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General theory of asymmetric steric interactions in electrostatic double layers

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We study the mean-field Poisson–Boltzmann equation in the context of dense ionic liquids where steric effects become important. We generalise lattice gas theory by introducing a Flory–Huggins entropy for ions of differing volumes and then compare the effective free energy density to other existing lattice gas approximations, not based on the Flory–Huggins Ansatz. Within the methodology presented we also invoke more realistic equations of state, such as the Carnahan–Starling approximation, that are not based on the lattice gas case. We solve the Carnahan–Starling model in the high density limit, and demonstrate a slow, power-law convergence at high potentials. We elucidate how equivalent convex free energy functions can be constructed that describe steric effects in a manner which is more convenient for numerical minimisation.

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1 Introduction

In the theory of ionic liquids¹ steric effects are of particular importance since the packing of ions can be especially dense.² If this is indeed the case, steric saturation impedes the solid establishment of the Gouy–Chapman double layer close to an electrified surface as the ions are not allowed to pack densely near the surface, and consequently cannot screen the high surface charge as would be the case for *e.g.* aqueous electrolytes.³ Instead they rather occupy several vicinal layers, completely saturating the sterically available volume.

The most common and simplest analytic approach to these effects is *via* the lattice gas mean-field approximation that became, particularly through the work of Kornyshev, a paradigmatic approximation in the context of ionic liquids.³ The methodological basis of the lattice gas mean-field approximation is the Poisson equation coupled with a lattice gas entropy, as opposed to the ideal gas (Boltzmann) entropy incorporated in the foundation of Poisson–Boltzmann theory (for a detailed introduction, see ref. 4). The mean-field lattice gas methodology introduced specifically within the context of ionic liquids can be, as we show below, furthermore extended to a general local thermodynamic approach for any model of inhomogeneous fluids, without any connection to the lattice gas framework.⁵ In this way one can connect the equation of state for any reference uncharged fluid, not only a lattice gas, with a solid description

of the same fluid with charged particles on the mean-field electrostatics level, generalizing in this way the Poisson–Boltzmann theory with consistent inclusion of the packing effects. We consider this to be an important formal and conceptual advance as it allows us to consistently compare various approximate models of steric effects in ionic liquids, while preserving the overall mean-field nature of the electrostatic part.

This approach is particularly relevant for the analysis of dense electric double layers as they arise in the context of ionic liquids or dense Coulomb fluids in general.⁶ We will use this general local thermodynamics approach in conjunction with two model equations of state: the asymmetric lattice gas approximation and the asymmetric Carnahan-Starling approximation, and compare their consequences. The size asymmetry as well as the charge asymmetry, as shown in Fig. 1, that this approach allows us to analyse, are fundamentally important for understanding the nature of the electrostatic double layers in ionic liquids. We, in particular, include the asymmetric lattice gas approximation into our discussion as its symmetric counterpart has been widely recognized as the standard theoretical approach³ but has, as such, resisted various attempts to be consistently generalized to a situation of asymmetric steric interactions for components of widely differing size. On the other hand, the Carnahan-Starling approximation for uncharged homogeneous fluids gives the results regarding thermodynamic observables that are almost indistinguishable from simulations⁷ and thus represents an excellent baseline to compare with.

Our approach to the asymmetric lattice gas statistics is based on an analogy with the standard Flory–Huggins methodology used in the context of polymer chains of differing lengths.⁸ While formulated in the context of interacting polymers,

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Fig. 1 A schematic representation of the asymmetric system composed of particles with unequal sizes and unequal valencies in the vicinity of a charged surface. The left side symbolically shows the underlying lattice for the Flory–Huggins lattice gas approximation.

the entropic part of Flory–Huggins theory refers only to the lattice statistics of variously sized objects,⁹ which is the sole aspect that we utilize in what follows. Asymmetric lattice gas mixtures have been addressed on various levels before,^{1,3,6,10-14} but mostly through *ad hoc* approximations, plausible expansions and phenomenological extensions of the symmetric lattice gas theories, with some similarities to the present approach, while yet not identical to it. The connection with Flory–Huggins theory now sets the calculation in the proper perspective of other physical problems that require a detailed counting of sterically available states for variously sized objects on a lattice. We believe that this is also the most natural framework for the appropriate lattice theory of asymmetry effects in ionic liquids.

Our purpose here is threefold. First we want to formulate a general local thermodynamic theory of mean-field electrostatic effects for non-homogeneous Coulomb systems that can be described with an equation of state in the reference *i.e.* an uncharged state. This will allow us to derive an appropriate generalized Poisson-Boltzmann equation for the fully coupled, charged system where the electrostatic part is consistently formulated on the mean-field level. We then define a model asymmetric lattice gas system, whose equation of state we derive based on the Flory-Huggins theory of lattice gases, at the same time putting into perspective also various other attempts in obtaining the appropriate asymmetric lattice gas statistics. This allows us finally to compare the asymmetric lattice gas with the asymmetric Carnahan-Starling theory with a well-known equation of state in the reference uncharged state. Based on this, we then draw the necessary conclusions regarding the applicability of the lattice gas approximation in the description of asymmetric dense ionic liquids and show that it misses qualitatively some important features exhibited clearly by the Carnahan-Starling approximation. Nonetheless, as the lattice gas model is and will foreseeably remain a workhorse of the ionic liquid theory, it is important to formulate it appropriately for the asymmetric case also so that its predictions can be compared with more advanced theoretical approaches as well as definitively assessed in comparison with experiments.

The plan of the paper is as follows: we will first formulate the local thermodynamic mean-field approach to Coulomb fluids and then apply it to the asymmetric lattice gas, derived within the Flory–Huggins lattice approximation, comparing its results with the asymmetric Carnahan–Starling approximation. As a sideline we then derive several useful general relations valid specifically for the asymmetric lattice gas approximation in the context of electrostatic double layers. We finally comment on the major deficiencies of the lattice gas approach when compared to the more advanced Carnahan–Starling approximation and draw some useful conclusions and possible directions for future research. The paper is written pedagogically and contains several known results that have been however rederived in a completely different framework.

