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Particle Indistinguishability Symmetry within a Field Theory. Entropic Effects

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Abstract: In this paper, we briefly discuss a field theory approach of classical statistical mechanics. We show how an essentially entropic functional accounts for fundamental symmetries related to quantum mechanical properties which hold out in the classical limit of the quantum description. Within this framework, energetic and entropic properties are treated at equal level. Based on a series of examples on electrolytes, we illustrate how this framework gives simple interpretations where entropic fluctuations of anions and cations compete with the energetic properties related to the interaction potential.

Keywords: Classical statistical mechanics; Entropy; Indistinguishability; Field theory; Electrolytes.

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1. Introduction

Ever since the work of Gibbs, well before quantum mechanics, one knows that it is impossible to define a purely classical statistical mechanics. More precisely, we now find that even in the classical limit, we cannot ignore those elements which escape this description. For instance, at equilibrium, there exists a minimum length to differentiate and therefore count different states in the phase space. This is the role of the de Broglie length and, more generally, we find quantities involving the Planck constant. Moreover, in classical statistical mechanics, we have to account for a symmetry related to the principle of indistinguishability as applied to identical particles which again finds its origin in quantum mechanics. For a discussion on the classical limit see Hill [1].

Adding elements of physics, inherent to the *quantum world*, to the classical description is a commonly accepted process. From our view point, this process is far from being an intuitive approach. Let us clarify. The deep-rooted classical description refers to entities which can be enumerated and localised as precisely as needed. This is in contrast to what occurs in the quantum world.

Similarly, in the quantum world, refering to objects such as particles is not the only way to describe the reality, and fields are frequently used for a more fundamental description. For a possibly unified framework, it is of interest to derive a field theory (FT) approach to classical statistical mechanics. Number of authors have elaborated a FT from the Gibbs partition function. Based on exact mathematical transforms of the partition function, their approach leads, we think, to formalisms which are difficult to apply and not specifically intuitive [2–26].

In a series of papers [27–32], we use an intuitive field theory approach in order to describe electrolytes at interfaces. The peculiarity of this approach is the use of a field which has a straightforward physical meaning. It represents the density of matter. This leads to a representation, in terms of fields, that is quite different from the particle description. In this paper, we present a brief exposé on how the quantum physical ingredients acquire a different semantic representation and treatment when considered from the angle of fields. We shall discuss what becomes of the indistinguishability symmetry (IS) of particles by describing this property in the context of various systems, such as electrolytes at interfaces. Studying these charged systems, our purpose is to illustrate, how this basic and fundamental physical property can, within a new specific framework, provide original insight and interpretations.

2. *Classical* statistical mechanics.

2.1. *Standard statistical mechanics.*

As noticed intuitively by Gibbs even the simple ideal gas is not trivial. For an ideal gas of N particles at equilibrium, in a volume V, at temperature T, the canonical partition function is written

$$Q(N,V,T) = \frac{V^N}{N!\Lambda^{3N}}, \tag{1}$$

where the enumeration of states requires an elementary volume in the phase space related to Λ, the de Broglie length. In this quantity we have the Planck constant characteristic of quantum effects. The other ingredient, deriving from the quantum world, which appears in this classical description, is according to the principle of indistinguishability, the factorial N term associated with indistinguishable particles. We also show the grand canonical ensemble description, which we shall be needing further in the paper. The grand partition function is

$$\Xi(V,\mu,T) = \sum_{N=0}^{\infty} e^{\beta\mu N} Q(N,V,T) \tag{2}$$

where β is the inverse temperature. The thermodynamic potential associated is the grand potential

$$-PV = -k_B T \hat{\rho} V \tag{3}$$

where $\hat{\rho} = \hat{N}/V$ is the average density. Hereafter hatted quantities represent averages. The grand potential can also be written in terms of other thermodynamic quantities

$$-PV = U - TS - \mu\hat{N} \tag{4}$$

$$= \frac{3}{2}k_BT\hat{N} + k_BT\hat{N}\left(-\frac{5}{2} + \ln\hat{\rho}\Lambda^3\right) - \mu\hat{N} \tag{5}$$

$$= k_BTV\hat{\rho}\left(\ln\frac{\hat{\rho}}{\bar{\rho}} - 1\right) \tag{6}$$

where $\bar{\rho} = e^{\beta\mu}/\Lambda^3$ is the activity.

