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FIELD THEORY FOR CLASSICAL SYSTEMS. ENTROPIC EFFECTS. APPLICATION TO NON HOMOGENEOUS ELECTROLYTES

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In a series of papers, we have presented a field theory to describe the liquid state. In contrast to other field theory approaches, we do not start from Gibbs partition function in terms of particles. The direct use of a field theory assumption leads to a simple formulation in terms of a Hamiltonian functional. The form of this functional is partly reminiscent of other field theory approaches and of the density functional theory. However, the formal similarity of the functional is misleading. In this paper, we intend to clarify some aspects which may lead to confusion when interpreting this field theory approach. We compare the role of quantum effects in the traditional approach and in field theory.

Key words: statistical mechanics, field theory, thermodynamics, entropy.

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I. INTRODUCTION

The formalism of the field theory (FT) has been successfully used in numerous domains of the statistical mechanics. For instance, this formalism has been widely used as a simple and robust tool to discuss the behaviour of complex systems in the domain of the so-called soft matter physics [1–7] in the field of the critical phenomena [8–11] and more specifically the topical subject of critical phenomena in ionic systems [12, 13]. Based on a coarse graining procedure, these approaches are essentially phenomenological. In parallel, microscopically exact approaches have also been derived [14–35]. In this case a field theoretical representation of the Gibbs partition function is obtained and the particle configuration space representation is replaced by the one in terms fields. Unfortunately, these approaches involve complex mathematical transformations and as a result the fields do not all have a straightforward physical meaning.

Alternatively [36–41], we have presented a microscopically exact field theory to describe the liquid state. This theory is exact in the following sense: there exists a mapping between our approach and the Mayer expansion of the usual statistical mechanics. Here, the field is namely the density of matter. In contrast to the other microscopical field theories, the construction of the theory is straightforward. It uses a standard field theory type construction. Such a construction is based on the existence and relevance of a mean field theory. In our case, the starting point is thermodynamics and this scheme leads, in our opinion, to a simple and clear formulation. In this respect, it is closer in spirit to the more intuitive phenomenological approaches. However, in contrast to these approaches, the Hamiltonian functional of this theory can be given explicitly and it has a simple form. There are in fact two contributions. One is local and is reminiscent of other field theory approaches and also of the density functional theory. The second, which is non-local, is directly related to the interaction potential between two space points. This potential is identical to the intermolecular pair potential used in standard theory [37]. In view of some similarities between our local Hamiltonian functional with functionals found within other approaches we will try to analyze more deeply the physical content of this functional and also how it is used in practical calculations. The paper is organized as follows. We will first elaborate the field theory using a simple thermodynamic construction. We start from the ideal gas and generalize to systems with interactions. To analyse the formalism we will focus on the role of the lattice space discretization of the partition function within an integral functional representation and discuss a renormalization procedure. This will put emphasis on the local term in the Hamiltonian which represents the specificity of this field theory approach and lead to a discussion on its physical significance. In particular, we show its role in the transcription of quantum mechanical properties true of particles in terms of fields.

The interest of a new way of elaborating these quantum mechanical properties within the FT will be illustrated using applications related to inhomogeneous electrolytes at interfaces. For these systems, the role of the local Hamiltonian is essential and describes the competition between purely entropic effects related with the existence of distinct ions and energetic properties related to the Coulomb potential. Within the FT formalism, we show that some phenomena which escape standard descriptions can easily be described and understood. We conclude by emphasing the interest of adopting a new formalism to shed a somewhat different light on some problems.