2 General formulation

We proceed by studying the Legendre transform of the free energy density $f(c_1,c_2)$ of an isothermal (T = const) binary mixture

$$f(c_1,c_2) - \mu_1 c_1 - \mu_2 c_2, \tag{1}$$

where $c_{1,2}$ are the densities of the two components, and the chemical potentials $\mu_{1,2}$ are defined as

$$\mu_{1,2} = \frac{\partial f(c_1, c_2)}{\partial c_{1,2}}.$$
 (2)

According to the well-known thermodynamic relationships⁵ the Legendre transform, eqn (1), equals

$$f(c_1, c_2) - \frac{\partial f(c_1, c_2)}{\partial c_1} c_1 - \frac{\partial f(c_1, c_2)}{\partial c_2} c_2 = -p(c_1, c_2), \qquad (3)$$

where $p(c_1,c_2)$ is the thermodynamic pressure, or the equation of state. For the inhomogeneous case we now invoke the local thermodynamic approximation so that the inhomogeneity is described solely *via* the coordinate dependence of the densities, but the form of the thermodynamic potential remains the same as in the bulk,

$$\mathscr{F} = \int_{\mathcal{V}} d^3 \mathbf{r} (f(c_1, c_2) - \mu_1 c_1 - \mu_2 c_2) = -\int_{\mathcal{V}} d^3 \mathbf{r} p(\mu_1, \mu_2).$$
(4)

In the case of charged particles one needs to consider also the electrostatic energy and its coupling to the density of the particles *via* the Poisson equation, on top of the reference free energy of uncharged particles. The corresponding thermodynamic potential of the charged binary mixture then assumes the form

$$\mathscr{F}[c_1, c_2, \mathbf{D}] = \int_{\mathbf{V}} d^3 \mathbf{r} (f(c_1, c_2) - \mu_1 c_1 - \mu_2 c_2) + \int_{\mathbf{V}} d^3 \mathbf{r} \left(\frac{\mathbf{D}^2}{2\varepsilon} - \psi (\nabla \cdot \mathbf{D} - e(Z_1 c_1 - Z_2 c_2)) \right),$$
(5)

where $\mathbf{D} = \mathbf{D}(\mathbf{r})$ is the dielectric displacement field, $\varepsilon = \varepsilon \varepsilon_0$ with ε being the relative dielectric permittivity, $Z_{1,2}$ are the valencies of the two charged species and $\psi = \psi(\mathbf{r})$ is now the Lagrange multiplier

field that ensures the local imposition of Gauss's law.¹⁵ We can write this expression in an alternative form as

$$\mathscr{F} = \int_{\mathcal{V}} d^{3}\mathbf{r} (f(c_{1}, c_{2}) - (\mu_{1} - eZ_{1}\psi)c_{1} - (\mu_{2} + eZ_{2}\psi)c_{2}) + \int_{\mathcal{V}} d^{3}\mathbf{r} \left(\frac{\mathbf{D}^{2}}{2\varepsilon} - \psi\nabla \cdot \mathbf{D}\right).$$
(6)

Invoking now the identity with eqn (4), discarding the boundary terms and minimizing with respect to \mathbf{D} , we get the final form of the inhomogeneous thermodynamic potential

$$\mathscr{F}[\psi] = -\int_{\mathcal{V}} d^3 \mathbf{r} \left(\frac{1}{2} \varepsilon (\nabla \psi)^2 + p(\mu_1 - eZ_1\psi, \mu_2 + eZ_2\psi) \right).$$
(7)

In the case of charged boundaries one needs to add a surface term $\psi D_n dS$, where D_n is the normal component of the electric displacement field at the surface, to the above equation. While the derivation of eqn (7) proceeded entirely on the mean-field level, it can be extended to the case when the Coulomb interactions are included exactly and the mean potential becomes the fluctuating local potential in a functional integral representation of the partition function.¹⁶

Let us note that the signs of the electrostatic terms in eqn (7) are consistent with the definition of the grand canonical partition function, *i.e.* $\Omega = -pV$, with $\Omega(\lambda, \beta) = \sum_{N=1}^{\infty} \lambda^N Q(N, \beta)/N!$, where $Q(N,\beta)$ is the canonical partition function for N particles. The absolute activity is defined as $\lambda = e^{\beta\mu}$. Since electrostatic interactions enter with a Boltzmann factor, $\lambda = e^{\beta\mu} \rightarrow e^{\beta\mu \mp eZ_{1,2}\psi}$, where - is valid for positive and + for negative ions.

For any equation of state $p(\mu_1,\mu_2)$ or indeed any model free energy $f(c_1,c_2)$ of the reference uncharged system, one now needs to evaluate the appropriate chemical potentials of the binary components from eqn (2), make a substitution

$$\mu_{1,2} \rightarrow \mu_{1,2} \mp eZ_{1,2}\psi$$

and finally derive the Euler-Lagrange equation for the local electrostatic potential of the form

$$\varepsilon \nabla^2 \psi - \frac{\partial p(\mu_1 - eZ_1 \psi, \mu_2 + eZ_2 \psi)}{\partial \psi} = 0, \qquad (8)$$

which contains a derivative of the pressure function of the uncharged reference system and generalizes a form already derived within a symmetric lattice gas approximation.¹⁷ Invoking furthermore the Gibbs–Duhem relation

$$c_{1,2} = \frac{\partial p}{\partial \mu_{1,2}}$$

we derive the Poisson equation as

$$\frac{\partial p(\mu_1 - eZ_1\psi, \mu_2 + eZ_2\psi)}{\partial \psi} = -eZ_1\frac{\partial p}{\partial \mu_1} + eZ_2\frac{\partial p}{\partial \mu_2}$$
(9)
$$= -e(Z_1c_1 - Z_2c_2) = -q.$$

where q is the local charge density. Also note that the charge density is a derivative with respect to the potential of a single function, a simple test of consistency for any proposed

approximate theory. Together with eqn (8) this constitutes a generalisation of Poisson–Boltzmann theory for any model of the fluid expressible *via* an equation of state in the local thermodynamic approximation. This also generalizes some results previously derived only for the lattice gas.

In the case of a single or two planar surfaces, with the normal in the direction of the *z*-axis, so that $\psi(\mathbf{r}) = \psi(z)$, the Poisson–Boltzmann equation possesses a first integral of the form

$$\frac{1}{2}\varepsilon\psi'^{2}(z) - p(\mu_{1} - eZ_{1}\psi(z), \mu_{2} + eZ_{2}\psi(z)) = -p_{0}$$
(10)

where p_0 is an integration constant equal to the osmotic pressure of the ions and determined by the boundary conditions. The disjoining (interaction) pressure for two charged surfaces, Π , is then obtained by subtracting the bulk contribution from the osmotic pressure p_0 . The first integral of the Euler–Lagrange equation can be used to construct an explicit 1D solution, $\psi = \psi(z)$ by quadrature.

