Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

Article

Theory of inhomogeneous calamitic Coulomb fluids

Rudolf, Podgornik [1,2,3] 0000-0002-3855-4637

[1] School of Physical Sciences and Kavli Institute for Theoretical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China
[2] Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
[3] Wenzhou Institute of the University of Chinese Academy of Sciences, Wenzhou, Zhejiang 325000, China
* Correspondence: podgornikrudolf@ucas.ac.cn
† Also affiliated with Department of Physics, Faculty of Mathematics and Physics, University of Ljubljana, SI-1000 Ljubljana, Slovenia and Department of Theoretical Physics, Jožef Stefan Institute, SI-1000 Ljubljana, Slovenia.

Abstract: A field theoretic representation of the classical partition function is derived for a system composed of a mixture of anisotropic and isotropic mobile charges that interact *via* long range Coulomb and short range nematic interactions. The field theory is then solved on a saddle-point approximation level, leading to a coupled system of Poisson-Boltzmann and Maier-Saupe equations. Explicit solutions are finally obtained for a calamitic counterion-only system in proximity of a charged planar wall. The nematic order parameter profile, the counterion density profile and the electrostatic potential profile are interpreted within the framework of a nematic-isotropic wetting phase with a Donnan potential difference.

Keywords: nematic interaction, Coulomb fluids, nematic wetting, electric double layer

---

0. Introduction

Coulomb fluids composed of anisotropic charge carriers are ubiquitous in many contexts. In fact it is worth noting that strong electrostatic interactions between rod-like charges were already invoked in the case of nematic ordering of tobacco mosaic virus (TMV) in the seminal work of Bernal and Fankuchen [1], which is also one of the first cases of the application of the Poisson-Boltzmann theory to biological systems [2]. Apart from the TMV, other charged rod-like viruses and virus-like nanoparticles have been used in functional materials assembly [3] whose formation is controlled by the electrostatic interaction with the substrate [4].

A strong electrostatic attraction between the substrate and the deposited filamentous viruses enhances a stable film formation, as is clear from the effect of the ionic strength and the pH of the solution [5,6]. Different types of filamentous viruses [7], as well as short fragments of DNA [8], F-actin [9], and cellular scaffold microtubules [10] all exhibit also properties of polyvalent rod-like ions as do also many other multivalent strongly anisotropic biological polyvalent ions [11] that can be either modeled as spatially distributed point charges or as higher order point multipoles [12–14]. Last but not least, ionic liquid crystals (ILCs) [15] are solvent-less ionic systems with a dual ionic and organic nature [16], that are composed of cations and anions with at least one ionic species and characterized by highly anisotropic molecular shape [17].

The calamitic shape leads to ordered structures whose formation exhibits features of liquid crystal ordering as well as long-range electrostatic interactions. It is this latter example that has recently witnessed a real proliferation of theoretical works set to illuminate the basic principles of order formation in these complex Coulomb systems.

© 2020 by the author(s). Distributed under a Creative Commons CC BY license.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

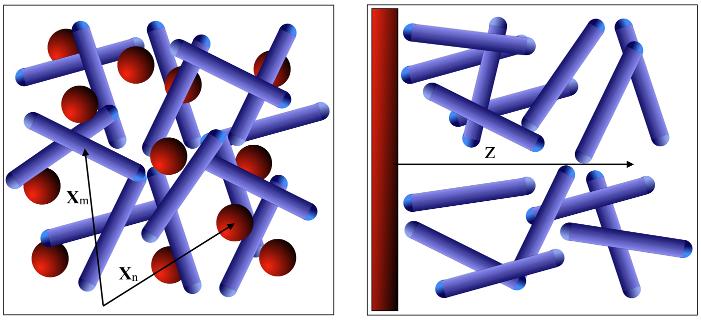

Figure 1. A schematic presentation of the system with calamitic cations and simple anions in the bulk (left). An inhomogeneous system of calamitic cationsclose to a charge surface (right). Both the cations as well as the anions are charged, though in general differently. Apart from long range Coulomb interactions the calamitic cations interact also via short range nematic interactions described by a Lebwohl-Lasher interaction potential.

The theoretical approaches to charged anisotropic systems in the bulk are varied and abundand. Here we delimit to a few that are directly relevant for subsequent developments. The work of Deutsch and Goldenfeld [18,19] for thin charged rods relies on a collective coordinate transformation method applied to the ordering of charged rods in 3D. In addition, for rod-like charged cylinders a generalized Onsager theory could also be used to describe the ordering transition with electrostatic interactions strongly modifying the hard core diameter of the rods as well as providing a mechanism for twisting interaction as first described by Odijk [20–22]. This approach has seen many further developments with different level modifications and extensions [23–27]. A generalized variational field theory of particles with rigid charge distributions [28] and an order parameter based mean-field approximation of rod-like polyelectrolytes [29] both lead to an ordering transition in 3D.

The properties of systems composed of a mixture of monopolar and dipolar charges or needle-like quadrupolar charges have also been analyzed in detail [30,31]. The nematic order and electrostatics in the case of ion-doped nematic electrolytes, with an anisotropic dielectric response, have been considered on a phenomenological level [32]. Bulk properties as well as electrical double layers in ionic liquid crystals have been analyzed in the work of Bier within the density functional approach [33,34] that was formulated for homogeneous as well as inhomogeneous systems with interfaces [35,36]. It is the latter case that is particularly interesting as it should exhibit features of both, the nematic ordering as well as the Gouy-Chapman-type electrostatic double layers.

The inhomogeneous charged rods problem, rather then the general problem of rod-like Coulomb fluids, has not been analyzed to the same degree as the bulk systems but this is exactly what we are interested in here. The inhomogeneous case of a system bounded by charged wall(s) with mobile dipolar charges [37–39], quadrupolar charges [12,40,41] and finite size dumbbell charges [13,42–44] have been investigated on different levels of approximations. Density functional theory was formulated for the case of inhomogeneous systems of charged anisotropic particles with interfaces [33,35,36], specifically a semiinfinite isotropic or nematic bulk system in contact with a charged hard wall exhibiting nematic wetting of the substrate, which is close to our point of departure.

In fact, our focus here will be on how to formulate a theory of an inhomogeneous system of anisotropic charges with Coulomb and nematic interactions - as in the case of calamitic cations close to an oppositely charged wall - based on a formalism that could be seen as a straightforward generalization of the Gouy-Chapman theory for simple ions. Thus, in what follows we will derive a statistical theory of a Coulomb system composed of anisotropic calamitic cations and point-like anions with microscopic interactions of Lebwohl-Lasher nematic as well as Coulomb type and derive its mean-field approximation form. We will then apply the general theory to the case of an inhomogeneous system, composed of a negatively charged planar interface in the presence of calamitic counterions, thus generalizing the standard counterion-only Gouy-Chapman problem of colloid physics. We will

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

derive the equations governing the density distribution and electrostatic potential on the mean-field level, in the case of a one dimensional system with an electrified interface. By solving the mean-field level equations that emerge as a coupled system of the Maier-Saupe and the Poisson-Boltzmann equation, we are able to derive some salient properties of inhomogeneous nematic ordering induced by the charged interface as well as the modifications in the electric double layer distribution wrought by the presence of nematic order. Our theory presents a natural generalization of the Gouy-Chapman theory to the case of nematogenic calamitic counterions.

1. Collective description of an anisotropic ionic liquid

1.1. Order parameters

Let us consider a system composed of monovalent anions (charge $-e$) and polyvalent rod-like cations (charge $+qe$) with chemical potential μ, a situation often encountered in many ionic liquid system with cations being extended stiff rods, while anions are considered to be point-like particles, see Fig. 1.

The respective microscopic order parameters are the *nematic order parameter density* defined as (see *e.g.* Ref. [45])

$$\hat{\mathcal{Q}}_{ij}(\mathbf{x}) \equiv \sum_{(+)} \tfrac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \tfrac{1}{3}\delta_{ij}\right)\delta\left(\mathbf{x}-\mathbf{x}_n\right) = \sum_{(+)} \hat{q}_{ij}(\mathbf{x}_n)\delta\left(\mathbf{x}-\mathbf{x}_n\right) \tag{1}$$

with $\mathbf{n}(\mathbf{x}_n)$ and $\hat{q}_{ij}(\mathbf{x}_n)$ the director and the orientational order parameter of the $n-th$ rod-like cation, together with the microscopic *charge density*

$$\hat{\rho}_{(\pm)}(\mathbf{x}) \equiv (+q,-1)\sum_{(\pm)} \delta\left(\mathbf{x}-\mathbf{x}_n\right) \tag{2}$$

so that the total charge density is $\hat{\rho}(\mathbf{x}) = \hat{\rho}_{(+)}(\mathbf{x}) + \hat{\rho}_{(-)}(\mathbf{x})$. The cations are polyvalent, with valency q, and the anions are univalent $q=1$. The ensemble averaged forms of the above order parameters are defined as

$$\left\langle \hat{\mathcal{Q}}_{ij}(\mathbf{x})\right\rangle = c_+(\mathbf{x})\,\mathcal{S}(\mathbf{x})\,\tfrac{3}{2}\left(\mathbf{n}_i(\mathbf{x})\mathbf{n}_j(\mathbf{x}) - \tfrac{1}{3}\delta_{ij}\right) \tag{3}$$

and

$$\left\langle \hat{\rho}_+(\mathbf{x})\right\rangle = qc_+(\mathbf{x}), \qquad \left\langle \hat{\rho}_-(\mathbf{x})\right\rangle = -c_-(\mathbf{x}), \tag{4}$$

where the corresponding thermodynamic densities of the rod cations and anions are $c_+(\mathbf{x}), c_-(\mathbf{x})$ and the nematic scalar order parameter is $\mathcal{S}(\mathbf{x})$.

The microscopic Hamiltonian is assumed to be of the general Lebwohl-Lasher type, though in the original formulation it was assumed to act only between nearest neighbors [46]. This constraint was relaxed in a recent analytical formulation [47]. By assumption then

$$\mathcal{H}[\mathbf{r}_n,\mathbf{n}_n] = \tfrac{1}{2}\sum_{n,m} u_{QQ}(\mathbf{x}_n-\mathbf{x}_m)\left(\left(\mathbf{n}_n\mathbf{n}_m\right)^2 - \tfrac{1}{3}\right) + \tfrac{1}{2}\sum_{n,m} u_{\rho\rho}(\mathbf{x}_n-\mathbf{x}_m), \tag{5}$$

where n,m run over all the particles in the system and $\mathbf{n}_n,\ \mathbf{n}_m$ are the unit directors of the n-th and m-th particles. The interaction strengths are all expressed in thermal units.

