

A variational field theory for solutions of charged, rigid particles

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Abstract

A general field theoretic formalism is developed for dealing with solutions of particles with rigid charge distributions. Combined with the mean-field approximation, the resulting theory extends the Poisson–Boltzmann equation to incorporate the presence of structured ions (e.g., uniformly charged rods or disks). When combined with a first-order variational approximation, the resulting theory, in the low density limit, is a generalization of the Debye–Hückel theory to extended charge distributions and reduces to the standard expressions when applied to point charges. A first-order variational theory is applied to solutions of uniformly charged disks and to solutions of uniformly charged disks with a neutralizing ring charge to examine the influence of electrostatic interactions on the isotropic–nematic transition.

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1. Introduction

In everyone's life, there are a few people who have a profound impact on the way one thinks. For me, Prof. Prausnitz is one of these people. The time I spent working with him was a time where I was flooded with new thoughts and ideas for research. Every other week or so, he would leave interesting articles on my desk—not just current research work but also “classic” papers—to keep me thinking. Conversations with him during our weekly research meetings easily flowed between thermodynamics, history, opera, art, literature, and current events. He is a true academic, who sought and respected knowledge in any field. He made me realize that the “technical” work we do is never truly isolated from other aspects of our lives. The designs we produce, experiments we devise, or the theories and models that we create are a consequence of our own experiences, biases, and personality. Engineering is fundamentally a creative subject.

Many colloidal and biological systems contain large, charged particles (e.g., proteins, DNA, or micelles) and electrolytes. Electrostatic interactions play a major role in determining the structure and thermodynamic properties of these systems. Most

of our current understanding of the role of electrostatic interactions comes from the Poisson–Boltzmann equation [1,2]. Although the Poisson–Boltzmann equation has been quite successful in describing many aspects of these interactions, there are many phenomena (e.g., overcharging, charge inversion, like-charge attraction, and polyelectrolyte collapse) that it cannot describe, even qualitatively, because it does not account for electrostatic correlations [3–6].

Because of the importance of correlation effects, there has been a lot of work on trying to incorporate their influence into the Poisson–Boltzmann equation. Some of these approaches include the modified Poisson–Boltzmann theory [7], integral equation theory such as the mean-spherical approximation [8] and the hypernetted-chain approximation [9], density functional theory [10], as well as many others.

The common feature of these theories is that they focus on the charged particles in the system and the correlations between them, although they differ in the manner in which these correlations are approximated. An alternate perspective is not to focus on the particles in the system, but rather to consider the electric potential and its variations (which are due to the thermal motion of the charged particles). This field theoretic approach has already been developed and applied [11–16] to a wide variety of electrolyte problems.

If fluctuations of the electric potential are neglected (i.e., the mean-field approximation), the field theory reduces [13,17] to a

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generalized version of the Poisson–Boltzmann equation, which may include non-electrostatic effects such as excluded-volume interactions. When the effects of fluctuations are relatively small, methods, such as the loop expansion or the variational perturbation method, are available to provide systematic improvements upon the mean-field approximation. Other expansion procedures have also been recently developed [18,19] which are accurate in situations where the fluctuations of the electric potential are extremely strong.

Most applications of the field theoretic approach to electrolyte solutions has been to systems containing point charges or spherically symmetric ions. Systems that include particles with non-spherical charge distributions (e.g., charged rods, disks, or helices) can exhibit interesting phenomena that are not possible for spherically symmetric particles, such as liquid crystalline phases, bundle formation, etc. In this work, a field theoretic formalism is developed to examine the properties of solutions of particles with rigid charge distributions. These types of systems occur in a wide variety of engineering applications, such as in protein purification and the design of home, personal, and health care products (e.g., paints, detergents, shampoos, etc.).

The remainder of the paper is organized as follows. In Section 2, the functional integral formulation of the grand partition function, for a system composed of particles with rigid charge distributions, is presented. Then in Section 3, two different approximation methods for evaluating the grand partition function are introduced: (i) the mean-field theory, and (ii) the variational method. The relationship between both these theories and the Poisson–Boltzmann equation is discussed. The simplification of the formalism in the case of translationally invariant and isotropic systems is examined in Section 4, where the relationship to the Debye–Hückel theory is demonstrated. The application of the theory to investigate the isotropic-nematic transition

$$\mathbf{A}(\boldsymbol{\Omega}) = \mathbf{A}(\theta, \phi, \psi) = \begin{pmatrix} \cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi & \cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi & \sin \theta \sin \psi \\ -\sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi & -\sin \psi \sin \phi + \cos \theta \cos \phi \cos \psi & \sin \theta \cos \psi \\ \sin \theta \sin \phi & -\sin \theta \cos \phi & \cos \theta \end{pmatrix} \quad (2)$$

of solutions of charged disks is presented in Section 5. Finally, Section 6 summarizes the main points of this paper and discusses areas for future work.