In the limiting case of an ideal gas, with the van't Hoff equation of state $p(c_1,c_2) = k_B T(c_1 + c_2)$ it is straightforward to see that the above theory reduces exactly to the Poisson–Boltzmann approximation.¹⁸ Furthermore, for the binary, symmetric lattice-gas

$$p(c_1, c_2) = -\frac{k_{\rm B}T}{a^3} \log(1 - a^3(c_1 + c_2))$$
(11)

where *a* is the cell size,¹⁹ the above formalism yields the results discussed at length by Kornyshev.³ From eqn (11) we also see one of the weaknesses of the lattice gas approach, as the pressure diverges only very weakly at close packing. We will compare with a more realistic equation of state later in this paper.

3 Asymmetric lattice gas

We start with the free energy density of mixing for a three component lattice gas system composed of species "1" at concentration c_1 , composed of N_1 subunits, and species "2" at concentration c_2 , composed of N_2 subunits, in a solvent of (water) molecules of diameter *a*. It can be expressed rather straightforwardly in terms of the volume fractions ϕ_1 and ϕ_2 after realizing that it is equivalent to the problem of polydispersed polymer mixtures on the Flory–Huggins lattice level.⁸ For a three component system the free energy can be obtained from the entropy of mixing simply as²⁰

$$\frac{f(\phi_1, \phi_2)a^3}{k_{\rm B}T} = \frac{\phi_1}{N_1}\log\phi_1 + \frac{\phi_2}{N_2}\log\phi_2 + (1 - \phi_1 - \phi_2)\log(1 - \phi_1 - \phi_2),$$
(12)

where the volume fractions ϕ_1 and ϕ_2 are defined as

$$\phi_{1,2} = a^3 c_{1,2} N_{1,2} = R_{1,2}{}^3 c_{1,2}, \tag{13}$$

and $N_{1,2} = (R_{1,2}/a)^3$ measures the relative volumes of species 1 and 2, with radii $R_{1,2}$, compared to the solvent with radius *a*. While the size-symmetric lattice gas has a venerable history (for an excellent review, see ref. 2) there have been fewer previous attempts to master the lattice gas mixtures in the context of size-asymmetric electrolytes,^{1,3,6,10–14} and the simple connection with the entropy of lattice polymers has apparently not been noted before.

Since there is no exact enumeration of the lattice statistics for equal and even less so for unequal, composed particles, it is difficult to compare various approximations referred above.^{6,10–14} What they do have in common is that they are never derived systematically but in one way or another incorporate a kind of mean-field statistical–mechanical Ansatz, based on the assumption that the probability that the next site to be occupied is empty, is assumed to be equal to the fraction of still empty sites.²¹ However, the features that all the approximations should exhibit, apart from consistency as defined by eqn (9), are that the osmotic pressures corresponding to different approximate lattice entropies reduce to

the ideal van't Hoff form, $\frac{p(\phi_1, \phi_2)a^3}{k_BT} \rightarrow \left(\frac{\phi_1}{N_1} + \frac{\phi_2}{N_2}\right)$, for small $p(\phi_1, \phi_2)a^3$

volume fractions and to $\frac{p(\phi_1, \phi_2)a^3}{k_B T} \rightarrow -\log(1 - (\phi_1 + \phi_2))$ for

high volume fractions. In the latter tight packing regime the nature of the composed particles is irrelevant and the osmotic pressure depends only on the volume fractions. None of the approximations referred to above satisfies all these requirements.

The reason that we base our asymmetric lattice statistics on the Flory–Huggins entropy is that first of all it exhibits all the stated properties, furthermore that it has already been applied to micelles, globular proteins and colloids, and finally that over the years its limitations have been thoroughly investigated (see ref. 22, and references therein).

The chemical potential for the free energy eqn (12), based on the Flory–Huggins entropy of mixing, is then obtained as

$$\mu_{1,2} = \frac{\partial f(c_1, c_2)}{\partial c_{1,2}} = \frac{\partial f(\phi_1, \phi_2)}{\partial \phi_{1,2}} a^3 N_{1,2}, \tag{14}$$

that can be evaluated explicitly yielding

$$\beta \mu_{1,2} = \log \phi_{1,2} + 1 - N_{1,2} (\log(1 - \phi_1 - \phi_2) + 1).$$
(15)

The Legendre transform eqn (1) then yields the osmotic pressure, again as a function of both volume fractions

$$-\frac{p(\phi_1, \phi_2)a^3}{k_{\rm B}T} = \log(1 - \phi_1 - \phi_2) + \phi_1\left(1 - \frac{1}{N_1}\right) + \phi_2\left(1 - \frac{1}{N_2}\right).$$
(16)

The form of this result is revealing as it states that the osmotic pressure is basically the lattice gas pressure of a symmetric mixture, corrected by the fact that $N_{1,2}$ subunits of species "1" and "2" do not represent separate degrees of freedom. Obviously, for a symmetric system with $N_{1,2} = 1$ this reduces exactly to the lattice gas symmetric binary mixture expression, eqn (11).

Introducing $\tilde{\mu}_{1,2} = \beta(\mu_{1,2} + N_{1,2} - 1)$ we can rewrite eqn (15) as

$$\phi_{1,2} = (1 - \phi_1 - \phi_2)^{N_{1,2}} e^{\tilde{\mu}_{1,2}}$$
(17)

Using this relation we can derive an explicit equation for

$$u = (1 - \phi_1 - \phi_2) \tag{18}$$

of the form

$$u(1+u^{N_1-1}e^{\tilde{\mu}_1}+u^{N_2-1}e^{\tilde{\mu}_2})=1, \qquad (19)$$

that yields $u = u(\tilde{\mu}_1, \tilde{\mu}_2; N_1, N_2)$. This allows us to finally write the osmotic pressure as a function of the two densities

$$-\frac{p(c_1, c_2)a^3}{k_{\rm B}T} = \log(1 - a^3(c_1N_1 + c_2N_2)) + a^3c_1(N_1 - 1) + a^3c_2(N_2 - 1),$$
(20)

or the two chemical potentials through $u = u(\tilde{\mu}_1, \tilde{\mu}_2; N_1, N_2)$ as

$$\frac{-\frac{p(\mu_1,\mu_2)a^3}{k_{\rm B}T} = \log u + u^{N_1} e^{\bar{\mu}_1} \left(1 - \frac{1}{N_1}\right) + u^{N_2} e^{\bar{\mu}_2} \left(1 - \frac{1}{N_2}\right).$$
(21)