The angular part of the Onsager's nematic interaction between two spherocylinders of length L and diameter $2D$ is $2L^2D\sin(\mathbf{n},\mathbf{n}')$ [22], where $\mathbf{n},\ \mathbf{n}'$ are the unit direction vectors of the two particles is also related to the above *Ansatz*. In fact it was shown by Doi [48] that

$$\sin(\mathbf{n},\mathbf{n}') = \tfrac{\pi}{4}\left(1-\tfrac{15}{16}\left(\mathbf{n}_i\mathbf{n}_j-\tfrac{1}{3}\delta_{ij}\right)\left(\mathbf{n}'_i\mathbf{n}'_j-\tfrac{1}{3}\delta_{ij}\right)\right), \tag{6}$$

where the next order term corresponds to 4th rank irreducible tensors. The Onsager interactions are thus - at least to the lowest order - equivalent to the first term in Eq. 5, where the nematic interaction has a delta function range. The theory presented here therefore incorporates to the lowest order also the standard Onsager results.

The interaction energy Eq. 5 can be clearly recast as

$$\mathcal{H}[\mathbf{r}_n,\mathbf{n}_n] = \tfrac{1}{2}\iint_V d\mathbf{x}d\mathbf{x}'\ \hat{\mathcal{Q}}_{ij}(\mathbf{x})u_{QQ}(\mathbf{x}-\mathbf{x}')\hat{\mathcal{Q}}_{ij}(\mathbf{x}') + \tfrac{1}{2}\iint_V d\mathbf{x}d\mathbf{x}'\ \hat{\rho}(\mathbf{x})u_{\rho\rho}(\mathbf{x}-\mathbf{x}')\hat{\rho}(\mathbf{x}'), \tag{7}$$

where we further assume that the orientational interaction is short-ranged and that the scalar part is due to the long-range electrostatic interactions. The coupling between the two is omitted to the lowest order but can be considered for e.g. dipolar or quadrupolar rods. The self-energies which were also omitted from the formula above can be absorbed into the chemical potential when defining the grand canonical partition function.

1.2. Grand canonical partition function

The grand canonical partition function for this two component system is defined standardly as

$$\Xi[\mathbf{r}_n,\mathbf{n}_n] = \sum_{N^+}\sum_{N_{(-)}}\frac{\lambda_{(+)}^{N^+}\lambda_{(-)}^{N^-}}{N^+!N^-!}\,\mathcal{Q}_{N^+N^-}[\mathbf{r}_n,\mathbf{n}_n] \tag{8}$$

while

$$\mathcal{Q}_{N^+N^-}[\mathbf{r}_n,\mathbf{n}_n] = \int\!\dots\!\int \mathcal{D}[\mathbf{x}_n]\mathcal{D}[\mathbf{n}_m]\ e^{-\beta\mathcal{H}[\mathbf{r}_n,\mathbf{n}_n]}, \tag{9}$$

where the integral over the orientational degrees of freedom, $[\mathbf{n}_m]$, is only over the cationic species. Introducing the "decomposition of unit" in the form

$$1 \equiv \int\mathcal{D}[\mathcal{Q}_{ij}(\mathbf{x})]\ \Pi_{\mathbf{x}}\delta(\mathcal{Q}_{ij}(\mathbf{x})-\hat{\mathcal{Q}}_{ij}(\mathbf{x}))\times\int\mathcal{D}[\rho(\mathbf{x})]\ \Pi_{\mathbf{x}}\delta(\rho(\mathbf{x})-\hat{\rho}(\mathbf{x})), \tag{10}$$

together with the functional integral representation with auxiliary potentials $\phi(\mathbf{x})$ and $\Phi_{ij}(\mathbf{x})$ for the functional delta functions, one then remains with the following form of the partition function

$$\begin{aligned}\Xi[\mathbf{r}_n,\mathbf{n}_n] = & \int\mathcal{D}[\mathcal{Q}_{ij}(\mathbf{x})]\mathcal{D}[\Phi_{ij}(\mathbf{x})]\times\\ & \int\mathcal{D}[\rho(\mathbf{x})]\mathcal{D}[\phi(\mathbf{x})]\ e^{-\beta\tilde{\mathcal{H}}[\mathcal{Q}_{ij}(\mathbf{x}),\,\rho(\mathbf{x})]}\times\\ & \sum_{N^+}\sum_{N_{(-)}}\frac{\lambda_{(+)}^{N^+}\lambda_{(-)}^{N^-}}{N^+!N^-!}\int\mathcal{D}[\mathbf{x}_n]\mathcal{D}[\mathbf{n}_m]\ e^{-\beta\tilde{\mathcal{H}}^*[\mathbf{x}_n,\mathbf{n}_m]}\end{aligned} \tag{11}$$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

where we introduced the field coupling part, $\mathcal{H}[\mathcal{Q}_{ij}(\mathbf{x}),\ \rho(\mathbf{x})]$, that stems from the two decompositions of unit as well as the interaction energy written with the collective coordinates, in the form

$$\begin{aligned}-\beta\tilde{\mathcal{H}}[\mathcal{Q}_{ij}(\mathbf{x}),\ \rho(\mathbf{x})] \quad = \quad & -\tfrac{1}{2}\iint_V d\mathbf{x}d\mathbf{x}'\ \mathcal{Q}_{ij}(\mathbf{x})u_{QQ}(\mathbf{x}-\mathbf{x}')\mathcal{Q}_{ij}(\mathbf{x}') - \tfrac{1}{2}\iint_V d\mathbf{x}d\mathbf{x}'\ \rho(\mathbf{x})u_{\rho\rho}(\mathbf{x}-\mathbf{x}')\rho(\mathbf{x}') - \\ & - i\int_V d\mathbf{x}\ \mathcal{Q}_{ij}(\mathbf{x})\Phi_{ij}(\mathbf{x}) - i\int_V d\mathbf{x}\ \rho(\mathbf{x})\phi(\mathbf{x}), \end{aligned} \tag{12}$$

while the configurational part in the internal space of the particles has the form

$$\begin{aligned}-\beta\tilde{\mathcal{H}}^*[\mathbf{r}_n, \mathbf{n}_n] \quad &= \quad i\int_V d\mathbf{x}\ \hat{\mathcal{Q}}_{ij}(\mathbf{x})\Phi_{ij}(\mathbf{x}) + i\int_V d\mathbf{x}\ \hat{\rho}(\mathbf{x})\phi(\mathbf{x}) = \\ &= \quad i\sum_{(+)}\tfrac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \tfrac{1}{3}\delta_{ij}\right)\Phi_{ij}(\mathbf{x}_i) +\ iq\sum_{(+)}\ \phi(\mathbf{x}_i) - i\sum_{(-)}\ \phi(\mathbf{x}_i), \end{aligned} \tag{13}$$

where we explicitly used the definitions of the microscopic scalar charge density and the microscopic tensor nematic order parameter density, Eqs. 2 and 1.

$\tilde{\mathcal{H}}^*[\mathbf{r}_n, \mathbf{n}_n]$ is diagonal in the internal space of the particles so that

$$\sum_{N^+}\sum_{N^-}\frac{\lambda_{(+)}^{N^+}\lambda_{(-)}^{N^-}}{N^+!N^-!}\int\mathcal{D}[\mathbf{x}_n]\mathcal{D}[\mathbf{n}_n]\ e^{-\beta\tilde{\mathcal{H}}^*[\mathbf{r}_n,\mathbf{n}_n]} \quad = \quad e^{-\beta\mathcal{H}}, \tag{14}$$

after summing separately and explicitly over both N^+ and N^-, with

$$-\beta\mathcal{H} = \lambda_{(+)}\int_V d\mathbf{r}e^{iq\phi(\mathbf{x})+\ln\mathcal{P}(\mathbf{x})} + \lambda_{(-)}\int_V d\mathbf{r}e^{-i\phi(\mathbf{x})}. \tag{15}$$

Here we introduced the orientational partition function of a single particle

$$\mathcal{P}(\Phi_{ij}(\mathbf{x})) \equiv \left\langle e^{i\frac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \frac{1}{3}\delta_{ij}\right)\Phi_{ij}(\mathbf{x})}\right\rangle_\Omega. \tag{16}$$

The orientational trace is defined in such a way that $< 1 >_\Omega = 1$. The log of this expression is actually the orientational entropy of the rods. Were the field $\Phi_{ij}(\mathbf{x})$ pure imaginary, the above distribution would correspond to the Bingham distribution, and the $\Phi_{ij}(\mathbf{x})$ field would be playing the role of the Bingham field.

Since the $\mathcal{Q}_{ij}(\mathbf{x})$ and $\rho(\mathbf{x})$ functional integrals in Eq. 11 are obviously Gaussian, these variables can be integrated out explicitly, yielding a pure field theoretical representation of the original configurational partition function Eq. 8 in terms of the tensor, $\Phi_{ij}(\mathbf{x})$, and scalar, $\phi(\mathbf{x})$, fields with

$$\Xi[\Phi_{ij}(\mathbf{x});\phi(\mathbf{x})] \quad = \quad \int\mathcal{D}[\Phi_{ij}(\mathbf{x})]\int\mathcal{D}[\phi(\mathbf{x})]\ e^{-\beta\underline{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\phi(\mathbf{x})]}, \tag{17}$$

where the effective field action is finally obtained in a highly non-linear form

$$\begin{aligned}-\beta\underline{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\ \phi(\mathbf{x})] \quad = \quad & -\tfrac{1}{2}\iint_V d\mathbf{x}d\mathbf{x}'\ \Phi_{ij}(\mathbf{x})u_{QQ}^{-1}(\mathbf{x}-\mathbf{x}')\Phi_{ij}(\mathbf{x}') - \tfrac{1}{2}\iint_V d\mathbf{x}d\mathbf{x}'\ \phi(\mathbf{x})u_{\rho\rho}^{-1}(\mathbf{x}-\mathbf{x}')\phi(\mathbf{x}') + \\ & + \lambda_{(+)}\int_V d\mathbf{x}\ e^{iq\phi(\mathbf{x})+\ln\mathcal{P}(\Phi_{ij}(\mathbf{x}))} + \lambda_{(-)}\int_V d\mathbf{x}\ e^{-i\phi(\mathbf{x})} - \\ & -\tfrac{1}{2}\ln\mathrm{Det}\big(u_{QQ}(\mathbf{x}-\mathbf{x}')\big) - \tfrac{1}{2}\ln\mathrm{Det}\big(u_{\rho\rho}(\mathbf{x}-\mathbf{x}')\big). \end{aligned} \tag{18}$$

The formal identity of the configurational, Eq. 8, and auxiliary field representations, Eq. 17, can be recapitulated as

$$\Xi[\mathbf{r}_n,\mathbf{n}_n] = \Xi[\Phi_{ij}(\mathbf{x});\phi(\mathbf{x})]. \tag{19}$$

The steps leading to this identity are analogous to the case of Edwards transform for the Coulomb fluid partition function [49], except for the orientational Lebwohl-Lescher part that leads to a tensor order parameter and a tensor auxiliary field.