II. A FIELD THEORY ASSUMPTION

The specificity of our FT approach is that we do not elaborate the formalism starting from the standard Gibbs partition function. Rather, from the starting point we assume both the existence of the approach and that

the field is namely the density of matter. From this assumption, we stress that changing from particles to fields leads to an entirely different representation. Typically, in standard statistical mechanics we consider a well identified number of particles with a given number of degrees of freedom, of translation for instance[1]. If we consider the grand canonical ensemble, we also need to sum over all possible number of particles. In contrast, in field theory, we do not have Gibbs ensembles and the partition function is a functional integral over all configurations of the density fields which are functions. The degrees of freedom of the system are those of these functions which take different values at each lattice site. By choosing the density of matter ρ as the elementary real valued field variable we imply that this quantity is not fixed and fluctuates. This leads us to fixing the chemical potential μ and adopt the grand potential. In FT, the grand potential is written as a functional integral

$$-\beta PV = -\ln \Xi = -\ln \left[\int \mathcal{D}\rho \, e^{-\beta H[\rho]} \right] \tag{1}$$

where $\mathcal{D}\rho$ is the measure and β is the inverse temperature. To elaborate the FT, we then have to find the functional of the field H, which we call Hamiltonian. Ultimately, the FT formalism must describe the standard classical statistical mechanics for particles.

A traditional way of elaborating field theories is to assume that some mean field theory represents a meaningful intuitive starting point from which the theory can be elaborated. The complete theory takes into account the fluctuations of the field. To illustrate this, we first consider the ideal gas and here the Hamiltonian functional will be denoted H_l. In order to obtain H_l, we impose that a mean field approximation will be sufficient to give the exact expression of the chemical potential, which for the ideal gas is exactly given by

$$\ln(\rho(i)\Lambda^3) - \beta\mu = 0 \tag{2}$$

where Λ is the thermal de Broglie wavelength, where we define a lattice of elementary spacing a, and i is the label of a lattice site, hence $\rho(i)$ is the density at site i and the measure will be simply $\mathcal{D}\rho = \prod_i [\mathrm{d}\rho(i)\, a^3]$.

A Hamiltonian which reproduces Eq. (2), in a mean field approximation is given by

$$\beta H_l[\rho] = \sum_i \rho(i) \left[\ln(\rho(i)/\bar{\rho}) - 1 \right] a^3 \tag{3}$$

where $\bar{\rho} = e^{\beta\mu}/\Lambda^3$ is the activity. For the ideal system, in the absence of any interaction potential, we note that this functional is local which justifies the subscript l. For a homogeneous gas, assuming $\rho(i) = \bar{\rho}$, we obtain the standard value of the grand potential for the ideal gas $-\beta PV = -\bar{\rho}V$. However, the mean field approximation of the FT is commonly accepted to be correct and correspond to the thermodynamics, only when the lattice cell a^3 is large. In this case, fluctuations within each cell can be neglected so that the density in each lattice site $\rho(i)$ can reasonably be assumed to be close to the average density $\bar{\rho}$. In the presence of an external field, these expressions can be generalized as long as the external potential varies sufficiently slowly, implying that it has negligible variations over a lattice distance a [37].

Clearly, a theory applicable only in the large a limit is of limited interest as it smooths out all physics at any smaller length scales. In principle, we intend to treat systems with interactions for which the scale is much smaller than this large limit for a. In [37], we show that taking the opposite limit for a can be done. In order to do that, we take advantage that all lattice sites are decoupled in the Hamiltonian Eq. (3). We calculate the exact expression of the partition function, that is the mean field expression plus the corrections valid for the large a limit. The partition function external potential V^{ext} is

$$\ln \Xi_0[\rho, V^{\mathrm{ext}}] = \sum_i^{V/a^3} \bar{\rho} a^3 e^{-V^{\mathrm{ext}}(i)} + \sum_i^{V/a^3} \psi[\bar{\rho} a^3 e^{-V^{\mathrm{ext}}(i)}] \tag{4}$$

where the function ψ is known [37]. The interesting point is that this function has terms which exhibit distinct powers of $\bar{\rho}a^3$, and in particular all different from the first term which corresponds to the exact thermodynamic result, extensive with the volume. More precisely, these terms are logarithmic or inverse powers of $\bar{\rho}a^3$ and therefore negligeable with respect to the thermodynamic term in the large a limit. In [37], we have proposed a renormalization procedure in order to obtain the thermodynamic result whatever the value of the arbitrary lattice spacing. The renormalized partition function is simply the partition function in (4) to which the ψ function has been subtracted. Only the remaining terms have the correct power in a, in order to give the thermodynamic value of the grand potential whatever the value of a as long as the variations of external potential remain negligible over this lattice length scale. Thus our Hamiltonian is not strictly H_l that appears in other approaches based on Sine–Gordon transformation since a renormalization procedure must be added to (3).