In the case of ions of the same size, we can set without any loss of generality that $N_1 = N_2 = 1$, so that

$$-\frac{p(\mu_1,\mu_2)a^3}{k_{\rm B}T} = \log u(\tilde{\mu}_1,\tilde{\mu}_2) = -\log(1+{\rm e}^{\tilde{\mu}_1}+{\rm e}^{\tilde{\mu}_2}), \quad (22)$$

a standard expression for the symmetric lattice gas.^{23,24}

The above equations present a complete set of relations satisfied by the asymmetric lattice gas, being a mixture of two differently sized ions. The addition of mean-field electrostatic interactions eqn (8) then modifies solely the chemical potentials so that

$$p(\mu_1,\mu_2) \to p(\mu_1 - eZ_1\psi,\mu_2 + eZ_2\psi)$$
 (23)

if the two species are oppositely charged, which we assume. The corresponding Poisson–Boltzmann equation is then obtained from eqn (8) and (9) in the form

$$\varepsilon \nabla^2 \psi = -e \left(Z_1 \partial_{\mu_1} - Z_2 \partial_{\mu_2} \right) p(\mu_1 - e Z_1 \psi, \mu_2 + e Z_2 \psi)$$

$$= -\frac{e}{a^3} \left(\frac{Z_1}{N_1} \phi_1(\psi) - \frac{Z_2}{N_2} \phi_2(\psi) \right).$$
(24)

where $\phi_{1,2}(\psi)$ are obtained from eqn (17) and (19) with $\tilde{\mu}_1 \rightarrow \tilde{\mu}_1 - \beta e Z_1 \psi, \tilde{\mu}_2 \rightarrow \tilde{\mu}_2 + \beta e Z_2 \psi$.

In complete analogy with the case of polyelectrolytes with added salt²⁵ it is clear that electroneutrality of the asymmetric lattice gas in the bulk is achieved only if it is held at a non-zero electrostatic potential, ψ_0 , that can be obtained from eqn (24) in an implicit form

$$(N_1 - N_2)\log u(\psi_0) = -(\tilde{\mu}_1 - \tilde{\mu}_2) + \log \frac{N_1 Z_2}{N_2 Z_1}.$$
 (25)

In what follows we then simply displace the origin of the electrostatic potential by ψ_0 , the Donnan potential, interpreted as the change in the electrostatic potential across the bulk reservoir–ionic liquid interface, or equivalently as a Lagrange multiplier for the constraint of global electroneutrality.²⁶

Paper

4 Asymptotic behaviour of the lattice gas model

We now consider the forms of the general equations derived above in the limiting cases of small and large electrostatic potentials of the lattice gas model:

4.1 Small potential and screening length

In the limit of $\psi \rightarrow 0$, one can derive

$$p(\mu_{1} + eZ_{1}\psi, \mu_{2} - eZ_{2}\psi) = p(\mu_{1}, \mu_{2})$$

- $e(Z_{1}\partial_{\mu_{1}} - Z_{2}\partial_{\mu_{2}})p(\mu_{1}, \mu_{2})\psi$
+ $\frac{1}{2}e^{2}(Z_{1}\partial_{\mu_{1}} - Z_{2}\partial_{\mu_{2}})^{2}p(\mu_{1}, \mu_{2})\psi^{2} + O(\psi^{3})$ (26)

where we took into account eqn (9). Just as in the non-linear case, see above, the term linear in ψ is connected with the displaced electrostatic potential, eqn (25). The linearized form of ψ_0 is then obtained approximately as

$$\psi_0 = \frac{e(Z_1\partial_{\mu_1} - Z_2\partial_{\mu_2})p(\mu_1, \mu_2)}{e^2(Z_1\partial_{\mu_1} - Z_2\partial_{\mu_2})^2p(\mu_1, \mu_2)}.$$
(27)

Obviously the expansion of the pressure for small values of the electrostatic potential is then quadratic in the difference $\psi - \psi_0$.

Furthermore, the Hessian of the pressure $p(\mu_1,\mu_2)$ is positive definite, *i.e.*

$$\frac{e^2}{\varepsilon} \left(Z_1^2 \frac{\partial^2 p}{\partial \mu_1^2} - 2Z_1 Z_2 \frac{\partial^2 p}{\partial \mu_1 \mu_2} + Z_2^2 \frac{\partial^2 p}{\partial \mu_2^2} \right) = \kappa^2 > 0, \quad (28)$$

while from eqn (7) it follows that κ is nothing but the inverse Debye length expressed through the second derivatives of pressure with respect to the chemical potentials of both charged species. Since the curvature tensor of the Legendre transform is the inverse of the curvature tensor of the function itself,²⁷ we can write

$$\sum_{m} \frac{\partial^2 p(\mu_1, \mu_2)}{\partial \mu_i \partial \mu_m} \frac{\partial^2 f(c_1, c_2)}{\partial c_m \partial c_k} = \delta_{ik}$$
(29)

where all the matrices are 2 \times 2. From here it follows rather straightforwardly that

$$\begin{aligned} \kappa^{2} &= \frac{e^{2} Z_{2}^{2} \frac{\partial^{2} f}{\partial c_{1}^{2}} + 2Z_{1} Z_{2} \frac{\partial^{2} f}{\partial c_{1} \partial c_{1}} + Z_{1}^{2} \frac{\partial^{2} f}{\partial c_{2}^{2}}}{\frac{\partial^{2} f}{\partial c_{1}^{2} \partial c_{2}^{2}} - \left(\frac{\partial^{2} f}{\partial c_{1} \partial c_{2}}\right)^{2}} \\ &= 4\pi \ell_{\mathrm{B}} N_{1} N_{2} \frac{u (Z_{1}^{2} c_{1} + Z_{2}^{2} c_{2}) + a^{3} c_{1} c_{2} (Z_{1} N_{2} + Z_{2} N_{1})^{2}}{(1 + (N_{1} - 1) a^{3} N_{1} c_{1} + (N_{2} - 1) a^{3} N_{2} c_{2})}, \end{aligned}$$

$$(30)$$

where we introduced the Bjerrum length $\ell_{\rm B} = e^2/(4\pi \varepsilon k_{\rm B}T)$. In general, the Debye length is therefore not a linear function of the concentrations. For the symmetric lattice gas, $N_1 = N_2 = 1$, and taking into account the definition eqn (18), the above result reduces to $\kappa^2 = 4\pi \ell_{\rm B}(Z_1^{\ 2}c_1 + Z_2^{\ 2}c_2 - a^3(Z_1c_1 - Z_2c_2)^2)$, which for bulk electroneutrality reduces further to the standard Debye expression.²³