The equivalence is formal and further steps are needed to actually calculate the functional integrals of the very non-linear field action. We will eventually take recourse to the saddle-point approximation which is, in the case of the Coulomb fluid, equivalent to the mean-field Poisson-Boltzmann approximation.

Notably, the two fluctuational *TrLog* expressions at the end of the above equation pertain to the Casimir-type fluctuation terms [49] and would be combined with the fluctuational determinant of the second order expansion of the above field theory. We will not delve into these details here and will omit them in what follows.

2. Field theory

2.1. Order parameters and auxiliary fields

We now investigate the consequences of the field-theoretical formulation of the partition function for the microscopic model under consideration. First we need to find a physical meaning of the two formal auxiliary fields that were introduced above. This proceeds similarly to the field-theoretical formulation of the Coulomb fluid partition function.

One notes that in the case of an added ghost source charge density, $\rho^0(\mathbf{x}) = \rho^0_+(\mathbf{x}) - \rho^0_-(\mathbf{x})$, and/or an added ghost quadrupolar orientational order density, $\mathcal{Q}^0{}_{ij}(\mathbf{x})$, Eq. 7 acquires two additional terms

$$\mathcal{H}[\mathbf{r}_n,\mathbf{n}_n] \longrightarrow \mathcal{H}[\mathbf{r}_n,\mathbf{n}_n] + \iint_V d\mathbf{x}d\mathbf{x}'\; \mathcal{Q}^0{}_{ij}(\mathbf{x})u_{QQ}(\mathbf{x}-\mathbf{x}')\hat{\mathcal{Q}}_{ij}(\mathbf{x}') + \iint_V d\mathbf{x}d\mathbf{x}'\; \rho^0(\mathbf{x})u_{\rho\rho}(\mathbf{x}-\mathbf{x}')\hat{\rho}(\mathbf{x}'). \tag{20}$$

Repeating now the steps leading to Eq. 18 one then obtains the effective field action for the two-component field theory with ghost sources as

$$-\beta\underline{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\;\phi(\mathbf{x})] \longrightarrow -\beta\underline{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\;\phi(\mathbf{x})] + i\int_V d\mathbf{x}\;\mathcal{Q}^0{}_{ij}(\mathbf{x})\Phi_{ij}(\mathbf{x}) + i\int_V d\mathbf{x}\;\rho^0(\mathbf{x})\phi(\mathbf{x}). \tag{21}$$

It then follows straighforwardly that

$$\frac{\delta\ln\Xi[\Phi_{ij}(\mathbf{x});\phi(\mathbf{x})]}{\delta\mathcal{Q}^0(\mathbf{x})} \equiv i\Big\langle\Phi_{ij}(\mathbf{x})\Big\rangle, \tag{22}$$

and similarly

$$\frac{\delta\ln\Xi[\Phi_{ij}(\mathbf{x});\phi(\mathbf{x})]}{\delta\rho^0{}_{ij}(\mathbf{x})} \equiv i\Big\langle\phi(\mathbf{x}')\Big\rangle. \tag{23}$$

Rearranging these equations obtained from Eq. 21, one can derive a set of two other equations stemming from the derivatives of Eq. 20, thus ending up with two general identities

$$\Big\langle\hat{\mathcal{Q}}_{ij}(\mathbf{x})\Big\rangle = -i\int_V d\mathbf{x}'\; u^{-1}_{QQ}(\mathbf{x}-\mathbf{x}')\Big\langle\Phi_{ij}(\mathbf{x}')\Big\rangle, \tag{24}$$

and analogously

$$\left\langle \hat{\rho}(\mathbf{x}) \right\rangle = -i \int_V d\mathbf{x}' \, u_{\rho\rho}^{-1}(\mathbf{x}-\mathbf{x}') \left\langle \phi(\mathbf{x}') \right\rangle, \tag{25}$$

that we will use later in their saddle-point variant. The latter identity establishes the thermodynamic average $i\langle \phi(\mathbf{x}) \rangle$ as the average of the *electrostatic potential*, and the former establishes the average $i\langle \Phi_{ij}(\mathbf{x}) \rangle$ as the average of the *nematic potential*. One should note that these are general expressions valid exactly without any approximations. Clearly, the auxiliary fields and the order parameters are dual to one another.

2.2. Thermodynamic relations

The fields and order parameters need to satisfy several thermodynamic relations. There is first the thermodynamic identity involving the fugacity and the average number of molecules in the system

$$\begin{aligned} N_+ &= \lambda_+ \frac{\partial \ln \Xi[\Phi_{ij}(\mathbf{x}); \phi(\mathbf{x})]}{\partial \lambda_+} = \\ &= \lambda_+ \int_V d\mathbf{x} \left\langle e^{iq\phi(\mathbf{x}) + \ln \mathcal{P}(\Phi_{ij}(\mathbf{x}))} \right\rangle \end{aligned} \tag{26}$$

and

$$\begin{aligned} N_- &= \lambda_- \frac{\partial \ln \Xi[\Phi_{ij}(\mathbf{x}); \phi(\mathbf{x})]}{\partial \lambda_-} = \\ &= \lambda_- \int_V d\mathbf{x} \left\langle e^{-i\phi(\mathbf{x})} \right\rangle. \end{aligned} \tag{27}$$

Another general relation is derived from the invariance of the functional integral with respect to the linear transformation of the fluctuating fields. This immediately yields two relations

$$\left\langle \frac{\delta \underline{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\ \phi(\mathbf{x})]}{\delta \Phi_{ij}(\mathbf{x})} \right\rangle = 0 \tag{28}$$

and

$$\left\langle \frac{\delta \underline{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\ \phi(\mathbf{x})]}{\delta \phi(\mathbf{x})} \right\rangle = 0, \tag{29}$$

where the averages stand for

$$\left\langle \ldots \right\rangle = \frac{\int \mathcal{D}[\Phi_{ij}(\mathbf{x})] \int \mathcal{D}[\phi(\mathbf{x})] \ \ldots \ e^{-\beta \underline{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\phi(\mathbf{x})]}}{\int \mathcal{D}[\Phi_{ij}(\mathbf{x})] \int \mathcal{D}[\phi(\mathbf{x})] \ e^{-\beta \underline{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\phi(\mathbf{x})]}}. \tag{30}$$

Distinguishing between the normalized

$$\left\langle\!\left\langle \ldots \right\rangle\!\right\rangle_\Omega = \frac{\left\langle (\ldots) e^{i\frac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \frac{1}{3}\delta_{ij}\right)\Phi_{ij}(\mathbf{x})} \right\rangle_\Omega}{\left\langle e^{i\frac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \frac{1}{3}\delta_{ij}\right)\Phi_{ij}(\mathbf{x})} \right\rangle_\Omega} \tag{31}$$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

and unnormalized orientational averages with respect to the distribution Eq. 16, one derives from Eqs. 28 and 29 that

$$\begin{aligned}\left\langle \hat{\mathcal{Q}}_{ij}(\mathbf{x})\right\rangle &= -i\int_V d\mathbf{x}'\ u^{-1}_{QQ}(\mathbf{x}-\mathbf{x}')\left\langle \Phi_{ij}(\mathbf{x}')\right\rangle = \\ &= -i\lambda_{(+)}\left\langle \frac{\partial \ln \mathcal{P}(\Phi_{ij}(\mathbf{x}))}{\partial \Phi_{ij}(\mathbf{x})} e^{iq\phi(\mathbf{x})+\ln \mathcal{P}(\Phi_{ij}(\mathbf{x}))}\right\rangle = \\ &= \lambda_{(+)}\left\langle \left\langle\!\left\langle \tfrac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \tfrac{1}{3}\delta_{ij}\right)\right\rangle\!\right\rangle_\Omega e^{iq\phi(\mathbf{x})+\ln \mathcal{P}(\Phi_{ij}(\mathbf{x}))}\right\rangle,\end{aligned} \tag{32}$$

where we took into account the definition of the double brackets Eq. 31. Furthermore by analogy

$$\begin{aligned}\left\langle \rho(\mathbf{x})\right\rangle &= -i\int_V d\mathbf{x}'\ u^{-1}_{\rho\rho}(\mathbf{x}-\mathbf{x}')\left\langle \phi(\mathbf{x}')\right\rangle = \\ &+ q\lambda_{(+)}\left\langle\ e^{iq\phi(\mathbf{x})+\ln \mathcal{P}(\Phi_{ij}(\mathbf{x}))}\right\rangle - \lambda_{(-)}\left\langle e^{-i\phi(\mathbf{x})}\right\rangle.\end{aligned} \tag{33}$$

Note the difference between the thermodynamic averages $\left\langle \dots \right\rangle$ and the orientational averages $\left\langle \dots \right\rangle_\Omega$.

On the saddle-point level we will soon see that the above two equations are actually the modified Maier-Saupe (MS) self-consistent equation and the modified Poisson-Boltzmann (PB) self-consistent equation for the tensor and scalar fields, respectively.

3. Mean-field approximation

3.1. Maier-Saupe and Poisson-Boltzmann equations

Since the field action Eq. 18 is non-linear, no further exact developments are feasible and one needs to resort to the *saddle-point approximation* that yields two mean-field equations for the two fields.

