour. Experimentally and in numerical simulations [5], we find systems where the electric capacitance decreases at low reduced temperature. This effect is non-intuitive as one can expect the electric response of the system to decrease with increasing thermal agitation which is what the Gouy–Chapman and MSA theories predict. This phenomenon appears at low reduced temperature when relatively the Coulomb interaction is stronger. Within the FT, the phenomenon can easily be understood from the previously described depletion in the density profiles which naturally accounts for the decrease in the electric capacitance. For point ions [6], we have obtained a simple analytic expression of the capacitance. This has been corrected to account for the size of the ions [7]. The comparison with the numerical simulations is rather good, and the simplicity of the expressions and of the corrections indicate that we capture the significant physical effect.

3.2. More entropic effects for multivalency

Entropic effects are also important for valence asymmetric systems: $z_+ : z_-$ electrolytes where the electroneutrality condition has now modified the number balance of the ions.

Anomalous capacitance for valence asymmetry. In [8], we have considered capacitance curves for different valencies, the curves are rather scattered but one finds that one should first redefine the temperature $T^* \to T_s^* = T^*/(z_+ z_-)$ which is also a scaling with the ionic strength. However, the ionic strength $z_+ z_-$ scaling does not discriminate between a 2:2 and a 4:1 electrolyte. The FT introduces a distinct parameter $z_{as} = (z_+ - z_-)/\sqrt{z_+ z_-}$ which is really characteristic of the valence asymmetry. In agreement with simulation results, FT is, to our knowledge, the only approach capable of predicting an increase of the differential capacitance peak with z_{as}. This parameter comes out naturally in FT as we can perform simple operations on the fluctuating fields and again it is related to the entropic Hamiltonian functional.

Potential of zero charge (PZC) for size and valence asymmetric systems. For the neutral interface, numerical simulation results show the existence of a spontaneous polarization due to the asymmetry in size and/or in valence [9]. The consequences of size asymmetry are rather intuitive as the smaller ions by reaching nearer the interface induce a polarization. Less intuitive is the polarization due to valence asymmetry. Indeed, in figure 1, standard approaches in liquid state physics [9] do not account for such effect. In contrast, FT predicts the polarization due to multivalency, and we show results obtained by adding the MSA theory for size asymmetry to the FT result for point ions (size asymmetry being immaterial for point
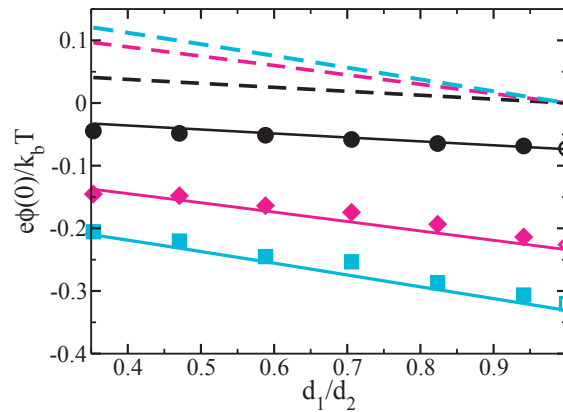
Figure 1. PZC for 3:1 electrolytes as a function of the d_1/d_2 ionic diameters ratio. The symbols are for the numerical simulation with the corresponding FT plus MSA predictions (see the text); concentrations are 0.033, 0.333, 0.666 mol l^{-1} from top down. The dashed lines are for the MSA in the reverse order for the concentrations.

(This figure is in colour only in the electronic version)

ions) [10]. The sign of the PZC is in agreement with the charge contact theorem [11] and with the simulation results. The simplicity of the correction suggests again that we focus on the adequate physical effect.

Ionic criticality and valence asymmetry. We have derived in the FT an equation of state for ionic systems. In the loop expansion, the pressure is a series in terms of η: $\beta P = \rho \left(1 - \frac{1}{3}\eta - \alpha_0 z_{as}^2 \eta^2 + \cdots\right)$. The linear term $-\eta/3$ is the standard Debye term; further we have a simple dependence with the z_{as} parameter. We have generalized this expression to account for hard sphere effects by using the MSA pressure[3] and calculated the asymmetry contribution α_0 using the MSA correlation function. The term in the pressure associated with valence asymmetric systems gives a simple description of the decreasing critical temperature and increasing critical density in agreement with Monte Carlo (MC) results [12]. Respectively for the 1:1, 2:1 and 3:1 electrolytes the critical temperatures and densities are $T^* = 0.079, 0.060, 0.038$ and $\rho^* = 0.0145, 0.021, 0.034$. This seems to indicate that this physical trend is likely to be associated with the simple number balance effect found in multivalent systems.

4. Conclusion

Within a FT framework, we have shown how the formalism can introduce a new point of view on Coulomb systems. The basic and fundamental quantum-mechanical counting of states can lead to important consequences in Coulomb systems which have at least two indistinguishable species. These entropic effects lead to an unavoidable correlation between charge and density fluctuations. This simple statement is sufficient to give meaningful interpretations; we believe that this is useful to complete the standard liquid state approaches generally focused on excluded volume effects.

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[3] Corresponds to replacing $K_D \to 2\Gamma$ the MSA screening distance parameter, $2\Gamma d = \sqrt{1 + 2K_D d} - 1$ where d is the ionic diameter.

References

[1] Di Caprio D and Badiali J P 2008 *J. Phys. A: Math. Theor.* **41** 125401
[2] Di Caprio D, Badiali J P and Stafiej J 2006 *Mol. Phys.* **104** 3443
[3] Di Caprio D, Stafiej J and Badiali J P 2005 Ionic soft matter: modern trends in theory and applications *Proc. NATO Advanced Res. Workshop* vol 206 (Dordrecht: Kluwer) p 1
[4] Di Caprio D, Stafiej J and Badiali J P 2003 *Mol. Phys.* **101** 2545
[5] Boda D, Henderson D and Chan K Y 1999 *J. Chem. Phys.* **110** 5346
      Boda D, Henderson D, Chan K Y and Wasan D T 1999 *Chem. Phys. Lett.* **308** 473
[6] Di Caprio D, Stafiej J and Borkowska Z 2005 *J. Electroanal. Chem.* **582** 41
[7] Di Caprio D, Valiskò M, Holovko M and Boda D 2007 *J. Phys. Chem.* C **111** 15700
[8] Di Caprio D, Valiskò M, Holovko M and Boda D 2007 *Mol. Phys.* **104** 3777
[9] Valiskó M, Henderson D and Boda D 2004 *J. Phys. Chem.* B **108** 16548
[10] Di Caprio D and Holovko M 2009 *J. Phys. Chem.* at press
[11] Holovko M and Di Caprio D 2008 *J. Chem. Phys.* **128** 174702
[12] Fisher M E, Aqua J N and Banerjee S 2005 *Phys. Rev. Lett.* **95** 135701