4.2 Large potential and close packing

The limits for
$$\psi \rightarrow \pm \infty$$
 of a lattice gas can be derived as

$$u = \begin{cases} e^{-(\tilde{\mu}_1 + \beta e Z_1 \psi)/N_1} & \psi \to +\infty \\ e^{-(\tilde{\mu}_2 - \beta e Z_2 \psi)/N_2} & \psi \to -\infty \end{cases}$$
(31)

implying

$$\phi_{1,2}(\psi \to \infty) = \begin{cases} 1 \\ e^{-(\tilde{\mu}_1 + \beta e Z_1 \psi) N_2 / N_1 + (\tilde{\mu}_2 - \beta e Z_2 \psi)} . \end{cases}$$
(32)

and

$$\phi_{1,2}(\psi \to -\infty) = \begin{cases} e^{-(\tilde{\mu}_2 - \beta e Z_2 \psi) N_1 / N_2 + (\tilde{\mu}_1 - \beta e Z_1 \psi)} \\ 1 \end{cases}.$$
(33)

where the upper formula is for "1" and the lower one for "2". Thus

$$-\frac{p(\psi \to \infty)a^{3}}{k_{\rm B}T} = -(\tilde{\mu}_{1} + \beta e Z_{1}\psi)/N_{1} + \left(1 - \frac{1}{N_{1}}\right) + e^{-(\tilde{\mu}_{1} + \beta e Z_{1}\psi)N_{2}/N_{1}}e^{(\tilde{\mu}_{2} - \beta e Z_{2}\psi)}\left(1 - \frac{1}{N_{2}}\right)$$
(34)

and

$$\frac{-p(\psi \to -\infty)a^{3}}{k_{\rm B}T} = -(\tilde{\mu}_{2} - \beta e Z_{2}\psi)/N_{2} + e^{-(\tilde{\mu}_{2} - \beta e Z_{2}\psi)N_{1}/N_{2}}e^{(\tilde{\mu}_{1} + \beta e Z_{1}\psi)}$$
$$\times \left(1 - \frac{1}{N_{1}}\right) + \left(1 - \frac{1}{N_{2}}\right)$$
(35)

The most striking feature of these limits is the linear behaviour of $p(\psi)$ for large positive or negative potentials, which gives rise to a V-like curve for symmetric particles. This linear behaviour is linked to the saturation of close packing of the lattice particles against a high potential surface. For particles of unequal size the two branches of $p(\psi)$ have different slopes.

5 A dense two-component lattice gas

For some cases in the theory of ionic liquids one can assume dense packing, without any intervening solvent, so that $\phi_1 + \phi_2 = 1$. The corresponding free energy can then be cast into a simplified form

$$\frac{f(\phi_1, \phi_2 = 1 - \phi_1)N_2a^3}{k_{\rm B}T} = \frac{\phi_1}{M}\log\phi_1 + \phi_2\log\phi_2.$$
 (36)

where $M = N_1/N_2$ is the effective size of species "1" compared to species "2". This implies furthermore that

$$\frac{\partial f}{\partial \phi_1} + \frac{\partial f}{\partial \phi_2} = 0 \to \mu_1 + M\mu_2 = 0.$$
 (37)

The equation analogous to eqn (19) then assumes the form

$$\phi_1 = (1 - \phi_1)^M e^{\beta \mu_1 - 1 + M} \tag{38}$$

and the Legendre transform of the free energy density follows as

$$-\frac{p(\phi_1,\phi_2=1-\phi_1)N_2a^3}{k_{\rm B}T} = \log\phi_2 + \phi_1\left(1-\frac{1}{M}\right).$$
 (39)

The Poisson–Boltzmann equation is then cast into a simplified form

$$\varepsilon \nabla^2 \psi = -e (Z_1 \partial_{\mu_1} - Z_2 \partial_{\mu_2}) p(\mu_1 - eZ_1 \psi, \mu_2 + eZ_2 \psi)$$

$$= \frac{e}{a^3 N_1} ((Z_1 + MZ_2) \phi_1 - MZ_2),$$
(40)

and the charge density is constrained to be between $-\frac{e}{a^3}\frac{Z_2}{N_2}$ and $\frac{e}{a^3}\frac{Z_1}{N_1}$.

6 Asymmetric Carnahan–Starling approximation

In order to show the interest and generality of our local thermodynamic approach we will now apply it in the case of the Carnahan–Sterling approximation for asymmetric binary hard sphere mixtures.²⁸ For a bulk, uncharged hard sphere fluid the Carnahan–Starling approximation is "almost exact".

The excess pressure in the Carnahan–Starling approximation derived *via* the "virial equation" is then equal to

$$\frac{p_{\rm exc}(c_1, c_2)}{ck_{\rm B}T} = \frac{\left(1 + \xi + \xi^2\right) - 3\xi(y_1 + \xi y_2) - 3\xi^3 y_3}{\left(1 - \xi\right)^3} \tag{41}$$

where $c_{1,2}$ are the densities of the two components and

$$\xi_{1,2} = \frac{4\pi}{3} R_{1,2}{}^3 c_{1,2}$$
 and $\xi = \xi_1 + \xi_2,$ (42)

where $R_{1,2}$ are the hard sphere radii of the two species. Furthermore,

$$y_{1} = \Delta_{12} \frac{R_{1} + R_{2}}{\sqrt{R_{1}R_{2}}} \quad y_{2} = \Delta_{12} \frac{\xi_{1}R_{2} + \xi_{2}R_{1}}{\sqrt{R_{1}R_{2}\xi}}$$

$$y_{3} = \left(\left(\frac{\xi_{1}}{\xi}\right)^{2/3} + \left(\frac{\xi_{2}}{\xi}\right)^{2/3}\right)^{3}$$
(43)

with

$$\Delta_{12} = \frac{\sqrt{\xi_1 \xi_2} (R_1 - R_2)^2}{\xi R_1 R_2}.$$
 (44)

The excess free energy then follows as

$$\frac{f_{\text{exc}}(c_1, c_2)}{ck_{\text{B}}T} = -\frac{3}{2}(1 - y_1 + y_2 + y_3) + \frac{3y_2 + 2y_3}{1 - \xi} + \frac{3}{2}\frac{1 - y_1 - y_2 - \frac{1}{3}y_3}{(1 - \xi)^2} + (y_3 - 1)\log(1 - \xi),$$
(45)

It is now straightforward to obtain the chemical potentials from the free energy as $\mu_{1,2} = \mu_{1,2}(c_1,c_2)$, invert them and then obtain the pressure equation as $p = p(\mu_1,\mu_2)$.