At the saddle-point the fields are pure imaginary, so that one can transform

$$\Phi_{ij}(\mathbf{x}) \longrightarrow -i\Phi^*_{ij}(\mathbf{x}) \quad \text{and} \quad \phi(\mathbf{x}) \longrightarrow i\phi^*(\mathbf{x}). \tag{34}$$

The thermodynamic averages $\left\langle \dots \right\rangle$ are given at the value of the mean-field, and the two self-consistent field equations, Eqs. 24, 25, are then reduced to

$$\begin{aligned}\left\langle \hat{\mathcal{Q}}_{ij}(\mathbf{x})\right\rangle &= -\int_V d\mathbf{x}'\ u^{-1}_{QQ}(\mathbf{x}-\mathbf{x}')\Phi^*_{ij}(\mathbf{x}') = \\ &= \lambda_{(+)}\left\langle\!\left\langle \tfrac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \tfrac{1}{3}\delta_{ij}\right)\right\rangle\!\right\rangle_\Omega e^{-q\phi^*(\mathbf{x})+\ln \mathcal{P}(-i\Phi^*_{ij}(\mathbf{x}))},\end{aligned} \tag{35}$$

as well as

$$\begin{aligned}\left\langle \rho(\mathbf{x})\right\rangle &= \int_V d\mathbf{x}'\ u^{-1}_{\rho\rho}(\mathbf{x}-\mathbf{x}')\phi^*(\mathbf{x}') = \\ &+ q\lambda_{(+)}\ e^{-q\phi^*(\mathbf{x})+\ln \mathcal{P}(-i\Phi^*_{ij}(\mathbf{x}))} - \lambda_{(-)}\ e^{+\phi^*(\mathbf{x})},\end{aligned} \tag{36}$$

with the orientational partition function Eq. 16 as

$$\mathcal{P}(-i\Phi^*_{ij}(\mathbf{x})) \equiv \left\langle e^{\frac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j-\frac{1}{3}\delta_{ij}\right)\Phi^*_{ij}(\mathbf{x})}\right\rangle_{\Omega}. \tag{37}$$

In what follows we will assume a short range attractive orientational potential and a Coulombic positional potential. This implies

$$u^{-1}_{QQ}(\mathbf{x}-\mathbf{x}') = -u^{-1}_{QQ}(0)\delta(\mathbf{x}-\mathbf{x}') \tag{38}$$

and

$$u^{-1}_{\rho\rho}(\mathbf{x}-\mathbf{x}') = -\varepsilon\nabla^2\delta(\mathbf{x}-\mathbf{x}') \tag{39}$$

where $\varepsilon \equiv \epsilon_0\epsilon$, with ϵ the dielectric permittivity of the solvent and ϵ_0 the permittivity of space.

With this in mind we then derive the tensorial part in the form of a modified Meier-Saupe equation

$$-u^{-1}_{QQ}(0)\;\Phi^*_{ij}(\mathbf{x}) + c_{(+)}\left\langle\!\!\left\langle \tfrac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \tfrac{1}{3}\delta_{ij}\right)\right\rangle\!\!\right\rangle_{\Omega} = 0. \tag{40}$$

We will see that the Maier-Saupe equation determines only the nematic order parameter but not the orientation in the ordered phase, which is assumed to be homogeneous. To describe orientational relaxation effects one needs also the elastic deformation energy which would stem from the expansion of the orientation interaction potential w.r.t. the gradient of the tensorial order.

The scalar part of the mean-field equations can be written in the form of the Poisson-Boltzmann equation as

$$\varepsilon\nabla^2\phi^*(\mathbf{x}) + qc_{(+)} - c_{(-)} = 0, \tag{41}$$

where we introduced the mean-field cationic and anionic densities as

$$\begin{aligned} c_{(+)}(\phi^*(\mathbf{x})) &= \lambda_{(+)}\; e^{-q\phi^*(\mathbf{x})+\ln\mathcal{P}(-i\Phi^*_{ij}(\mathbf{x}))} \\ c_{(-)}(\phi^*(\mathbf{x})) &= \lambda_{(-)}\; e^{+\phi^*(\mathbf{x})}. \end{aligned} \tag{42}$$

The two mean-field equations Eqs. 40 and 41 correspond to the nematic and electrostatic degrees of freedom in a similar manner that the Edwards and the polymer Poisson-Boltzmann equation correspond to polymer and electrostatic degrees of freedom for charged flexible polymers [50,51]. Consequently any other degree of freedom would introduce its own mean-field equation.

Inserting the mean-field *Ansatz* into the free energy Eq. 18 we obtain the general form of the mean-field free energy $\mathcal{F}[\Phi^*_{ij}(\mathbf{x});\ \phi^*(\mathbf{x})]$ as a functional of the *mean-field nematic potential*, $\Phi^*_{ij}(\mathbf{x})$, and the *mean-field electrostatic potential*, $\phi^*(\mathbf{x})$ as

$$\begin{aligned} \beta\mathcal{F}[\Phi^*_{ij}(\mathbf{x});\ \phi^*(\mathbf{x})] = \; = \; & -\tfrac{1}{2}\iint_V d\mathbf{x}d\mathbf{x}'\;\Phi^*_{ij}(\mathbf{x})u^{-1}_{QQ}(\mathbf{x}-\mathbf{x}')\Phi^*_{ij}(\mathbf{x}') - \tfrac{1}{2}\iint_V d\mathbf{x}d\mathbf{x}'\;\phi^*(\mathbf{x})u^{-1}_{\rho\rho}(\mathbf{x}-\mathbf{x}')\phi^*(\mathbf{x}') - \\ & -\lambda_{(+)}\int_V d\mathbf{x}\; e^{-q\phi^*(\mathbf{x})+\ln\mathcal{P}(-i\Phi_{ij}(\mathbf{x}))} - \lambda_{(-)}\int_V d\mathbf{x}\; e^{+\phi^*(\mathbf{x})}. \end{aligned} \tag{43}$$

The mean field free energy can be derived also from the Onsager theory as was done by Doi [48]. We recapitulate this alternative derivation as it applies to our model in the Appendix.

The mean-field theory for calamitic cations thus decouples into the MS equation for simple liquid crystals and the PB equation for simple Coulomb fluids, except that formally the electrostatic potential of the calamitic cations is transformed to $q\phi^*(\mathbf{x}) \longrightarrow q\phi^*(\mathbf{x}) - \ln\mathcal{P}(-i\Phi^*_{ij}(\mathbf{x}))$.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

The theory was formulated specifically for a rod-like cationic species and a point-like anionic species, but based on the methodology other possibilities are just as amenable to the same procedure of deriving the field theory as well as the mean-field equations.

3.2. Solution of the mean-field equations

There are of course countless cases that one can dwell on in order to apply the general theory, and therefore some selectivity is in order. In what follows we shall delimit ourselves to the case of a rod-like counterion-only system in the presence of a single electrified surface so that the only spatial dependence is in the direction of the surface normal, which we choose to coincide with the z axis. This tallies with the paradigmatic case in the solution of the ordinary PB equation for a counterion-only system.

The scalar mean-field equation in this case is the modified Poisson-Boltzmann equation that is obtained as

$$\varepsilon \phi^{*\prime\prime}(z) + q c_{(+)}(\phi^*(z)) = 0, \tag{44}$$

where $\phi^{*\prime\prime}(z) = \frac{d^2\phi^*(z)}{dz^2}$ is the second derivative of the mean potential with respect to z and $c_{(+)}(\phi^*(z))$ is given by Eq. 42. Comparing the above expression with the standard PB equation for a point-like counterion-only case, the difference is manifest in the sense that the mean-field single ion free energy includes also the orientational entropy of the rods, equal to $\ln \mathcal{P}(-i\Phi^*_{ij}(\mathbf{x}))$. We will solve this equation later.

First we analyse the tensor mean-field equation, *i.e.*, the modified Maier-Saupe equation. Since the tensor auxiliary field and the tensor order parameter are dual, we can assume a non-vanishing orientational order characterized with the director $\hat{\mathbf{n}}$

$$\Phi^*_{ij}(zz) \quad = \quad s(z)\,\tfrac{3}{2}\left(\hat{\mathbf{n}}_i\hat{\mathbf{n}}_j - \tfrac{1}{3}\delta_{ij}\right), \tag{45}$$

and analyze the mean-field equations as to whether this *Ansatz* indeed solves them. The director $\hat{\mathbf{n}}$ is not specified but would be set by *e.g.* Rapini-Papoular surface free energy, which we did not invoke explicitly since the Maier-Saupe equation is local and thus valid for any local orientation. The parameter $s(z)$ is proportional but not equal to the nematic order parameter.

One can recall, Eq. 3 and Eq. 45, which means that

$$\begin{aligned} \mathcal{Q}^*_{ij} = u^{-1}_{QQ}(0)\Phi^*_{ij} = u^{-1}_{QQ}(0)s\,\tfrac{3}{2}\left(\hat{\mathbf{n}}_i\hat{\mathbf{n}}_j - \tfrac{1}{3}\delta_{ij}\right) = \\ = c_+\,\mathcal{S}\,\tfrac{3}{2}\left(\hat{\mathbf{n}}_i\hat{\mathbf{n}}_j - \tfrac{1}{3}\delta_{ij}\right) \end{aligned} \tag{46}$$

wherefrom we derive the connection between the nematic order parameter $\mathcal{S}$ and the parameter s introduced in Eq. 45 as

$$\mathcal{S} = \frac{s}{u_{QQ}(0)\,c_+}, \tag{47}$$

where c_+ is given by Eq. 42. In the above formula s is a coefficient of $\Phi^*_{ij}(z)$ in Eq. 45, while $\mathcal{S}$ is an orientational order parameter, so that it is strictly limited to the interval $0 \leq \mathcal{S} \leq 1$.