From this point the generalization to the interacting gas is straightforward. The equivalent procedure starting from a simple mean field expression of the chemical potential leads when there are interactions to the Hamiltonian [44]

$$\beta H[\rho] = \beta H_l[\rho] + \frac{1}{2} \sum_{i \neq j} \rho(i) a^3 \beta v(i,j) \rho(j) a^3 \tag{5}$$

[1]Note that in the following we limit our discussion to systems in equilibrium and assume that we have integrated over the kinetic degrees of freedom.

where v is the interaction potential. Assuming a vanishing lattice spacing a and applying the renormalization procedure used in the case of the ideal system, we show that the expansion of this field theory is equivalent to the standard expansion in terms of Mayer graphs [37]. Therefore this Hamiltonian is not an approximate functional.

It is important to realize that the renormalization procedure elaborated for the ideal system does not impinge on the physical quantities related to the interactions. Practically, this is due to the fact that the ideal system Hamiltonian is local whereas the interaction contribution couples distinct lattice sites. Therefore the renormalization necessary to absorb divergences in the vanishing a limit only deals with the contributions from the local Hamiltonian H_l and does not affect the excess quantities related to the interaction. Then, once the supplementary terms have been discarded with the renormalization, the remaining terms lead to the precise combinatoric coefficients required to map the FT expansion onto the standard Mayer expansion of the liquid state theory.

Also, being able to renormalize the theory for an arbitrary external potential shows that generating functional techniques can be applied and as a consequence the renormalization remains valid when calculating any other quantity. In this renormalization process, the key point is to free oneself from the arbitrary lattice spacing a by taking the vanishing a limit when one describes the system with interactions. This is to some extent similar to what is stated by Hill [42] when he discusses the classical limit of the quantum statistical mechanics. Namely, for the ideal gas the classical physical behaviour is obtained taking the vanishing Planck constant h limit and in this case one finds there are no restriction on Λ. On the contrary, when there are interactions, it becomes necessary to consider not only the vanishing h limit, but also discuss the thermal Λ with respect to the interaction range.

We can summarize this Section by saying that the partition function written as a functional integral with the Hamiltonian (5) together with a renormalization procedure on the local part of the Hamiltonian leads to a theory which is an exact alternative to the standard statistical mechanics. From now on, to simplify notations, it is possible to abandon the lattice space representation of the Hamiltonian as, after renormalization, expressions are independent from the precise choice of a in the vanishing lattice space limit.

III. CLASSICAL STATISTICAL MECHANICS: THE QUANTUM MECHANICAL PARADIGM

The aim of this Section is to gain a better understanding of the role and physical meaning of the local Hamiltonian contribution H_l. We can start by noting that although we use the denomination of classical statistical mechanics there is no purely classical theory but just a classical limit of the quantum description [42]. In this limit we have to comply with two properties which have a meaning only in the quantum world. These properties are namely, the Heisenberg uncertainty principle and the property of indistinguishability for standard boson type particles. For systems in thermodynamic equilibrium the former property after integration over the kinetic momenta leads to the introduction of Λ that depends on the Planck constant. Λ is the minimal length where one is allowed to devise on the position of a particle when the momentum is calculated from the Maxwell velocity distribution law. Thus in the thermodynamic domain a particle cannot be localized better than in a volume Λ^3. We can say that any particle occupies an effective volume Λ^3. The second property leads, in partition functions, to the introduction of a factorial of the number of particle as the consequence of their indistinguishability. This term is the sign of our inability to write the partition function without going through two successive steps. The first is describing the theory for labelled particles then formally delabeling them [43, 44].