Introduced in the context of the ideal gas, these basic quantum mechanical ingredients also apply to the interacting systems. The partition function will then include the factorial term for indistinguishability and the de Broglie length for systems at equilibrium. It is the physical content of these properties and in particular the symmetry related to indistinguishability that we shall debate in the framework of a FT. Indistinguishability is one possible origin of entropy: by permutation, many states correspond to identical values of the system's energy.

2.2. Field theory approach.

The approach we use is based directly on a FT type assumption and not on an elaboration of the Gibbs partition function. As traditional in FT, we assume there is an intuitive construction of the Hamiltonian functional from a physically relevant mean field equation. To find this equation, we can use the following line. The fundamental choice of our FT is to take directly the density of matter $\rho(\mathbf{r})$ as the elementary real valued field variable. As the densities fluctuate, it is tempting to fix the chemical potential μ and study the grand potential. We then have a functional integral according to

$$-\beta PV = \ln\Xi = \ln\left[\int \mathcal{D}\rho \, e^{-\beta H[\rho]}\right]. \tag{7}$$

To find the Hamiltonian functional H we start from a relevant mean field approximation for the chemical potential

$$\ln(\rho(\mathbf{r})\Lambda^3) + \int \rho(\mathbf{r}')v(|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}' - \beta\mu = 0. \tag{8}$$

After integration of the mean field equation $\delta H/\delta\rho = 0$, in terms of the field, we obtain

$$\beta H[\rho] = \int \rho(\mathbf{r})\left[\ln(\rho(\mathbf{r})/\bar{\rho}) - 1\right]d\mathbf{r} + \int \rho(\mathbf{r})\rho(\mathbf{r}')v(|\mathbf{r} - \mathbf{r}'|)\,d\mathbf{r}d\mathbf{r}'. \tag{9}$$

This Hamiltonian functional is extremely simple. The first term is an integral representation of the grand potential for the ideal gas eq. (6). We shall refer to this term as the entropic functional, although strictly speaking there is more than the entropy, for instance the kinetic energy. The second term is a mean field approximation of the potential energy. What is seemingly a simple analysis is misleading. As stressed by Evans in [33], when comparing DFT and field theory approaches, the Hamiltonian is just an element of the functional integral eq. (7) which at the end gives the partition function. Therefore, this functional cannot be assimilated to the thermodynamic potential, as it is the case in a DFT approach.

Consequently, it is wrong to associate the ideal gas with the first term of the Hamiltonian, in the same way we would not attribute the factorial of the number of particles to the sole ideal gas. The problem stems from the fact that for an ideal gas, in the absence of interactions, we are left to focus on the property of indistinguishability and the different notions overlap. Truly, the role of the first term in the Hamiltonian is to provide quantum mechanical properties for interacting systems just as well as for ideal systems. In contrast to the arguments shown in [33], based on a phenomenological Hamiltonian, the specificity of this FT is that we can demonstrate that the Hamiltonian is exact [27]. Though fields have a number of degrees of freedom distinct from that of particles, our functional is constructed in order to give the correct enumeration of states. In our functional, we have the elementary volume in the phase space Λ^3 and a functional, depending on the density field, which substitutes the property of indistinguishability for particles. Significantly, in expansions, we observe that whenever there are n iterations of the field at a given point, these fields are associated precisely with the corresponding $1/n!$ coefficient, as a consequence of the entropic functional. This property corresponds to the particle indistinguishability in terms of fields [27]. In this paper, we do not want to enter in mathematical aspects developped in [27]. However, it must be remarked that the existence of a renormalisation indicates that the formalism used is more sophisticated than just the introduction of a logarithmic functional in the Hamiltonian.