Then we see that the exponent in Eq. 37 equals

$$\tfrac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \tfrac{1}{3}\delta_{ij}\right)\Phi^*_{ij}(z) \quad = \quad \tfrac{9}{4}s(z)\left((\mathbf{n}\cdot\hat{\mathbf{n}})^2 - \tfrac{1}{3}\right). \tag{48}$$

Multiplying both sides of Eq.40 by $\left(\hat{\mathbf{n}}_i\hat{\mathbf{n}}_j - \frac{1}{3}\delta_{ij}\right)$ this turns out to yield

$$s(z) \quad = \quad \tfrac{3}{2}u_{QQ}(0)c_{(+)}(\phi^*(z))\left\langle\!\!\left\langle (\mathbf{n}\cdot\hat{\mathbf{n}})^2 - \tfrac{1}{3}\right\rangle\!\!\right\rangle_{\Omega}, \tag{49}$$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

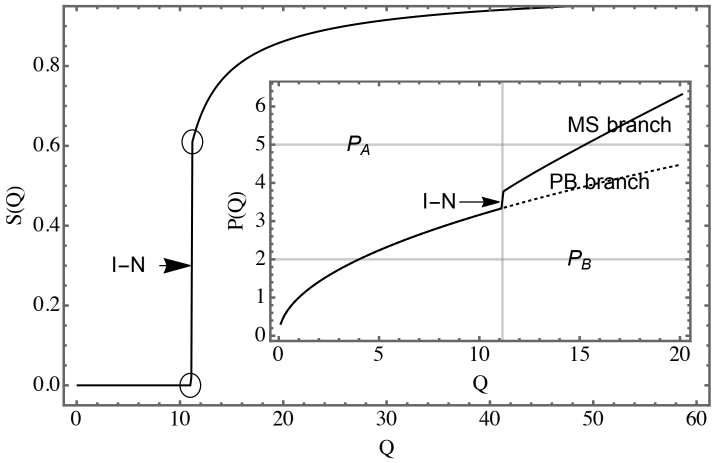

Figure 2. Solution of the Maier-Saupe equation with the phase portrait. The dependence of the nematic order parameter $\mathcal{S}$ on the dimensionless variable Q, defined in Eq. 58. The isotropic-nematic (IN) transition takes place at a critical value $Q_c = 11.15$ and the jump in the order parameter amounts to 0.604 as indicated by the two circles. (Inset) Phase portrait of $P(Q)$ obtained from the mean-field equation, Eq. 59. The solution starts with P_0 obtained from the boundary condition and then moves towards $P = 0$ far away from the surface. If P_0 is above the transition point (P_A intercept) the solution first follows the MS branch (full line) and then at the transition migrates to the PB branch (dotted line) that it follows until the electrostatic field levels off to zero far away from the surface, just as in the case of point-like counterions. On the other hand, if P_0 is below the transition point (P_B intercept), the solution simply follows the PB line as if the counterions are point-like.

Since the above relation is a local one, it remains the same at any position z, and the explicit dependence on the coordinate can be dropped in what follows.

Developing further, this eventually yields

$$\left\langle\!\!\left\langle (\mathbf{n}\cdot\hat{\mathbf{n}})^2 - \tfrac{1}{3} \right\rangle\!\!\right\rangle_\Omega = \left\langle\!\!\left\langle \cos\theta^2 - \tfrac{1}{3} \right\rangle\!\!\right\rangle_\Omega = \frac{\partial}{\partial\gamma} \ln J(\gamma), \tag{50}$$

where $\gamma = \frac{9}{4}s$ and from the definition Eq. 31 it follows that

$$\left\langle\!\!\left\langle \cos\theta^2 - \tfrac{1}{3} \right\rangle\!\!\right\rangle_\Omega = \frac{\left\langle \left(\cos\theta^2 - \frac{1}{3}\right) e^{\gamma\left(\cos\theta^2 - \frac{1}{3}\right)} \right\rangle_\Omega}{\left\langle e^{\gamma\left(\cos\theta^2 - \frac{1}{3}\right)} \right\rangle_\Omega}, \tag{51}$$

which can be indeed written as the logarithmic derivative in Eq. 50. Above the $J(\gamma)$ function has been defined as

$$J(\gamma) = \int_0^1 dz\, e^{\gamma\left(z^2 - \frac{1}{3}\right)} = \frac{e^{\frac{2}{3}\gamma}}{\sqrt{\gamma}} D(\sqrt{\gamma}), \tag{52}$$

with $D(x)$ as the Dawson's integral [52]. The Maier-Saupe expression can then be cast definitively as

$$\gamma = \tfrac{27}{8} u_{QQ}(0) c_+ \frac{\partial}{\partial\gamma} \ln J(\gamma) \tag{53}$$

where $\gamma = \frac{9}{4}s$ and the nematic order parameter is extracted from Eq. 47 as $\mathcal{S} = \gamma/(\frac{9}{4}u_{QQ}(0)\, c_+)$.

Note again that the mean-field Maier-Saupe equation is a local equation that pertains to every point in the domain, which is a consequence of the fact that in the *Ansatz* Eq. 38 we only considered

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

local nematic interactions. A similar path can be pursued also in 2D except that instead of the Dawson integral one ends up with a modified Bessel function integral [53].

Eq. 53 corresponds exactly to the Kleinert formulation [52] of the Maier-Saupe theory, if one takes the coupling strength of nematic interactions equal to $\mathcal{A}_0 = \frac{3}{2}u_{QQ}(0)c_+$, *i.e.*, to the local strength of the nematic potential multiplied by the local density. Obviously, the larger the local density of the rods, the smaller needs to be the orientational interaction driving the isotropic nematic transition.

The solution of the Maier-Saupe equation for $0 \leq \mathcal{S} \leq 1$ exhibits a first order transition at a critical value of $c_{(+)}$, where the order parameter makes a discontinuous jump from an isotropic phase to a nematic phase. More about this solution below.

3.3. First integral and the phase portrait analysis

Introducing now the generalized van't Hoff osmotic pressure as

$$p(\phi^*(z), s(z)) \quad = \quad c_+(\phi^*(z), s(z)), \tag{54}$$

it is possible to write the mean-field equations in a "Lagrangian" form (see Ref. [54])

$$\begin{aligned} \varepsilon\phi^*(z)'' &= \frac{\partial p(\phi^*(z), s(z))}{\partial \phi^*(z)}, \\ s(z) &= -\tfrac{2}{3}u_{QQ}(0)\frac{\partial p(\phi^*(z), s(z))}{\partial s(z)}. \end{aligned} \tag{55}$$

Proceeding now as in the case of the first integral of the Gouy-Chapman theory [55], by multiplying the first equation by $\phi^{*\prime}$ and the second one by $s'(z)$ and then summing them up, we obviously remain with

$$\frac{\partial p}{\partial \phi^*}\phi^{*\prime} + \frac{\partial p}{\partial s(z)}s'(z) = \Big(\varepsilon\phi^*(z)''\phi^*(z)' + \tfrac{3}{2}u_{QQ}(0)^{-1}s(z)s'(z)\Big) = \frac{d}{dz}\Big(\tfrac{1}{2}\varepsilon(\phi^{*\prime}(z))^2 - \tfrac{3}{4}\,u_{QQ}(0)^{-1}s^2(z)\Big), \tag{56}$$

which can be cast into the form of the first integral that generalizes the standard Poisson-Boltzmann result

$$\tfrac{1}{2}\varepsilon(\phi^{*\prime}(z))^2 - \tfrac{3}{4}\frac{s^2(z)}{u_{QQ}(0)} - p(\phi^*(z), s(z)) = const. \tag{57}$$

Because of the assumption of the short range nematic interactions, the field $s(z)$ has no associated "dynamics", *i.e.*, the first integral contains no derivatives of $s(z)$.

The "Lagrange equations" Eq. 55 can be solved and plotted in a phase portrait mode that has been invoked previously by Pandit and Wortis to describe the phase equilibria in lattice models with surfaces and interfaces [56]. The phase portrait method allows for an easy and physical visualization of the types of solutions of the mean-field theories and has been successfully applied also to the case of the Poisson-Boltzmann-type theories [57].

One can now obtain the full implicit form of the solution of the mean-field equations by introducing two new variables

$$\begin{aligned} P &= \sqrt{u_{QQ}(0)\varepsilon}\,\phi^{*\prime}(z) \\ Q &= u_{QQ}(0)\lambda_{(+)}\,e^{-q\phi^*(z)+\ln J\left(\gamma(z)\right)} = u_{QQ}(0)\,c, \end{aligned} \tag{58}$$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

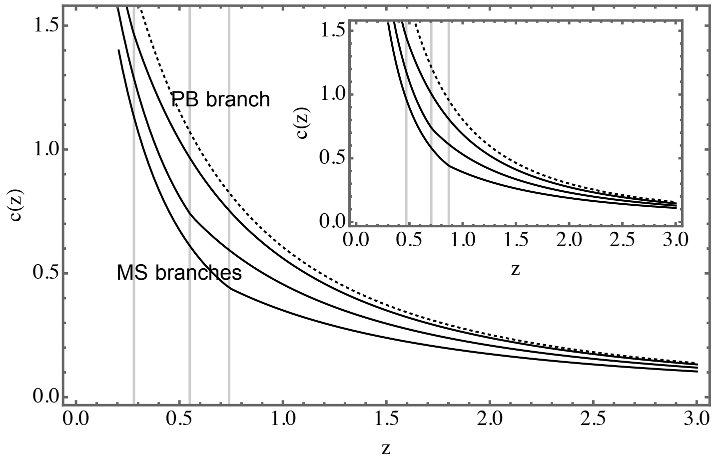

Figure 3. The counterion density profile $c(z)$ at a charged wall, parameterized by c_0 and $u_{QQ}(0)$, obtained from Eq. 65. The distance from the surface z is measured in units of $2q^2/\varepsilon = 8\pi\ell_B\lambda_+$. The parameters are $c_0 = 3.$ and $u_{QQ}(0) = .1$ for the PB branch (dotted curve), while $u_{QQ}(0) = 3., 6., 10.$ on the MS branches (from left to right, full curves). In the inset the only change is $c_0 = .6$, corresponding to a larger surface charge, consistent with the I-N transition at larger values of z. The density profile is continuous everywhere, but displays a discontinuity of the derivative at the I-N transition close to the wall, where the local density more steeply than the GC prediction. The transition point is indicated by the vertical gray lines. For z larger then the I-N transition value the density profile seems to decay in the GC manner but with a smaller renormalized value of the surface charge.

where $c \equiv c_+$ is the counterion density, Eq. 54. Q can thus be interpreted as the dimensionless density of the calamitic counterions. It follows from the first integral Eq. 57 that

$$P = \pm\sqrt{2Q + \tfrac{8}{27}\gamma^2(Q)}, \tag{59}$$

where for a single charged surface the constant in the first integral can be obtained as vanishing, just as in the standard Gouy-Chapman case, meaning that the osmotic pressure of the system is zero. The solution of the problem is therefore completely specified by the dependence $P = P(Q)$, while $\gamma(Q)$ is a solution of

$$\gamma(Q) = \tfrac{27}{8} Q \, \frac{\partial}{\partial\gamma(Q)} \ln J\big(\gamma(Q)\big). \tag{60}$$

Numerical solutions of the above equations are presented in Fig. 2 in the form of the dependence of the nematic order parameter $\mathcal{S}(Q)$ or equivalently the parameter s on the dimensionless calamitic counterion density: $s = s(Q)$, with the jump from zero to 0.604 at the critical value $Q = 11.15$, obviously corresponding to a first order isotropic-nematic transition.