The ideal gas as a reference for the quantum mechanical properties

The canonical partition function of the ideal gas $Q_{\rm ig}(N,V,T)$ is determined by the two quantum properties mentioned above. We have

$$Q_{\rm ig}(N,V,T) = \frac{V^N}{N!\Lambda^{3N}}, \tag{6}$$

for a system of N particles at equilibrium, in a volume V at temperature T. In this expression, we have to compare for each particle the available volume V to the effective volume Λ^3 and to divide the result by all possible permutations of the indistinguishable particles. Thus although we started by integrating separately each particle, finally the N particles cannot be really considered as independent entities. In the quantum world, although there are no interactions, particles still know of each other's existence. In the grand canonical description the partition function is given by

$$\Xi_{\rm ig}(V,\mu,T) = \sum_{N=0}^{\infty} e^{\beta\mu N} Q_{\rm ig}(N,V,T) \tag{7}$$

where β is the inverse temperature. The thermodynamic potential associated with the grand potential is $-\beta PV = -\bar{\rho}V$ and indeed the Hamiltonian H_l (3) is simply a transcription. The previous results are the only exact results we know and we consider that a field theory must reproduce such exact results whatever the lattice spacing a. In the previous section we have seen that this can be realized provided a renormalization procedure is introduced. If the partition function is calculated by expanding the exponential of the local functional — and, to our knowledge, we have no other choice — not all terms have to be kept, we drop those depending on a and those that are diverging. By such a procedure the quantum remeniscences are exacty taken into account. This derivation shows that functional H_l and its renormalization is precisely the exact representation of the quantum mechanical properties in the framework of the FT.

A system with interactions

The generalization of the partition functions to interacting systems is obtained by replacing $Q_{\rm ig}(N,V,T)$ in the previous relation by $Q(N,V,T)$ given by

$$Q(N,V,T) = Q_{\rm ig}(N,V,T) \times \int \prod_{i=1,N} \frac{d\mathbf{r}_i}{V} \exp\left(-\sum_{i\neq j} \beta v(r_{ij})\right). \quad (8)$$

In order to calculate $Q(N,V,T)$, our main task consists in the calculation of the $3N$ dimensional integral that reveals all the specificities of the liquid via the sum of pair potential acting between the N particles. Let us return to the field theory. The pair potential introduces a coupling between two points in space as shown in equation (5). Our main task is then to consider the coupling between the pair potential and the local part of the Hamiltonian. In [37], we have shown that the local part leads to introduce first a Gaussian quantity coupling two space points and then an operator acting on this Gaussian quantity (Eq. (39) in ref [37]). The treatment of this operator, representative of quantum effects via H_l, generates an expansion in terms of Feynman diagrams and finally we obtain the complete theory. Thus in field theory the effects of the pair potential and the reminiscence of quantum effects have equal importance in the progress of the theory. Note that the functional H_l appears in the DFT approach [45] but with a totally different point of view. To find the equilibrium properties we need a minimization of the density functional rather than an elaborate integral functional over all fluctuations of the density fields as performed in the FT.

To summarize, first we impose that the field theory reproduces exactly the quantum properties which determine the ideal gas thermodynamics. This can be done by using the local functional given by Eq. (3) but we also have to add to it a renormalization condition. The quantum effects via a local functional H_l leads to an operator acting on a gaussian function containing the interaction between two points in space. This operator produces a mixing between quantum effects and interactions which is rather different to that existing in standard liquid state theory or in DFT. Although it is understood that in the end the results are identical.