2.3. Breaking the Indistinguishability Symmetry.

Following Lin's assertion that "Symmetries are in principle ugly" [34], the interest of analysing a system in terms of its symmetries, lies precisely in the description of systems where these symmetries are broken. The most obvious way to break the IS of particles is clearly to consider distinguishible species, such as mixtures. To illustrate our point, we take a peculiar mixture, i.e. electrolytes. Electrolytes have at least two species, cations and anions, but their densities are not entirely free. We generally have the overall electroneutrality condition as a consequence of the long range Coulomb potential although locally the densities are free to fluctuate [35]. In this context, we can anticipate the following argument. From the point of view of mixtures, we shall focus on the density fluctuations of each species $\rho_\pm(\mathbf{r})$, cations and anions which have a bearing on combinatorics entropy. From the angle of Coulomb systems, we analyse properties related to the charge density $q(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$, which is a linear combination of the specie's density fields. The charge field is directly related with the energy.

A particular feature of our FT formulation is that the entropic contribution (i.e. enumeration of states) and the interaction potential are both treated as functionals of the density fields. Consequently, an interesting feature of our FT formulation is that the entropic contribution due to the enumeration of states, in relation to indistinguishability, and the contribution related to the interaction potential appear at the same level in the Hamiltonian. Thus the fluctuations of entropy and fluctuations related to the interaction have to be combined. We reckon that in the FT framework the calculation of the functional integral will evidence strong correlations between these different properties thereby allowing original interpretations. In the case of electrolytes, intuitively, when we alter the charge distribution, i.e. the Coulomb energy, we also modify the relative number of the species i.e. their purely entropic combinatorics contribution.

We examin hereafter simple point ions focusing on the competition between combinatorics entropy and Coulomb energetic effects and we bypass excluded volume effects. We also start from the more simple symmetric 1:1 electrolyte and generalise to the case of asymmetric in valence systems.

3. Entropic effects in electrolytes.

3.1. Role of the entropic functional in perturbation theory.

In the mean field approximation, using the full entropic functional, the response to a charged interface corresponds to the non linear Gouy-Chapman theory [36]. Beyond mean field approximation, it is interesting to analyse the role of the entropic functional when discussing fluctuations. We will need to expand the entropic part of the Hamiltonian which for 1:1 Coulomb systems is

$$H^{ent} = \int d\mathbf{r} \left\{ \rho_+(\mathbf{r}) \left[\ln(\rho_+(\mathbf{r})/\bar{\rho}_+) - 1 \right] + \rho_-(\mathbf{r}) \left[\ln(\rho_-(\mathbf{r})/\bar{\rho}_-) - 1 \right] \right\}, \tag{10}$$

where $\bar{\rho}_\pm = e^{\beta\mu_\pm}/\Lambda_\pm^3$ and in this context $\bar{\rho} = \bar{\rho}_+ + \bar{\rho}_-$. As above mentioned, there are separate terms corresponding to each ion. However, for the study of Coulomb systems, the more natural variables are the charge density $q(\mathbf{r})$ and the total density $s(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})$. Each of the two terms, originally independent with respect to each ion, in the entropic functional, will mix the two ionic fields, as $\rho_\pm(\mathbf{r}) = (s(\mathbf{r}) \pm q(\mathbf{r}))/2$. As a consequence, the higher than quadratic terms, in the expansions, will include products of δq and δs, the dimensionless excess fields. The expansion is a sum of local coupling terms. The first terms are shown as follows

$$\delta H^{ent} = -\frac{\bar{\rho}}{2} \int \delta q^2(\mathbf{r})\delta s(\mathbf{r}) \, d\mathbf{r} + \frac{\bar{\rho}}{12} \int \delta q^4(\mathbf{r}) \, d\mathbf{r} \, ... \, . \tag{11}$$

We treat the quadratic terms separately because they include the interaction potential and they are diagonal in the q and s fields. For point ions, quadratic terms result in the well known Debye limiting law in the bulk [37].

In the following, we examine hard planar neutral interfaces, i.e. an electrolyte confined to half space and a uniform dielectric constant. We shall evidence that these a priori simple systems exhibit non trivial electrostatic phenomena.