Fig. 2 also shows the phase portrait of the system $P = P(Q)$, Eq. 58. The dotted line in the inset corresponds to the pure PB branch (isotropic branch) while the solid line MS branch (nematic branch) separates from the PB branch at the nematic transition point.

The surface charge density at the bounding surface sets the boundary value to

$$P_0^2 = u_{QQ}(0)\varepsilon\, \phi^{*\prime}(z=0)^2 = u_{QQ}(0)\frac{\sigma^2}{\varepsilon}, \tag{61}$$

which follows directly from the Gauss boundary condition for the electrostatic field at a surface with surface charge density σ, *i.e.* $\varepsilon\phi^{*\prime}(z=0) = \sigma$. The solution then amounts to the $P(Q)$ curve starting at P_0 and then moving along the solution line to $P = 0$.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

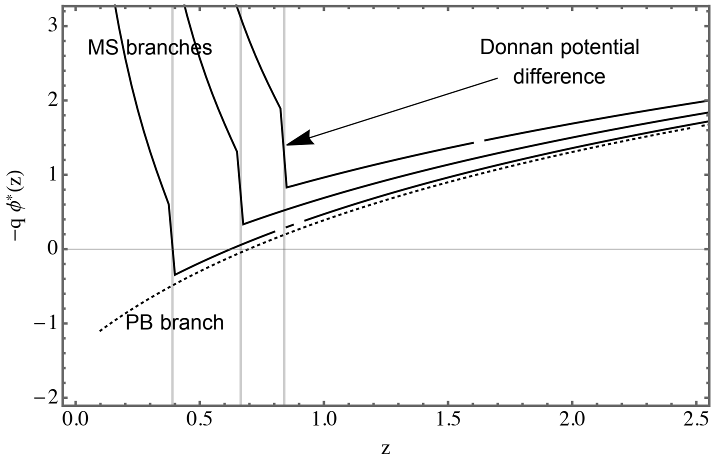

Figure 4. Dimensionless mean electrostatic potential from Eq. 66 as a function of the distance from the surface z, measured in units of $\sqrt{8\pi\ell_B\lambda_+}$. The parameters are $c_0 = 3.$ and $u_{QQ}(0) = .1$ for the PB branch (dotted curve), while $u_{QQ}(0) = 3., 6., 10.$ on the MS branches (from left to right, full curves). As c_0 increases (not shown) the curves are systematically displaced towards larger values of the z coordinate, *viz.*, the I-N transition is displaced away from the surface. At the I-N transition, indicated by the gray vertical lines, there is a discontinuous jump corresponding to the Donnan potential difference, $q\varphi^*_D \simeq 0.99$, corresponding to the phase boundary in the system. Note that the transition lines seem to be skewed and not vertical, but this is purely an artifact of the discrete sampling of the curve.

For P_0 large enough (see the P_A intercept in Fig. 2) the solution first follows the MS branch in the ordered phase until it reaches the transition point. The system thus exhibits an *ordered wetting phase* close to the surface, with a phase boundary at the transition point corresponding to a finite thickness of the wetting layer. After that the solution migrates to the PB branch of a disordered system that it follows until the electrostatic field levels off to zero far away from the surface. On the other hand for P_0 smaller then a critical value (see the P_B intercept in Fig. 2) there is no wetting and the system remains disordered along the whole $P(Q)$ solution, following the PB line as if the counterions are point-like.

Clearly far away from the charged surface the system is disordered while in the proximity to the surface, where electrostatic attraction between the cations and the negatively charged surface increases their local concentration, it orders up, creating a surface wetting layer of the nematic phase.

The final dependence of the mean-field calamitic counterion density as well as the electrostatic potential on the separation from the bounding surface, z, is obtained by integrating the first integral, Eq. 57, as

$$\int_{\phi_0^*}^{\phi^*(z)} \frac{d\phi^*(z)}{\sqrt{\frac{3}{4}u_{QQ}(0)^{-1}s^2(z) + p(\phi^*(z), s(z))}} = q\sqrt{\frac{2}{\varepsilon}}z, \tag{62}$$

where ϕ_0^* is the value at the charged surface. This expression can be modified by taking into account the connection between Q and $\phi^*(z)$ from Eq. 58, leading to

$$\int_{Q(z)}^{Q_0} \frac{dQ}{Q\,\sqrt{2Q + \frac{8}{27}\gamma^2(Q)}} = q\sqrt{\frac{2}{u_{QQ}(0)\varepsilon}}\,z. \tag{63}$$

The value of Q_0 is obtained from the boundary condition and Eq. 61 in the form

$$P_0^2 = u_{QQ}(0)\frac{\sigma^2}{\varepsilon} = 2Q_0 + \tfrac{8}{27}\gamma^2(Q_0), \tag{64}$$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

which yields $Q_0 = Q_0(\sigma, u_{QQ}(0))$. Clearly Q_0 can be either on the MS branch or the PB branch, as is clear from Fig. 3, and consequently the functional dependence on z will depend on the Q_0, too. In the case of an isotropic solution, the equation Eq. 63 yields correctly the standard counterion-only Gouy-Chapman result, as it should.

Evaluating now the integral in Eq. 63 numerically we obtain the general solution to the problem, including the migration from the PB to the MS branch. First we make the substitution $Q = u_{QQ}(0)c$, where c is the calamitic counterion density. Then

$$\int_{c(z)}^{c_0} \frac{dc}{c\,\sqrt{2c + \frac{8}{27}\gamma^2(c)}} = q\sqrt{\frac{2}{\varepsilon}}\,z, \tag{65}$$

with $2q^2/\varepsilon = 8\pi\ell_B\lambda_+$ and ℓ_B the Bjerrum length. The dimensionless distance is thus $\sqrt{8\pi\ell_B\lambda_+}z$. c_0 is the density of the counterions at the bounding charged wall at $z = 0$. c_0 and $u_{QQ}(0)$, implicit in $\gamma(c)$, are the two parameters of the density profile. Inverting the dependence $z = z(c)$ one finally obtains $c(z)$, the dependence of the calamitic counterion density on the separation from the charged wall.

One notices, see Fig. 3, that the $c(z)$ dependence is continuous but displays a discontinuity in the derivative at the isotropic - nematic transition. Nevertheless we will see that the underlying electrostatic potential does display a discontinuity at the wetting phase boundary.

Naively one would assume that the mean field electrostatic potential is proportional to the log of the density, just as in the standard GC case. However, the calamitic counterions also contain the orientational entropy as part of the mean field energy, see Eq. 58, and thus the electrostatic potential is given rather by

$$-q\phi^*(z) = \log \frac{c(z)}{\lambda_{(+)}J\big(\gamma(z)\big)}. \tag{66}$$

While the spatial density profile is itself continuous with the derivative being discontinuous at the I-N transition, the electrostatic potential is discontinuous and displays a *Donnan potential difference* at the transition point.

The Donnan potential difference, ϕ_D^*, can be obtained straightforwardly from Eq. 66 as

$$q\phi_D^* = \log J\big(\gamma_{I-N}\big) = \log J\big(\tfrac{9}{4}s_{I-N}\big), \tag{67}$$

where s_{I-N} is the jump of the orientational order parameter at the $I - N$ transition, P_A case in Fig. 2, and is therefore universal for all the electrostatic potential curves. The value of the Donnan potential difference across the phase boundary can be read off the graph, Fig. 4, as 0.99, which equals exactly $\log J\big(\frac{9}{4} \times 0.604\big)$ according to Eq. 67.

On the other hand, should the Q_0 that corresponds to the boundary condition Eq. 61 fall below the critical value of 11.1, P_B case in Fig. 2, the solution for the electrostatic potential remains on the PB branch for all values of z, displaying no discontinuities.

4. Discussion and conclusions

While one can formulate the theory of inhomogeneous charged calamitic systems on different levels of approximations, we were specifically motivated to remain as close as possible to the Gouy-Chapman theory of point-like ions, the reason being that the Poisson-Boltzmann mean-field framework presents the foundation for the soft matter electrostatics and serves as a standard against which the new developments are usually compared with.

The main feature of the theory presented is the two mean-field equations which present generalizations of the standard Maier-Saupe and Poisson-Boltzmann equations. Their solution for a single charged surface with calamitic counterions leads to the existence of a nematic wetting layer, driven by the interplay of nematic and electrostatic interactions between charged rods and

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

the bounding surface charges. The phase boundary at a finite distance from the surface is in addition characterized by a Donnan potential difference corresponding to the nematic order parameter jump.

Among the possible and obvious generalizations of the present theory we should mention two explicitly. The first one is the non-locality of the nematic interactions which implies the following form for the $u_{QQ}^{-1}(\mathbf{x}-\mathbf{x}')$ interaction

$$u_{QQ}^{-1}(\mathbf{x}-\mathbf{x}') \longrightarrow u_{QQ}^{-1}(0)\left(1+\xi^2\nabla^2\right)\delta(\mathbf{x}-\mathbf{x}'), \tag{68}$$

where ξ is the nematic order correlation length. The non-local form of the interaction potential in its turn leads to a non-local form of the Maier-Saupe equation, Eq. 40, and one ends up with a system of two coupled non-linear differential equations. The no doubt complicated solutions would reduce to those studied above when the nematic correlation length ξ is much smaller then the electrostatic correlation length, *i.e.*, either the Gouy-Chapman length or the Debye length, depending on the composition of the system.

The other possible and obvious generalization would be to include the higher multipolar moments into the interaction energy, Eq. 5, such as the quadrupolar electrostatic term. Formally this can be seen as leading to a modification in Eq. 16 of the form

$$\Phi_{ij}(\mathbf{x}) \longrightarrow \Phi_{ij}(\mathbf{x}) + t\nabla_i\nabla_j\phi(\mathbf{x}), \tag{69}$$

where t is the strength of the quadrupolar moment of the charged rod. This generalization would treat the rod-rod electrostatic interactions more accurately, allowing for the existence of the Odijk effect (preferred perpendicular orientation of the rods) but would again imply a more complicated form of the Poisson-Boltzmann equation of the type that was derived in Refs. [12,49].

In addition, one can also use the present theory to calculate the effective macroscopic dielectric function in the same way as was already done by Andelman *et al.* [37,58,59] in a different context. This can be pursued either from writing the Poisson-Boltzmann equation in the standard form, but with a modified dielectric constant, or by analyzing the second variational derivative of the free energy with respect to the electrostatic fields. Both methodologies yield an explicit expression for the dielectric constant, either local or a non-local one [60].