IV. APPLICATIONS TO INHOMOGENEOUS ELECTROLYTES

The field theory has been illustrated in various examples describing electrolytes at interfaces [36–41]. Hereafter, we briefly recall some key elements of discussion common to the various systems. To study the local Hamiltonian, the interest in treating electrolytes is that for these systems we have particles with both properties i.e. each type of ions is indistinguishable within the same species but cations and anions are clearly distinguishable. Such properties must be visible in H_l and have physical consequence. These physical properties can be foreseen in that for this system we have two representations or viewpoints. We can think in terms of mixtures and choose for the fields the ionic densities or focus on the electrostatic properties and consider the charge and the conjugated total density field. These viewpoints are intimately related and as a consequence there will be couplings between purely entropic fluctuations related to the relative number distribution of the two ions and the Coulomb properties associated to the charge density. In this Section, we will consider point ions in order to focus on the competition between the Coulomb potential and the quantum mechanical effects as controlled by the Hamiltonian H_l. To be more general, we can consider excess quantities with respect to a neutral system with volume excluded interactions. We will also start from the more simple symmetric 1:1 electrolyte and generalize to the case of systems asymmetric in valence systems. These systems represent yet another domain to study the implications of H_l as the number balance between ions is modified due to the electroneutrality condition. The objective is to illustrate the role of the functional H_l and its physical consequence. In particular, we will show that in perturbation theory, this terms leads to local couplings between the fields which are non-trivial and have a clear consequence on the physical properties of the system.

A. Symmetric systems

The Hamiltonian H_l in the case of ionic systems is

$$\begin{aligned}\beta H_l &= \int \rho_+(\mathbf{r})\left[\ln(\rho_+(\mathbf{r})/\bar{\rho}_+)-1\right]d\mathbf{r} \\ &+ \int \rho_-(\mathbf{r})\left[\ln(\rho_-(\mathbf{r})/\bar{\rho}_-)-1\right]d\mathbf{r} \\ &= \int \frac{s(\mathbf{r})+q(\mathbf{r})}{2}\left[\ln\left(\frac{s(\mathbf{r})+q(\mathbf{r})}{2\bar{\rho}}\right)-1\right]d\mathbf{r} \\ &+ \int \frac{s(\mathbf{r})-q(\mathbf{r})}{2}\left[\ln\left(\frac{s(\mathbf{r})-q(\mathbf{r})}{2\bar{\rho}}\right)-1\right]d\mathbf{r} \quad (9)\end{aligned}$$

where $\bar{\rho}_\pm = e^{\beta\mu_\pm}/\Lambda_\pm^3$ and are equal for the symmetric electrolyte and in this context $\bar{\rho} = \bar{\rho}_+ + \bar{\rho}_-$. The second form is introduced because it is more practical to study the Coulomb potential and we introduce the charge field $q(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$ and the total density field $s(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})$. We can immediately note that if the ionic fields for cations and anions appear in separate terms in the first form of Eq. (9), this is no longer the case in the second form where the two fields q and s appear simultaneously in all terms of H_l. The full Hamiltonian is obtained by including the interactions

$$\beta H[q,s] = \beta H_l[q,s] + \beta H^{\rm Coul}[q] \quad (10)$$

where $\beta H^{\rm Coul}[q]$ is the standard Coulomb term. In the following, we will calculate the integral functional in perturbation theory, studying the fluctuations around the mean field approximation. We will only need to consider the neutral interface as quantities like the differential capacitance will be obtained in the linear response

regime from the neutral interface properties. For the non-charged interface, the mean field approximation solution is trivial. The charge profile across the system is zero and for point ions the density is constant throughout the interface. The expansion of the Hamiltonian around the mean field approximation is a sum of local coupling terms. The first terms beyond the quadratic terms are shown as follows

$$\beta\delta H_l[q,s] = -\frac{\bar{\rho}}{2}\int \delta q^2(\mathbf{r})\delta s(\mathbf{r})\, d\mathbf{r} + \frac{\bar{\rho}}{12}\int \delta q^4(\mathbf{r})\, d\mathbf{r}\ \ldots \tag{11}$$

where $\delta q = q/\bar{\rho}$ and $\delta s = (s-\bar{\rho})/\bar{\rho}$ are dimensionless excess fields. The quadratic Hamiltonian is