3.2. Entropic effects for inhomogeneous electrolytes.

Ionic depletion at a neutral interface

In [28], we have shown the existence of an ionic depletion profile of the total density s, at neutral interface, although there is, logically, no profile for the charge density q at neutral interface. From a standard perspective, this phenomenon can be rationalised as the cost of rupturing the ionic atmosphere near the surface, leading to a depletion of both the ionic profiles. From the FT approach, we observe that the theory predicts a profile of the quadratic fluctuations of the charge. Physically, some fluctuations are frustrated at the vicinity of the interface due to the absence of ions in the other half space. The role of the entropic functional is to imply that this coulombic effect on the charge fluctuations be coupled to the total density field although the quantity is not directly related to the Coulomb interaction. We would like to emphasise that the outcome is a consequence of the first term of eq. (11), which combines both the

square of the charge density and the total density. The result obtained, at the first level in loop expansion of the FT, is consistent with the pressure calculated at the same level of approximation. Hence, the theory verifies the exact condition given by the contact theorem. We underline that this equation relates the bulk pressure to the contact value of the density at the interface, and corresponds to the mechanical equilibrium condition of the system. Although intuitively obvious, this equilibrium is not implied in "popular" approaches like the Gouy-Chapman or the MSA (Mean Spherical Approximation) [38] theories. The two different interpretations i.e. the one concerning the ionic cloud which refers to an energetic balance and the FT involving the entropy are not in contradiction. In both cases, the temperature plays a central role. In the first case, we emphasise the thermal agitation controlling the extension of the ionic atmosphere. In the FT, the temperature sets the scale for the entropic effects – the energetic effects being present in the quadratic charge fluctuations.

The anomalous capacitance behaviour.

Another phenomenon which has been lately examined in detail, is the anomalous capacitance behaviour. Experimentally and in numerical simulations, scientists have shown systems where the electric capacitance decreases at low reduced temperature [39–49]. This phenomenon is non intuitive as one expects the electric response of the system to decrease with increasing thermal agitation as in Gouy-Chapman and MSA theories. The phenomenon appears at low reduced temperature when the Coulomb interaction becomes stronger. Within the FT, this behaviour can be comprehended when seen in terms of the ionic depletion effect. The decrease in the density profiles naturally leads to a decrease in the electric response, i.e. the electric capacitance. Note that in this case, the calculation of the capacitance involves both terms in eq. (11). For point ions [29], we have a simple analytic expression of the capacitance. This expression has been modified to account for the size of the ions [31]. The comparison with the numerical simulations is positive and the simplicity of the expressions and of the relevant corrections indicate that "we capture the significant physical effect".

3.3. *Entropic effects for multivalent electrolytes*

Entropic effects are bound to play an important role in valence asymmetric systems, $z_+ : z_-$ electrolytes. The electroneutrality condition has modified the number balance of the ions and therefore the combinatoric entropic balance between the species.

Anomalous capacitance for multivalent electrolytes.

In [32], we have considered capacitance curves for different valencies. The curves are scattered but we come to the conclusion that one should first redefine the temperature $T^* \rightarrow T_s^* = T^*/(z_+ z_-)$, a scaling with the ionic strength. This transformation is evident in FT and can be associated with a scaling of the charge density field $Q = q/(z_+ z_-)$. In so doing, 1:1 electrolyte quadratic terms in the Hamiltonian are restored, and are the basis for our calculation. 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 truly characteristic of the valence asymmetry [30, 32]. The Hamiltonian is then

$$\beta \delta H = -\frac{\bar{\rho}}{2} \int \delta s(\mathbf{r}) \delta Q^2(\mathbf{r}) d\mathbf{r} + \frac{\bar{\rho}}{12} \int \delta Q^4(\mathbf{r}) d\mathbf{r} - \frac{\bar{\rho} z_{as}}{6} \int \delta Q^3(\mathbf{r}) d\mathbf{r} + \frac{\bar{\rho} z_{as}^2}{12} \int \delta Q^4(\mathbf{r}) d\mathbf{r} + . \quad (12)$$

where, in comparison to eq. (11), we have extra terms depending on z_{as}. The FT predictions, in relation to this parameter, indicate an increase of the differential capacitance peak, clearly shown in numerical simulations. To our knowledge, this behaviour has not been evidenced by any other theory. In the case of multivalent ions, it is the last term of the entropic functional eq. (12) which plays a central role.