7 Asymptotic behaviour of the Carnahan–Starling free energy density

In the limit of large potentials ψ , as occurs near an electrode, the second, wrongly charged, component of the fluid is excluded and the dominant physics is the packing of a single component system under the constraints coming from the electrostatic interactions. In this limit of $\xi \rightarrow 1$ we can substitute $y_{1,2} = 0$ and $y_3 = 1$. The most important divergence in this limit thus stems from the denominator in eqn (45).

The free energy density of a Carnahan–Starling liquid near close packing has a singularity of the form

$$f(c) = \frac{c_0 k_{\rm B} T}{\left(1 - c/c_0\right)^2} \tag{46}$$

where c_0 is the close packing volume fraction of the component dominating near the electrode. With this assumption we can take the Legendre transform of the most singular, diverging part of the free energy to find the large potential limit of $p(\psi)$. For large positive ψ (assuming that $eZ_2\psi \gg \mu$) this limit turns out to be

$$p(\psi) = Z_2 e c_0 \psi - \frac{3}{2} (2c_0 k_B T)^{1/3} (Z_2 e c_0 \psi)^{2/3}$$
(47)

where we have used the fact that negative ions of valence Z_2 dominate.

In the high packing limit $p(\psi)$ is therefore linear in the potential, and is given by the spatial charge density at close packing exactly like for the lattice gas. However, unlike the lattice gas, the approach to the high field limit is very slow. In fact from eqn (9) it follows that

$$-q(\psi) = \frac{\partial p(\psi)}{\partial \psi} = Z_2 e c_0 - \left(\frac{2c_0 k_B T}{\psi}\right)^{1/3} (Z_2 e c_0)^{2/3}.$$
 (48)

The spatial charge density is negative for large positive potentials. The correctness of this law is demonstrated in Fig. 2 which plots $(1/c_0Z_2e)dp/d\psi$ as a function of $\psi^{-1/3}$. The curve linearly extrapolates to unity for large ψ . There is a very clear contrast to the case of the lattice gas model where the cross-over to close packing occurs for much smaller values of the potential.

7.1 Solution for the high field Carnahan–Starling limit

The solution for the generalized Poisson–Boltzmann equation in the high field limit can be found from the solution of the integral problem

$$\int d\psi \left(ec_0 Z_2 \psi - \omega (ec_0 Z_2 \psi)^{2/3} + p_0 \right)^{-1/2} = \sqrt{\frac{2}{\varepsilon}} \int dz \qquad (49)$$

with $\omega = 3(2c_0k_BT)^{1/3}/2$; we neglect μ compared to $Z_2e\psi$. This integral can be transformed by substituting $(ec_0Z_2\psi)^{1/3} = y$, giving

$$3\int \frac{\mathrm{d}yy^2}{\left(y^3 - \omega y^2 + p_0\right)^{1/2}} = \sqrt{\frac{2e^2 c_0^2 Z_2^2}{\varepsilon}} \int \mathrm{d}z, \qquad (50)$$



Fig. 2 Study of the evolution of the charge density $-q = dp(\psi)/d\psi$ in units of close packed charge density Z_2ec_0 and variables adapted to the Carnahan–Starling fluid, eqn (45), (blue solid line). The large field behaviour is linear in $1/\psi^{1/3}$, as surmised in deriving eqn (48). Same data as Fig. 7 for large positive potentials. The lattice gas model (red dashed line) gives much more rapid cross-over to saturation at large potentials. Horizontal (yellow dash-dotted) line is to guide the eye and corresponds to the close packing charge density.

a form which can be solved by using elliptic functions. If we make the further approximation that p_0 is small we can find much simpler expressions:

$$z(\psi) - z_0 = \frac{\sqrt{2\varepsilon}}{ec_0 Z_2} \left[\left((Z_2 e \psi c_0)^{1/3} - \omega \right)^{3/2} + 3\omega \left((Z_2 e \psi c_0)^{1/3} - \omega \right)^{1/2} \right]$$
(51)

Here, $z(\psi)$ gives the distance from a plate which corresponds to a potential ψ . It is obviously the inverse function of $\psi(z)$. We perform a "numerically exact" calculation of the curve $z(\psi)$ (in the units of the Bjerrum length) in Fig. 3 inset, where we place a positive electrode at z = 0. The main figure of Fig. 3 contains three curves: The blue dotted curve explodes part of the inset and is overlayed with a red dotted curve corresponding to eqn (51). On this scale the results are indistinguishable. The green curve is evaluated by assuming a perfect packing of the fluid against the electrode. Eqn (51) is clearly a much better description of the high electrostatic potential physics.

Eqn (51) can also be combined with eqn (48) to find z(q) and thus the evolution of the spatial charge density with distance from an electrode as well as the variation of the local charge density with the potential.

8 Differential capacitance

Together with the boundary condition $D_n = \sigma$, where σ is the surface charge density, one can derive the equivalent of the Grahame equation in the form

$$\frac{\sigma^2}{2\varepsilon} - p(\mu_1 - eZ_1\psi_0, \mu_2 + eZ_2\psi_0) = -p_0,$$
 (52)



Fig. 3 Solution of eqn (50) for Carnahan–Starling 1:1 electrolyte in units of the Bjerrum length. Blue dotted line: an exact numerical calculation of the function $z(\psi)$. The solid curve is given in the inset (blue solid line). The high field limit is studied in the main panel. Red dotted line: an approximation valid for large fields from eqn (51). Green dashed line profile calculated from assuming a perfect packing of the fluid against the electrode. Blue dotted and red dotted curves correspond almost perfectly, with no extra fitting parameters.