$$\beta\delta H^{\text{quad}} = \frac{\bar{\rho}}{2}\int [\delta q^2(\mathbf{r}) + \delta s^2(\mathbf{r})]\, d\mathbf{r} + \frac{\beta e^2\bar{\rho}}{8\pi\varepsilon}\int \frac{\delta q(\mathbf{r})\delta q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \tag{12}$$

where e is the elementary electric charge and ε is permittivity. The quadratic terms from H_l are naturally associated to the interaction potential as it is also bilinear and can be treated in a similar way. Thus, in expansion theory, δH_l will provide vertices and the bilinear terms in (12) the connections between the vertices. Note that the quadratic terms are diagonal in the q and s fields and for point ions, they lead at the quadratic level of approximation to the well known Debye limiting law in the bulk [48]. After renormalization, the expansion δH_l can be greatly simplified and vertices can be substituted by

$$\frac{1}{(2n)!m!}\delta q^{2n}\delta s^m \tag{13}$$

where only even terms in the charge are present for a $1:1$ symmetric electrolyte. Therefore, although it is not the case in H_l, the vertices now have the expected symmetry factors and all standard combinatoric rules in the expansions can be used. The consequence is that in expansions we will now use the above vertices and that in the bilinear terms only the interactions remain (here, the Coulomb potential). We now give a few examples of behaviours which can be predicted using this expansion.

Ionic depletion at a neutral interface

We first start by considering the neutral interface for which there is no charge density profile. However, at this interface, the quadratic charge fluctuations are not constant and at the one loop level approximation, we show that they have a depleted profile. The physical interpretation is that these fluctuations are modified when we approach the interface because of the absence of ionic system in one half space and thus some fluctuations are frustrated. In [36], we have shown that this profile is directly associated to the existence of an ionic depletion profile for the total density. Indeed, the expression of the total density shows that it is the term $\delta q^2\delta s$ in δH_l which is responsible for transposing a property associated to the charge field, thus related to the Coulomb potential, to an effect on the total density field. The contact value of this profile is precisely the value of the pressure βP, calculated at the same level of approximation. This means that the quantities fulfil the so-called contact theorem. Common approaches like the Gouy-Chapman theory or the MSA approximation [49] do not satisfy this condition. These approaches focus on the equations directly associated to the Coulomb potential and discard any correlation between the charge and the total density. Typically, in the MSA approximation the total density profile is that of neutral hard spheres. The consistency of the contact theorem is restored because we account for the competition between entropic effects for indistinguishable and distinguishable species (ions of the same/different kind) and Coulombic effects.

Anomalous capacitance behaviour

The above profile on the density is related to another surprising phenomenon, which is the anomalous behaviour of the electric differential capacitance as a function of the temperature. Experimentally and in numerical simulations, scientists have found systems where the electric capacitance decreases at low reduced temperature. The study of this phenomenon has lead to a substantial literature [38, 50–59]. This phenomenon is non-intuitive as one expects the electric response of the system to decrease with increasing thermal agitation as predicted by the Gouy-Chapman or MSA approaches. The phenomenon appears at low reduced temperature when the Coulomb interaction becomes stronger. When considering the ionic depletion profile, one can easily understand that the lack of ions is correlated with a less efficient electric response. This depletion is the more pronounced precisely at low reduced temperature. In [38], we have obtained a simple analytic expression of the differential capacitance using the charge-charge correlation function and in expansions we note that the corrections to the correlation involve the $\delta q^2\delta s$ and the δq^4 couplings in equation (11). In a second step, having captured the main physical behaviour, it is possible from a simple modification to account for the size of the ions [39]. We can note that originally, this effect was found in molten salts, which are dense systems - therefore attributed to excluded volume effects. Here, predicted by a point ion model, we show that this is not the case.