2. Development of the general formalism

In this section, a field theory formulation of the statistical mechanics of a solution of rigid, charged particles is developed. The particles are assumed to be immersed in a continuum dielectric constant which varies in space according to $\epsilon(\mathbf{r})$. Also, located throughout the system is a fixed, immobile charge distribution $\Sigma(\mathbf{r})$ (e.g., due to a charged surface).

Particles of type α are at a fixed chemical potential μ_α , and acting on each particle is an external potential $u_\alpha(\mathbf{r}, \boldsymbol{\Omega})$. The particles interact with each other through an electrostatic field, which has a total energy E^{elec} . The particles also interact with each other through non-electrostatic interactions, with potential

E^{ref} . The grand partition function Z_G of total volume V and temperature T is given by [20]

$$Z_G[\gamma, \Sigma] = \sum_{N_1=0}^{\infty} \cdots \sum_{N_M=0}^{\infty} \prod_{\nu} \frac{1}{N_{\nu}! \Lambda_{\nu}^{3N_{\nu}}} \times \int \prod_{\tau} d\mathbf{r}_{\tau} d\boldsymbol{\Omega}_{\tau} e^{-\beta E^{\text{elec}} - \beta E^{\text{ref}} + \sum_{\alpha,k} \gamma_{\alpha}(\mathbf{r}_{\alpha,k}, \boldsymbol{\Omega}_{\alpha,k})} \quad (1)$$

where $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, N_α is the number of particles of type α , $r_{\alpha,k}$ is the position of the k th point charge of type α , $\boldsymbol{\Omega}_{\alpha,k}$ is its orientation, Λ_α is the thermal wavelength of an ion of type α , and $\gamma_\alpha(\mathbf{r}, \boldsymbol{\Omega}) = \beta[\mu_\alpha - u_\alpha(\mathbf{r}, \boldsymbol{\Omega})]$. The integration over the orientation $\boldsymbol{\Omega}$ of a particle is given explicitly by

$$\int d\boldsymbol{\Omega} \rightarrow \int_0^\pi \frac{\sin \theta d\theta}{2} \int_0^{2\pi} \frac{d\varphi}{2\pi} \int_0^{2\pi} \frac{d\psi}{2\pi}$$

where θ , φ , and ψ are the Euler angles that denote the particle orientation.

Consider a rigid, charged particle of type α that is located at the origin. When the particle is in a reference orientation, the location of a particular segment s of the particle is given by $\delta\mathbf{R}_\alpha(s)$, which characterizes the displacement of the segment from the origin; the charge density at this location is given by $q_\alpha(s)$. The charge distribution $Q_\alpha(\mathbf{r}, \boldsymbol{\Omega})$ of the particle when it is in the orientation $\boldsymbol{\Omega}$ is

$$Q_\alpha(\mathbf{r}, \boldsymbol{\Omega}) = \int ds q_\alpha(s) \delta(\mathbf{r} - \mathbf{A}(\boldsymbol{\Omega}) \cdot \delta\mathbf{R}_\alpha(s))$$

where \mathbf{A} is the rotation matrix, which describes the transformation of the particle from its reference orientation to the orientation $\boldsymbol{\Omega}$. One example of the rotation matrix is [21]

In the case of a point charge of magnitude q_α , the charge distribution is given by:

$$Q_\alpha(\mathbf{r}, \boldsymbol{\Omega}) = q_\alpha \delta(\mathbf{r})$$

The charge distribution for a uniformly charged, rigid rod of length l and overall charge q_α is given by

$$Q_\alpha(\mathbf{r}, \boldsymbol{\Omega}) = q_\alpha \int_0^1 ds \delta\left(\mathbf{r} - \hat{\mathbf{n}}(\boldsymbol{\Omega})l\left(s - \frac{1}{2}\right)\right) \quad (3)$$

where $\hat{\mathbf{n}}$ is a unit vector that points parallel to the orientation of the rod, and s denotes the distance along the rod.

The overall charge density $\mathcal{Q}(\mathbf{r})$ of the system is given by

$$\mathcal{Q}(\mathbf{r}) = \sum_{\alpha,k} Q_\alpha(\mathbf{r} - \mathbf{r}_{\alpha,k}, \boldsymbol{\Omega}_{\alpha,k}) + \Sigma(\mathbf{r}) \quad (4)$$

where $\mathbf{r}_{\alpha,k}$ is the position of the k th particle of type α , $\boldsymbol{\Omega}_{\alpha,k}$ denotes the orientation of the k th particle of type α , and $\Sigma(\mathbf{r})$ is a fixed charge density.

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