assuming that the bound surface is located at z = 0, *i.e.* $\psi_0 = \psi(z = 0)$. From the Grahame equation one can next derive the differential capacitance \mathscr{C} as

$$C(\psi_0) = \frac{\partial \sigma(\psi_0)}{\partial \psi_0} = \frac{\varepsilon e}{\sigma(\psi_0)} \left(-Z_1 \frac{\partial p}{\partial \mu_1} + Z_2 \frac{\partial p}{\partial \mu_2} \right)$$

$$= \frac{-\varepsilon e(Z_1 c_1 - Z_2 c_2)}{\pm \sqrt{2\varepsilon(p - p_0)}},$$
 (53)

with \pm depending on the sign of the surface charge. Taking into account the definition of the Bjerrum length, $\ell_{\rm B}$

$$C^{2}(\psi_{0}) = 2\pi k_{\mathrm{B}} T \ell_{\mathrm{B}} \frac{(Z_{1}c_{1}(\psi_{0}) - Z_{2}c_{2}(\psi_{0}))^{2}}{p(\psi_{0}) - p_{0}}.$$
 (54)

Invoking the Poisson–Boltzmann equation for this case, an alternative form of the differential capacitance is

$$\mathscr{C}(\psi_0) = \varepsilon (\log \psi_0')'$$

= $\sqrt{2\varepsilon} \frac{\partial}{\partial \psi_0} \sqrt{p(\mu_1 - eZ_1\psi_0, \mu_2 + eZ_2\psi_0) - p_0},$ (55)

the form that we use in our numerical work, shown in Fig. 4, where we plot the dimensionless quantity $C\beta e^2/\epsilon^2$ that is obtained from the above relation. *In vacuo* $\epsilon^2/\beta e^2 \approx 13 \ \mu\text{F m}^{-2}$. It is interesting to note that even if we shift the minimum of the curve $p(\psi)$ to occur at $\psi = 0$ this does not imply that $\psi = 0$ is also a stationary value of the differential capacitance. This is clearly visible in the curves of Fig. 4, where in denser fluids the maximum of the curves is shifted to positive potentials. We mark the position of the minimum in $p(\psi)$ by a slight break in the solid lines. This displacement of the maximum of the capacitance from the minimum of p is trivially understood if one assumes that the expansion of $p(\psi)$ includes a term in ψ^3 .



Fig. 4 Top: differential capacitance in dimensionless form $\beta e^2 C/\epsilon^2$ for a volume asymmetric lattice gas 1:1 electrolyte. Bottom: volume asymmetric Carnahan–Starling fluid, from eqn (55). Each curve is for a different value of the chemical potential, μ . Strongly negative chemical potentials give a minimum in the curves near $\psi = 0$, together with two asymmetric maxima. As the chemical potential increases the curves develop a peak near (but not at) $\psi = 0$. The chemical potential has been shifted such that the minimum of $p(\psi)$ is at $\psi = 0$. In both cases the positively charged component has a volume 1.5³ larger than the negative component. Curves: bottom to top at $\psi = 0$ corresponding to $\beta\mu = [-8, -7, -6, -5, -4, -3, -2, \text{ and } -1, 0]$.

We see that the qualitative behaviour of the curves generated for the lattice model, as well as for the Carnahan–Starling fluid, is rather similar.

Finally, in Fig. 5, we compare our theory for differential capacitance of an asymmetric lattice gas electrolyte with a simple semiempirical modification proposed by Kornyshev,³ based on the assumed dependence of the maximal possible local concentration of the two types of ions on the local electrostatic potential. This cross-over modification is built to correctly interpolate between the maximal packing value characteristic for the cation-rich and anion-rich layers and can be guessed with the help of simple physical arguments. Indeed, we see that the wings of the capacitance curves are



Fig. 5 A comparison between the theory for the dimensionless capacitance $C\beta e^2/\epsilon^2$ of an asymmetric lattice gas 1:1 electrolyte and a simple semiempirical modification.³ Blue solid lines: approximate treatment; yellow dashed lines: results of the lattice gas model. Curves: bottom to top at $\psi = 0$ corresponding to values of the chemical potential, $\beta \mu = [-9, -5, \text{ and } -1]$.

reproduced rather well by the approximation. However, the detailed form of the side peaks is clearly different in the two approaches for strongly negative values of the chemical potential.

9 Conclusions

By using general arguments based upon local thermodynamics, we generalized the Poisson–Boltzmann mean-field theory of Coulomb fluids to the case where the reference, uncharged fluid need not be ideal. We formulated the general theory in particular cases of an asymmetric lattice gas based on the Flory–Huggins mixing entropy and an asymmetric Carnahan– Starling fluid, that both describe the steric effects at various levels of approximations and are particularly relevant for the analysis of dense electric double layers as arising in the context of ionic liquids or dense Coulomb fluids. The use of properties of Legendre transforms allows us to efficiently translate between forms of the free energy; this includes a standard formulation in terms of the electrostatic potential, and a dual formulation (see Appendix) in terms of the electric displacement field.

We analyzed in detail the size asymmetry and its effect on the salient properties of electric double layers. As part of our analysis we also formulated a thermodynamic description of an asymmetric lattice gas, derived within the Flory–Huggins lattice approximation. This allows the lattice gas approximation, which in its symmetric form already serves as the most popular description of the steric effects in the context of Poisson– Boltzmann theory,² to be further extended to the case of ubiquitous size-asymmetric dense ionic mixtures. It is probably in the latter case that it will prove to be most useful specifically in the context of ionic liquids.¹ The Flory–Huggins approach for steric asymmetry in itself does not deal with the possible shape asymmetry of the ions.²⁹ One possible way to incorporate this on a Poisson–Boltzmann-like level is to describe the ions through their charge multipoles, which certainly takes, at least to some extent, into account the electrostatic aspect of the shape asymmetry^{30,31} but does not address its steric part. The appropriate framework for that would be in a liquid crystal context where orientational ordering is ubiquitous.³²

For the Carnahan-Starling fluid we have found an asymptotic form that gives a rather simple analytic relation between potential and distance, eqn (51), as well as the relation between potential and local charge density, eqn (48). It is clear that the description of charged fluids as lattice gases or as charged hard spheres gives very different phenomenology in high field regions. The lattice gas crosses over very rapidly to a close packed system, whereas much higher fields are needed to compress the hard sphere system, leading to very slow cross-overs $1/\psi^{1/3}$ in physical properties such as charge density. The lattice gas-based theories of finite size effects, which because of their simplicity gained a pronounced following in the context of the ionic fluids and are quite suitable for drawing qualitative conclusions regarding the packing effects, should thus be used with caution when quantitative conclusions are what is aimed at. For this Carnahan-Starling theory or even better direct numerical simulations should be sought after as an alternative.