B. Multivalent electrolytes

Another domain to illustrate the role of H_l is to consider valence asymmetric systems that is $z_+ : z_-$ electrolytes. The relation between the ionic density fields and the charge field are modified according to $q = z_+\rho_+ - z_-\rho_-$. This new relation modifies the expression for H_l, equation (9)

$$\beta H_l = \int \frac{z_- s(\mathbf{r}) + q(\mathbf{r})}{z_+ + z_-} \left[\ln\left(\frac{z_- s(\mathbf{r}) + q(\mathbf{r})}{(z_+ + z_-)\bar{\rho}} \right) - 1 \right] d\mathbf{r} + \int \frac{z_+ s(\mathbf{r}) - q(\mathbf{r})}{z_+ + z_-} \left[\ln\left(\frac{z_+ s(\mathbf{r}) - q(\mathbf{r})}{(z_+ + z_-)\bar{\rho}} \right) - 1 \right] d\mathbf{r} \quad (14)$$

In the expansion, the coupling Hamiltonian now becomes

$$\beta\delta H_l[q,s] = -\frac{\bar{\rho}}{2z_+z_-} \int \delta q^2(\mathbf{r}) \delta s(\mathbf{r})\, d\mathbf{r} + \frac{\bar{\rho}(z_+^2 + z_-^2 - z_+z_-)}{12 z_+^3 z_-^3} \int \delta q^4(\mathbf{r})\, d\mathbf{r} - \frac{\bar{\rho}(z_+ - z_-)}{6 z_+^2 z_-^2} \int \delta q^3(\mathbf{r})\, d\mathbf{r}\ \ldots \quad (15)$$

and the quadratic Hamiltonian

$$\beta\delta H^{\mathrm{quad}} = \frac{\bar{\rho}}{2} \int \left[\frac{1}{z_+z_-} \delta q^2(\mathbf{r}) + \delta s^2(\mathbf{r}) \right] d\mathbf{r} + \frac{\beta e^2 \bar{\rho}^2}{8\pi\varepsilon} \int \frac{\delta q(\mathbf{r}) \delta q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (16)$$

Defining a scaling parameter $z_f = \sqrt{z_+ z_-}$ and rescaling the charge field by defining $\delta Q = \delta q / z_f$ and introducing the asymmetry parameter $z_{as} = (z_+ - z_-)/\sqrt{z_+ z_-}$, we can rewrite the expansion of the Hamiltonian

$$\beta\delta H_l[q,s] = -\frac{\bar{\rho}}{2} \int \delta Q^2(\mathbf{r}) \delta s(\mathbf{r})\, d\mathbf{r} + \frac{\bar{\rho}}{12} \int \delta Q^4(\mathbf{r})\, d\mathbf{r} + \frac{\bar{\rho} z_{as}^2}{12} \int \delta Q^4(\mathbf{r})\, d\mathbf{r} - \frac{\bar{\rho} z_{as}}{6 z_+^2 z_-^2} \int \delta Q^3(\mathbf{r})\, d\mathbf{r}\ \ldots \quad (17)$$

and the quadratic Hamiltonian

$$\beta\delta H^{\mathrm{quad}} = \frac{\bar{\rho}}{2} \int \left[\delta Q^2(\mathbf{r}) + \delta s^2(\mathbf{r}) \right] d\mathbf{r} + \frac{\beta z_f^2 e^2 \bar{\rho}^2}{8\pi\varepsilon} \int \frac{\delta Q(\mathbf{r}) \delta Q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (18)$$

In these new expressions, we find terms which are exactly the same ones as for the 1 : 1 symmetric system written with δQ in replacement of δq. This shows that these terms correspond to the same physics as for the 1 : 1 electrolyte once the charge is rescaled by z_f. This coefficient corresponds to the scaling of the ionic force when changing from a 1 : 1 to a $z_+ : z_-$ electrolyte. Note that this parameter is the same for a 4 : 1 and a 2 : 2 electrolyte. This suggests that there is another parameter which plays an important role. Indeed, the terms where there is z_{as} are really the terms characteristic of the asymmetry. We hereafter study the consequence of these terms.