Potential of zero charge (PZC) for size and valence asymmetric systems.

In [50], Torrie et al. have shown the existence of a spontaneous polarisation of the neutral interface due to the asymmetry in valence. Twenty years later, Henderson et al. [51] have generalised the study by considering both asymmetry in size and/or in valence. The asymmetry in size is evident – smaller ions, by reaching nearer the interface, induce a polarisation. Less evident is the polarisation due to valence asymmetry. From a superficial analysis, we come to the conclusion that the charge profile is constant and vanishing all the way accross the interface in the absence of charge at the interface. In contrast, numerical simulations show that there is indeed a charge profile. In [51], the authors, searching for simple analytic approaches, were able to demonstrate the size effect. However, none of the standard liquid state theories account for the valence effect [51, 52] except for the MPB approach used in [50] and more recently in a version of the DFT [53]. These approaches are mathematically demanding. Conversely, we find that FT predicts the polarisation due to multivalency with simple analytic expressions. Explicit dependence on the z_{as} asymmetry parameter allows generalisation for any valences. The charge profile thus calculated is consistent with the exact condition given by the charge contact theorem [54]. Given the crude point ion model, comparison with the numerical simulation results [30] shows an unexpected convergence. Note that in the calculation of the PZC, it is the third term in the expansion of the entropic functional eq. (12) which has been used.

In all the examples considered, we find simple analytic expressions which explain the physical behaviour as a function of few physical parameters. Using FT, the specific emphasis on the entropic functional leads to a new understanding of the phenomena and our results indicate that we incorporate the relevant physics. We should also point out that in the previous examples, different terms in the expansion eq. (11) and (12) are used in the calculation. From the use of different terms, we come to the conclusion that we require specifically the entropic functional given in our Hamiltonian. This functional also tells us that there is an unavoidable coupling between the charge and the total density field. For multivalent systems, we point out that there are few theoretical results. In FT, we have a systematic parametrisation of these systems in terms of the z_{as} asymmetry parameter. Finally, we also specify that the use of a point ion model indicates that excluded volume effects are not relevant to the different problems considered.

4. Conclusion.

In this paper, we have given examples concerning electrolytes stressing the particular role of the entropic functional in our FT approach. We emphasise, that "switching" from the traditional particle description to a field description, by means of the use of an intuitive field representing directly the particle density distribution, is not a minor process. In the classical description, particles are localised objects which we label, before possibly delabelling them. Fields are objects defined everywhere in space, and they are indexed simply by the space coordinates. The degrees of freedom of particles and fields are a priori incommensurate. The transcription of fundamental properties for particles in terms of fields is

necessary in order to achieve the correct physical representation. This is why the entropic functional was written. The framework presented leads, in our opinion, to an essentially new approach.

Bringing the purely combinatorics entropic aspects to the same level as the interaction potential level clears the path to a different interpretation in terms of coupling and competition between combinatorics entropy and energy. Apart from the simplicity and consistency of the results, which seem to indicate that we draw on a meaningful description, we want to stress specific features of the FT approach.

In classical statistical mechanics, we are accustomed to describing localised particles and potentials coupling these particles at different points in space. We associate the description with a labeling process. In the end, this process is cancelled by introducing the factorial of the number of particles. This is not a trivial issue. It introduces another correlation over the whole system, which adds to the point to point correlation given by the interaction potential. In contrast, in the FT, the field is delocalised whilst the entropic functional is local. The entropic effect of the IS appears, in expansions, as local coupling of the field. As previously mentioned, these terms are powers of the field at a given point which have a physical meaning. This process seems to us more natural than introducing a supplementary non local coupling via the factorial permutations of the ensemble of particles.

Another interesting feature of the FT, is that we can simply perform linear combinations of the fluctuating fields and not only on the average quantities. This is shown on the charge and total density fields which are linear combinations of ionic species fields. At present, we cannot work out the equivalent of such simple transformations in terms of particles. Our theory can be generalised to mixtures, where the choice of adequate linear combinations of the fields would reflect specific properties of the interactions between the species. This would put in evidence properties related to the IS and which is broken in various ways in mixtures.

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