As a final note we remark that local thermodynamics is the major obstacle to further refine the outlined approach and that it will be regrettably very difficult to circumvent. In this respect 1D models with possibly exact solutions should in our opinion contribute to a better – if by necessity simplistic – understanding of these complicated sterically constrained systems with Coulomb interactions.^{33–35}

10 Appendices

10.1 Numerical methods

We wrote numerical codes to study the double Legendre transformed free energy

$$f(c_1,c_2) - \mu(c_1 + c_2) - \psi(Z_1c_1 - Z_2c_2)$$
(56)

where $\tilde{\psi} = -\psi$. We do this by working with the effective coordinates

$$n = (c_1 + c_2)$$

$$q = (Z_1 c_1 - Z_1 c_2)$$
(57)

So that we are interested in stationary points of the function.

$$\tilde{f}(n,q) - \mu n - \tilde{\psi}q \tag{58}$$

where we have expressed the free energy as a function of the two independent coordinates, n the number density and q the charge density.

We proceed by constructing an intermediate function $g_{\mu}(q)$ by numerical minimisation of eqn (58), with fixed μ and q, with $\tilde{\psi} = 0$. The function $g_{\mu}(q)$ is then passed to the Chebfun library^{36,37} which evaluates $g_{\mu}(q)$ for different specific

values of q and builds a Chebyshev approximant accurate to a relative accuracy of 10^{-15} . From this function we build the Legendre transform from q to $\tilde{\psi}$ by standard operations on g_{μ}^{27} .

$$g_{\mu}(q) \to g_{\mu}{}'(q) \to (g_{\mu}{}')^{-1}(\tilde{\psi}) \to \int^{\psi} (g_{\mu}{}')^{-1}(\psi') d\psi'$$
 (59)

These steps are all performed by manipulation of the Chebyshev series, while maintaining close to machine precision in the evaluations. The result is an approximant to $p(\tilde{\psi})$. The last step is to transform back to $p(\psi)$ which requires a flip-in sign of the potential axes.

The functions $p(\psi)$ and $g_{\mu}(q)$ encode complementary information on the physical system. We can find the equilibrium charge density at a given potential from the relation

$$q(\psi) = -\frac{\mathrm{d}p}{\mathrm{d}\psi} \tag{60}$$

and we find the potential at imposed charge density from

$$\psi(q) = -\frac{\mathrm{d}g_{\mu}}{\mathrm{d}q} \tag{61}$$

The non-standard signs in these relations come from the difference between ψ and $\tilde{\psi}$.

Fig. 6 shows the numerical minimization result for the intermediate function $g_{\mu}(q)$, eqn (58), and the pressure, which is obtained from eqn (59) and a flip-in sign of the potential axes. $p(\psi)$ displays a characteristic V-like shape either of symmetric or asymmetric type, depending on the size of the ions. In Fig. 7 we



Fig. 6 Top: $g_{\mu}(q)$, an effective potential in units of $k_{\rm B}Tc_0$ at imposed local charge density, in units of ec_0 , for a Carnahan–Starling 1:1 electrolyte. The divergences correspond to the close packing with density c_0 for the symmetric fluid. Blue solid line: symmetric particle sizes. Gold dash-dotted line: asymmetric particle sizes with larger negative particles. Symmetric system with particle size $\ell_{\rm B}/4$, for an asymmetric system the larger particle has a doubled volume. Bottom: the function $p(\psi)$ in units of $k_{\rm B}Tc_0$ for the same two sets of parameters. Blue solid line: symmetric particle sizes. Seen from afar the function displaying a characteristic symmetric V-like behaviour. Gold dash-dotted line: asymmetric particle sizes, with larger particles giving a smaller slope in the pressure function.



Fig. 7 A comparison of symmetric Carnahan–Starling and lattice gas 1:1 electrolyte near $\psi = 0$. Top, $p(\psi)$ in units of $k_{\rm B}Tc_0$, and bottom, charge density $-q(\psi) = dp/d\psi$ in units of closely packed charge density ec_0 . Blue solid line for a Carnahan–Starling fluid, converges extraordinarily slowly to the final value, (see Fig. 2), and is much broader at the minimum then the lattice gas (red dash-dotted line). Physical parameters are such that the blue solid lines and red dash-dotted lines asymptotically correspond to the same slope; the chemical potentials are chosen to give the same Debye length in the bulk (corresponding to the same curvature at the origin in the curve for p), giving tangential curves at the origin in the lower panel for q.

compare the numeric results regarding the pressure and the charge density of the Carnahan–Starling fluid and the asymmetric lattice gas. An important and qualitative difference can be observed with the Carnahan–Starling fluid showing a much slower convergence to the asymptotic value for the large potential.

The question finally arises as to how to use the numerically determined curves for $p(\psi)$ in other external codes. Inspiration comes from the Carnahan–Starling approximation for the pressure which is a ratio of polynomials in the density. Such a general form is an example of a Padé approximant that yields a high precision representation of the function $p(\psi)$ with an approximation as a ratio of two cubic polynomials that yields a rather good fit. Use of two quartics gives results which are visually perfect. Thus the present functional forms can be easily exported (this is even part of the chebfun library) to simple, fast approximations that can be used in other simulation codes.

Clearly these methods are completely general and can be applied to even more elaborate equations of state, extrapolated from the best virial expansions.³⁸

10.2 Convex formulation for Poisson-Boltzmann free energies

As an alternative to writing the Poisson–Boltzmann functional in terms of the potential ψ with the help of the function $p(\psi)$ we can generate an equivalent convex formulation using the displacement field **D**. As shown in ref. 39 and 40 this exact transformation requires the Legendre transform of the function $p(\psi)$. However, we have already evaluated this object, it is just $g_{\mu}(q)$, eqn (59). We can thus at once conclude that the general convex Poisson–Boltzmann function equivalent to those discussed above is

$$f(\mathbf{D}) = \frac{\mathbf{D}^2}{2\varepsilon} + g_{\mu}(\operatorname{div}\mathbf{D} - \rho_{\rm e})$$
(62)

with ρ_e the externally imposed charge density. This form can be particularly interesting for the numerical work when coupling to other conformational degrees of freedom such as polymer chains or biomolecules. While we do not have an analytic expression for g_{μ} for the Carnahan–Starling fluid it is again easy to generate the curve as a Chebyshev polynomial and export them to an accurate and efficient form for use in other codes.

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