

Field theory for classical systems. Entropic effects. Application to non homogeneous electrolytes

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We consider a field theory approach of the liquid state. The Hamiltonian includes the standard interaction as for particles and a term which takes into account the indistinguishability symmetry property known for particles in terms of fields. This term is essentially entropic and accounts for the combinatorics of the particles. The peculiarity of this framework is that these energetic and entropic properties are treated at equal level when we describe the fluctuations of the fields. Such new formalism leads to new interpretations of different physical problems. The approach is exact [1].

The role of the combinatorics entropy is evidently emphasized in the case of ionic systems where there are at least two distinct species and one has to account for their combinatorics. For an ionic system at a neutral interface, we show the existence of a depletion profile for the total density. This phenomenon gives a simple interpretation of the so-called anomalous behaviour of the electric capacitance with the temperature [2]. Within a basic point ion model, we show that an entropic coupling between the total density and the charge field is important. Expressions are then corrected to include excluded volume effects [3]. The formalism can easily be generalised to asymmetric in valence electrolytes where the ionic number balance is modified in order to satisfy the electroneutrality condition [4]. The simple parametrisation of these systems illustrates the capabilities of the approach.

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