A variation on the geometry of the model could be pursued for a system confined between two charged surfaces with point-like co-ions. In this case one can either expect a surface nematic wetting transition or indeed a Fredericksz-type transition with a nematic phase between the surfaces and isotropic layers vicinal to the surfaces. These variations in the geometry setup would allow for interesting phenomena also in terms of the effective electrostatic interactions between the bounding surfaces that would no doubt deviate from the standard expectations.

5. Acknowledgement

This work was funded by the Key project #12034019 of the National Science Foundation of China. I would also like to acknowledge the support of the School of physics, University of the Chinese Academy of Sciences, Beijing and of the Institute of physics, Chinese Academy of Sciences, Beijing. Finally I would like to thank D. Andelman for illuminating and helpful discussions.

6. Appendix

Here we will give a short derivation of the mean-field free energy as a function of the scalar and tensor auxiliary fields based on the position and orientation dependent number density. The result will coincide with what we obtained via the field theory saddle point derivation.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

We start by introducing the number density of molecules at $\mathbf{r}$ whose orientation is given by the unit vector $\mathbf{n}$ as $f(\mathbf{x},\mathbf{n})$, so that the number density is defined as

$$\int f_\pm(\mathbf{x},\mathbf{n})d\mathbf{n} = c_\pm(\mathbf{x}), \tag{70}$$

with $\rho(\mathbf{x}) = \sum_\pm q_\pm c_\pm(\mathbf{x})$ being the total charge density. The nematic order parameter density is analogously defined as

$$\int \tfrac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \tfrac{1}{3}\delta_{ij}\right) f_+(\mathbf{x},\mathbf{n})d\mathbf{n} = Q_{ij}(\mathbf{x}). \tag{71}$$

We will later introduce these definitions into the free energy via the appropriate Lagrange multiplier functions.

The free energy as a functional of $f(\mathbf{x},\mathbf{n})$ is next written down in an Onsager form, meaning ideal entropies and the second order interaction terms, assumed of the form [48]

$$\begin{aligned} -\beta\tilde{\mathcal{H}}[f_\pm(\mathbf{x},\mathbf{n})] \quad = \quad & -\iint d\mathbf{n}d\mathbf{x}\sum_\pm \Big(f_\pm(\mathbf{x},\mathbf{n})\ln f_\pm(\mathbf{x},\mathbf{n}) - f_\pm(\mathbf{x},\mathbf{n}) - \mu_\pm f_\pm(\mathbf{x},\mathbf{n})\Big) + \\ & -\tfrac{1}{2}\iint d\mathbf{n}d\mathbf{x}\iint d\mathbf{n}'d\mathbf{x}' \sum_\pm q_\pm f_\pm(\mathbf{x},\mathbf{n})\, u_{\rho\rho}(\mathbf{x}-\mathbf{x}')\, q_\pm f_\pm(\mathbf{x}',\mathbf{n}') + \\ & -\tfrac{1}{2}\iint d\mathbf{n}d\mathbf{x}\iint d\mathbf{n}'d\mathbf{x}'\, \tfrac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \tfrac{1}{3}\delta_{ij}\right) f_+(\mathbf{x},\mathbf{n})\, u_{QQ}(\mathbf{x}-\mathbf{x}')\tfrac{3}{2}\left(\mathbf{n}'_i\mathbf{n}'_j - \tfrac{1}{3}\delta_{ij}\right) f_+(\mathbf{x}',\mathbf{n}'). \end{aligned} \tag{72}$$

$\mu_\pm$ is the corresponding chemical potential. The above expression is related to the standard Onsager theory of nematic ordering when one realizes that the Onsager interaction proportional to

$$\tfrac{1}{2}\int d\mathbf{x}\iint d\mathbf{n}d\mathbf{n}' f_+(\mathbf{x},\mathbf{n})f_+(\mathbf{x},\mathbf{n}')\sin(\mathbf{n},\mathbf{n}') \tag{73}$$

is to the lowest order equivalent to the nematic interaction as discussed before, Eq. 6.

The free energy can then be written with the Lagrange multiplier functions for the scalar charge density, $\phi(\mathbf{x})$, and the tensor nematic order parameter density, $\Phi_{ij}(\mathbf{x})$, that take into account the above two definitions. Minimizing this free energy with respect to the orientational density distribution function one gets the relations for chemical potentials of the Boltzmann form, for the calamitic cations

$$f_+(\mathbf{x},\mathbf{n}) = e^{\beta\mu_+}\ e^{-q_+\phi(\mathbf{x}) + \ln\mathcal{Z}(\Phi_{ij}(\mathbf{x}))} \tag{74}$$

and the simple anions

$$f_-(\mathbf{x},\mathbf{n}) = f_-(\mathbf{x}) = e^{\beta\mu_-}\ e^{-q_-\phi(\mathbf{x})} \tag{75}$$

with the orientational partition function that is defined exactly as in the field-theoretical case

$$\mathcal{Z}(\Phi_{ij}(\mathbf{x})) = \left\langle e^{-\frac{3}{2}\left(\mathbf{n}_i\mathbf{n}_j - \frac{1}{3}\delta_{ij}\right)\Phi_{ij}(\mathbf{x})}\right\rangle_\Omega. \tag{76}$$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

Eliminating finally the number density and the nematic order parameter density fields one remains with the free energy as a function of the two Lagrange multiplier functions, the scalar electrostatic potential and the tensor nematic potential

$$\begin{aligned}-\beta\tilde{\mathcal{H}}[\Phi_{ij}(\mathbf{x});\phi(\mathbf{x})] &= +\lambda_+\int d\mathbf{x}\, e^{-q+\phi(\mathbf{x})+\ln\mathcal{Z}(\Phi_{ij}(\mathbf{x}))} + \lambda_-\int d\mathbf{x}\, e^{+q-\phi(\mathbf{x})} + \\ &+ \tfrac{1}{2}\iint d\mathbf{x}d\mathbf{x}'\,\phi(\mathbf{x})\, u_{\rho\rho}^{-1}(\mathbf{x}-\mathbf{x}')\,\phi(\mathbf{x}') + \tfrac{1}{2}\iint d\mathbf{x}d\mathbf{x}'\,\Phi_{ij}(\mathbf{x})\, u_{QQ}^{-1}(\mathbf{x}-\mathbf{x}')\,\Phi_{ij}(\mathbf{x}',\mathbf{n}').\end{aligned} \tag{77}$$

In fact, this is nothing but the mean-field free energy that was derived before from a field theoretical representation of the partition function, Eq. 43.

References

1. Bernal, J.; Fankuchen, I. The isotropic-nematic transition in charged liquid crystals. *J. Gen. Physiol.* **1941**, *25*, 147–165.
2. Šiber, A.; Božič, A.L.; Podgornik, R. Energies and pressures in viruses: contribution of nonspecific electrostatic interactions. *Phys. Chem. Chem. Phys.* **2012**, *14*, 3746. doi:https://doi.org/10.1039/C1CP22756D.
3. Busseron, E.; Ruff, Y.; Moulin, E.; Giuseppone, N. Supramolecular self-assemblies as functional nanomaterials. *Nanoscale* **2013**, *5*, 7098–7140. doi:10.1039/C3NR02176A.
4. Culver, J.N.; Brown, A.D.; Zang, F.; Gnerlich, M.; Gerasopoulos, K.; Ghodssi, R. Plant virus directed fabrication of nanoscale materials and devices. *Virology* **2015**, *479-480*, 200 – 212. 60th Anniversary Issue, doi:https://doi.org/10.1016/j.virol.2015.03.008.
5. Rong, J.; Niu, Z.; Lee, L.A.; Wang, Q. Self-assembly of viral particles. *Current Opinion in Colloid & Interface Science* **2011**, *16*, 441 – 450. doi:https://doi.org/10.1016/j.cocis.2011.09.001.
6. Yang, S.H.; Chung, W.J.; McFarland, S.; Lee, S.W. Assembly of Bacteriophage into Functional Materials. *The Chemical Record* **2013**, *13*, 43–59, [https://onlinelibrary.wiley.com/doi/pdf/10.1002/tcr.201200012]. doi:https://doi.org/10.1002/tcr.201200012.
7. Tang, J.X.; Wong, S.; Tran, P.T.; Janmey, P.A. Counterion induced bundle formation of rodlike polyelectrolytes. *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 796, [https://onlinelibrary.wiley.com/doi/abs/10.1002/bbpc.19961000620]. doi:https://doi.org/10.1002/bbpc.19961000620.
8. Bellini, T.; Cerbino, R.; Zanchetta, G. DNA-based soft phases. *Top Curr Chem* **2012**, *318*, 225–279. doi:doi:10.1007/128_2011_230.
9. Sanders, L.K.; Xian, W.; Guáqueta, C.; Strohman, M.J.; Vrasich, C.R.; Luijten, E.; Wong, G.C.L. Control of electrostatic interactions between F-actin and genetically modified lysozyme in aqueous media. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 15994–15999, [https://www.pnas.org/content/104/41/15994.full.pdf]. doi:10.1073/pnas.0705898104.
10. Needleman, D.J.; Ojeda-Lopez, M.A.; Raviv, U.; Miller, H.P.; Wilson, L.; Safinya, C.R. Higher-order assembly of microtubules by counterions: From hexagonal bundles to living necklaces. *Proceedings of the National Academy of Sciences* **2004**, *101*, 16099–16103, [https://www.pnas.org/content/101/46/16099.full.pdf]. doi:10.1073/pnas.0406076101.
11. Teif, V.B.; Bohinc, K. Condensed DNA: condensing the concepts. *Progress in biophysics and molecular biology* **2011**, *105*, 208–222. doi:doi.org/10.1016/j.pbiomolbio.2010.07.002.
12. Kanduč, M.; Naji, A.; Jho, Y.S.; Pincus, P.A.; Podgornik, R. The role of multipoles in counterion-mediated interactions between charged surfaces: strong and weak coupling. *J. Phys.: Condens. Matter* **2009**, *21*, 424103.
13. Bohinc, K.; Lue, L. The Interaction Between Like-Charged Nanoparticles Mediated by Rod-Like Ions. *Journal of Nanoscience and Nanotechnology* **2015**, *15*, 3468–3475.
14. Kanduč, M.; Naji, A.; Jho, Y.S.; Pincus, P.A.; Podgornik, R. Charged nanorods at heterogeneously charged surfaces. *J. Phys.: Condens. Matter* **2018**, *149*, 134702.
15. Alvarez Fernandez, A.; Kouwer, P. Key Developments in Ionic Liquid Crystals. *Int J Mol Sci.* **2016**, *17*, 731. doi:10.3390/ijms17050731.
16. Shi, R.; Wang, Y. Dual Ionic and Organic Nature of Ionic Liquids. *Scientific Reports* **2016**, *6*, 19644.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