Anomalous capacitance for multivalent electrolytes

The study of the differential capacitance curves for asymmetric electrolytes as shown in [40]. The Scaling of the electric charge or equivalently of the dimensionless temperature with the ionic strength parameter z_f is shown to rescale the essentials of the differences between the curves which are seen to tend towards the 1:1 symmetric electrolyte result. However, as mentioned above 4 : 1 and 2 : 2 electrolytes which share the same parameter z_f still exhibit a slightly different physics. The remaining difference is associated to the parameter z_{as} which is truly characteristic of the valence asymmetry [40, 41]. The dependence with this parameter indicates an increase of the differential capacitance peak, clearly found in numerical simulations. To our knowledge, this behaviour has not been explained by another approach. It is the new terms in δH_l (Eq. 17), which depend on z_{as}, absent in symmetric electrolytes, which are responsible for this behaviour.

The potential of zero charge (PZC) for size and valence asymmetric systems

Another effect of the valence asymmetry is the existence of a polarization for the neutral interface. Such an effect has been shown by Torrie *et al.* [60] and more recently discussed by Henderson *et al.* [61] who have considered both asymmetry in size and/or in valence. The authors, searching for simple analytic approaches, were able to account for the size effect. However, none of the standard liquid state theories account for the valence effect [61, 62] except for the MPB approach used in [60] and more recently in a version of the DFT [63]. These approaches are mathematically demanding. Conversely, we find that FT predicts the polarization due to multivalency with simple analytic expressions which can be applied directly to any valences. The charge profile thus calculated is consistent with the exact condition given by the charge contact theorem [64] and comparison with the numerical simulation results [41] shows an unexpected convergence if we note that a simple point ion model has been used.

V. CONCLUSION

In this paper, we have shown how to construct a simple field theory approach of the standard statistical mechanics. Noting that there is no real classical statistical mechanics, we discuss the specificity of the FT. The characteristics consists in a new way of including quantum mechanical properties like the indistinguishability of particles into a local Hamiltonian in the theory. This specific way of introducing such properties leads, in this framework, to treating them in the same way as the interaction potential. As an illustration, some properties of electrolytes can be understood in a new way. The indistinguishability of ions of the same kind as opposed to cations and anions is shown to have entropic effects which compete with the energetic effects of the Coulomb potential. For symmetric and asymmetric electrolytes, we have detailed the transformations of the local Hamiltonian when going from the ionic density fields description to the charge and total density fields. This transformation is required to go from the original form expressing the indistinguishability to a form more convenient to study the Coulomb systems. Our point is to illustrate that, in FT, working on fields there is a simple algebra which introduces efficiently the appropriate physical parameters and

allows for simple calculations and interpretations. Finally, it is interesting to note that in the context of particles with defined locations the property of indistinguishability introduces a non local coupling over the whole system. On the contrary for fields which are essentially non local variables, the same property takes a local form, which appears practical for calculations.

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ТЕОРІЯ ПОЛЯ ДЛЯ КЛАСИЧНИХ СИСТЕМ. ЕФЕКТИ ЕНТРОПІЇ. ЗАСТОСУВАННЯ ДО НЕОДНОРІДНИХ ЕЛЕКТРОЛІТІВ

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У серії робіт ми виклали теорію поля для опису рідкого стану. На противагу до інших підходів теорії поля, ми не виходимо з представлення Ґіббса для статистичної суми частинок. Пряме використання припущень теорії поля приводить до простого формулювання в термінах функціонала Гамільтона. Форма цього функціонала частково нагадує інші підходи теорії поля та теорії функціонала густини. Проте формальна подібність функціонала є помилковою. У цій статті ми намагаємося вияснити деякі аспекти, які можуть викликати непорозуміння, коли інтерпретувати цей підхід теорії поля. Ми порівнюємо роль квантових ефектів у традиційному підході та в теорії поля.