17. Goossens, K.; Lava, K.; Bielawski, C.W.; Binnemans, K. Ionic Liquid Crystals: Versatile Materials. *Chem. Rev.* **2016**, *116*, 4643–4807.
18. Deutsch, J.M.; Goldenfeld, N.D. Ordering in charged rod fluids. *J. Phys. A: Math. Gen.* **1982**, *15*, L71–L73.
19. Deutsch, J.; Goldenfeld, N. The isotropic-nematic transition in charged liquid crystals. *J. Phys* **1982**, *43*, 651–654.
20. Odijk, T. Theory of Lyotropic Polymer Liquid Crystals. *Macromolecules* **1986**, *19*, 2313.
21. der Schoot, P.V.; Odijk, T. Structure factor of a semidilute solution of rodlike macromolecules. *Macromolecules* **1990**, *23*, 4181–4182. doi:https://doi.org/10.1021/ma00220a023.
22. Vroege, G.J.; Lekkerkerker, H.N.W. Phase transitions in lyotropic colloidal and polymer liquid crystals. *Macromolecules* **1992**, *55*, 1241–1309.
23. Wensink, H.H.; Trizac, E. Generalized Onsager theory for strongly anisometric patchy colloids. *J. Chem. Phys.* **2014**, *140*, 024901.
24. Constantinescu, A.; Jho, Y. Nematic Phase Emergence in Solutions of Similarly Charged Rodlike Polyelectrolytes. *Journal of the Physical Society of Japan* **2014**, *83*, 014002.
25. Bruinsma, R. Liquid crystals of polyelectrolyte networks. *Phys. Rev. E* **2001**, *63*, 061705. doi:10.1103/PhysRevE.63.061705.
26. Eggen, E.; Dijkstra, M.; van Roij, R. Effective shape and phase behavior of short charged rods. *Phys. Rev. E* **2009**, *79*, 041401. doi:10.1103/PhysRevE.79.041401.
27. Potemkin, I.I.; Khokhlov, A.R. Nematic ordering in dilute solutions of rodlike polyelectrolytes. *J. Chem. Phys.* **2004**, *120*, 10848–10851, [https://doi.org/10.1063/1.173939]. doi:10.1063/1.1739393.
28. Lue, L. A variational field theory for solutions of charged, rigid particles. *Fluid Phase Equilibria* **2006**, *241*, 236 – 247. A Festschrift in Honor of John M. Prausnitz, doi:https://doi.org/10.1016/j.fluid.2005.11.007.
29. Carri, G.; Muthukumar, M. Attractive interactions and phase transitions in solutions of similarly charged rod-like polyelectrolytes. *Journal of Chemical Physics* **1999**, *111*, 1765.
30. Levy, A.; Andelman, D.; Orland, H. Dipolar Poisson-Boltzmann approach to ionic solutions: A mean field and loop expansion analysis. *J. Chem. Phys.* **2013**, *139*, 164909. doi:10.1063/1.4826103.
31. Frydel, D. *Mean Field Electrostatics Beyond the Point Charge Description*; Wiley Pub., 2016; pp. 209–260.
32. Ravnik, M.; Everts, J. Topological-Defect-Induced Surface Charge Heterogeneities in Nematic Electrolytes. *Phys. Rev. Letts.* **2020**, *125*, 037801.
33. Bier, M. *Interfaces in fluids of charged platelike colloids*; Max-Planck-Institut fuer Metallforschung, Stuttgart (Disertation), 2007.
34. Kondrat, S.; Bier, M.; Harnau, L. Phase behavior of ionic liquid crystals. *J. Chem. Phys.* **2010**, *132*, 184901. doi:https://doi.org/doi.org/ 10.1063/ 1.3417384.
35. Bier, M.; Harnau, L.; Dietrich, S. Free isotropic-nematic interfaces in fluids of charged platelike colloids. *J. Chem. Phys.* **2005**, *123*, 114906.
36. Bier, M.; Harnau, L.; Dietrich, S. Surface properties of fluids of charged platelike colloids. *J. Chem. Phys.* **2006**, *125*, 184704.
37. Abrashkin, A.; Andelman, D.; Orland, H. Dipolar Poisson-Boltzmann Equation: Ions and Dipoles Close to Charge Interfaces. *Phys. Rev. Lett.* **2007**, *99*, 077801. doi:10.1103/PhysRevLett.99.077801.
38. Azuara, C.; Orland, H.; Bon, M.; Koehl, P.; Delarue, M. Incorporating Dipolar Solvents with Variable Density in Poisson-Boltzmann Electrostatics. *Biophysical Journal* **2008**, *95*, 5587 – 5605. doi:https://doi.org/10.1529/biophysj.108.131649.
39. Budkov, Y. Statistical field theory of ion-molecular solutions. *Phys. Chem. Chem. Phys.* **2020**, *22*, 14756–14772. doi:https://doi.org/10.1039/d0cp02432e.
40. Slavchov, R.I.; Ivanov, T.I. Quadrupole terms in the Maxwell equations: Born energy, partial molar volume, and entropy of ions. *J. Chem. Phys.* **2014**, *140*, 074503. doi:10.1063/1.4865878.
41. Urbanija, J.; Bohinc, K.; Bellen, A.; Maset, S.; Iglic, A.; Kralj-Iglic, V.; Sunil Kumar, P.B. Attraction between negatively charged surfaces mediated by spherical counterions with quadrupolar charge distribution. *J. Chem. Phys.* **2008**, *129*, 105101, [https://doi.org/10.1063/1.2972980]. doi:10.1063/1.2972980.
42. Kim, Y.W.; Yi, J.; Pincus, P.A. Attractions between Like-Charged Surfaces with Dumbbell-Shaped Counterions. *Phys. Rev. Lett.* **2008**, *101*, 208305. doi:10.1103/PhysRevLett.101.208305.
43. Bohinc, K.; Iglič, A.; May, S. Interaction between macroions mediated by divalent rod-like ions. *Europhysics Letters (EPL)* **2004**, *68*, 494–500. doi:10.1209/epl/i2004-10250-2.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 December 2020 doi:10.20944/preprints202012.0323.v1

44. May, S.; Bohinc, K. *Mean-Field Electrostatics of Stiff Rod-Like Ions*; Pan Stanford Publishing Pte. Ltd., 2014; pp. 335–346.
45. Frenkel, D. *Statistical Mechanics of Liquid Crystals*; Les Houches, Session LI, 1991; pp. 693–759.
46. Lebwohl, P.A.; Lasher, G. Nematic-Liquid-Crystal Order—A Monte Carlo Calculation. *Phys. Rev. A* **1972**, *6*, 426–429. doi:10.1103/PhysRevA.6.426.
47. Lu, B.S. Multiscale approach to nematic liquid crystals via statistical field theory. *Phys. Rev. E* **2017**, *96*, 022709.
48. Doi, M. Molecular dynamics and rheological properties of concentrated solutions of rodlike polymers in isotropic and liquid crystalline phases. *Journal of Polymer Science: Polymer Physics Edition* **1981**, *19*, 229–243.
49. Naji, A.; Kanduč, M.; Forsman, J.; Podgornik, R. Perspective: Coulomb fluids -weak coupling, strong coupling, in between and beyond. *J. Chem. Phys.* **2013**, *139*, 150901.
50. Podgornik, R. Self-consistent-field theory for confined polyelectrolyte chains. *J. Phys. Chem.* **1992**, *96*, 884–896. doi:https://doi.org/10.1021/j100181a066.
51. Borukhov, I.; Andelman, D.; Orland, H. Polyelectrolyte Solutions between Charged Surfaces. *Europhysics Letters (EPL)* **1995**, *32*, 499–504. doi:10.1209/0295-5075/32/6/007.
52. Kleinert, H. *Collective Classical and Quantum Fields*; World Scientific, Singapore, 2018.
53. Kumari, S.; Ye, F.; Podgornik, R. Ordering of adsorbed rigid rods mediated by the Boussinesq interaction on a soft substrate. *The Journal of Chemical Physics* **2020**, *153*, 144905, [https://doi.org/10.1063/5.0022556]. doi:10.1063/5.0022556.
54. Maggs, A.C.; Podgornik, R. General theory of asymmetric steric interactions in electrostatic double layers. *Soft Matter* **2016**, *12*, 1219–1229. doi:10.1039/C5SM01757B.
55. Markovich, T.; Andelman, D.; Podgornik, R. *Handbook of Lipid Membranes*; Taylor and Francis, 2020; chapter Charged Membranes: Poisson-Boltzmann theory, DLVO paradigm and beyond.
56. Pandit, R.; Wortis, M. Surfaces and interfaces of lattice models: Mean-field theory as an area-preserving map. *Phys. Rev. B* **1982**, *25*, 3226–3241. doi:10.1103/PhysRevB.25.3226.
57. Gavish, N.; Promislow, K. On the structure of generalized Poisson-Boltzmann equations. *Euro. Journal of Applied Mathematics* **2016**, *27*, 667–685. doi:https://doi.org/doi.org/10.1017/S0956792515000613.
58. Levy, A.; Andelman, D.; Orland, H. Dielectric Constant of Ionic Solutions: A Field-Theory Approach. *Phys. Rev. Lett.* **2012**, *108*, 227801. doi:10.1103/PhysRevLett.108.227801.
59. Adar, R.M.; Markovich, T.; Levy, A.; Orland, H.; Andelman, D. Dielectric constant of ionic solutions: Combined effects of correlations and excluded volume. *J. Chem. Phys.* **2018**, *149*, 054504, [https://doi.org/10.1063/1.5042235]. doi:10.1063/1.5042235.
60. Avni, Y.; Adar, R.M.; Andelman, D. Charge oscillations in ionic liquids: A microscopic cluster model. *Phys. Rev. E* **2020**, *101*, 010601. doi:10.1103/PhysRevE.101.010601.

Author Contributions: The author designed and performed the research as well as analysed the results described in this paper.

Funding: This research was funded .

Acknowledgments: The author acknowledges funding from the Key project #12034019 of the National Science Foundation of China.

Conflicts of Interest: There are no obvious conflicts of interests.