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A minimizing principle for the Poisson-Boltzmann equation

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Abstract – The Poisson-Boltzmann equation is often presented via a variational formulation based on the electrostatic potential. However, the functional has the defect of being non-convex. It cannot be used as a local minimization principle while coupled to other dynamic degrees of freedom. We formulate a convex dual functional which is numerically equivalent at its minimum and which is more suited to local optimization.

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The Poisson-Boltzmann treatment of free ions is widely used in simulations with implicit solvents. It successfully describes the mean field screening properties of ionic solutions. At the most phenomenological level it is found by balancing two crucial features of the ionic system: The electrostatic energy coming from Coulomb's law, plus the ideal entropy of mixing of the ions. Written in terms of ion concentrations c_j , or the charge concentrations $\rho_j = c_j q_j$ we find the free energy of a solution from

$$F = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \rho(\mathbf{r}) \frac{1}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}') + k_B T \int d^3\mathbf{r} \sum_j (c_j \ln(c_j/c_{j0}) - c_j), \quad (1)$$

where the total charge density $\rho = \sum_j \rho_j + \rho_f$. ρ_f is an external fixed charge density —associated with surfaces or molecular sources. The c_{j0} are the reference densities of component j ; they are a convenient way of parametrizing the chemical potential of the ions, $\mu_j = -k_B T \ln c_{j0}$.

If we minimize this functional of c_j then we find an effective free energy for the source field ρ_f , [1]. The problem in this formulation is the appearance of the long-ranged Coulomb interaction [2] which renders the evaluation and minimization less efficient than might be wished.

We start with a few points of notation: We will use the symbol f to describe a density of free energy of an electrolyte in mean field theory. We will freely integrate by parts in our expressions dropping terms which are zero in periodic boundary conditions. The transformations that

we perform conserve the stationary point of the mean field solution no matter the arguments of the functional f .

In eq. (1) one conventionally decouples the electrostatic interactions by introducing the potential as an additional variational field. If we do so then we find that

$$f = \rho\phi - \epsilon \frac{(\nabla\phi)^2}{2} + \sum_j k_B T (c_j \ln(c_j/c_{j0}) - c_j). \quad (2)$$

We see at once that we have gained in locality of the formulation; the other advantage is that it is valid for arbitrary spatial variation in the dielectric properties, $\epsilon(\mathbf{r})$. Unfortunately, the counterpart is that the resulting free energy is no longer convex. We do not have a minimizing principle, rather a stationary principle. This excludes some of the simplest optimization strategies that one might want apply —such as simultaneous annealing of conformational and electrostatic degrees of freedom. From eq. (2) one studies the differential

$$df = \sum_j dc_j (q_j \phi + k_B T \ln(c_j/c_{j0})) + d\phi (\rho + \nabla \cdot \epsilon \nabla \phi).$$

We now impose that the coefficient of dc_j is zero so that

$$q_j \phi + k_B T \ln(c_j/c_{j0}) = 0. \quad (3)$$

Substituting back into eq. (2) we find the standard form for the Poisson-Boltzmann functional [3–7]:

$$f = \rho_f \phi - \epsilon \frac{(\nabla\phi)^2}{2} - k_B T \sum_j c_{j0} e^{-q_j \phi}. \quad (4)$$

We take the variations of this functional with respect to ϕ to find:

$$\rho_f + \nabla \cdot \epsilon \nabla \phi + \sum_j q_j c_{j0} e^{-\beta q_j \phi} = 0. \quad (5)$$

For illustrative purposes we will often quote the symmetric ion system for which $q_j = \pm q$ and

$$f = \rho_f \phi - \epsilon \frac{(\nabla \phi)^2}{2} - 2k_B T c_0 \cosh(\beta q \phi). \quad (6)$$

Equation (6) continues to be awkward numerically since clearly both the derivative and the cosh functions are unbounded below; simple annealing procedures are thus unstable if one is interested in joint relaxation of conformational and ionic degrees of freedom. One has to solve the partial differential equation (5) in practical applications [8,9].

The purpose of this paper is to derive functionals that are equivalent to those given above which combine the advantages of the convexity of eq. (1) and the locality of eq. (2). We show how to find functions which are *numerically equivalent* to those widely used in the literature. We consider this *absolutely crucial* since much time has already been invested in calibration of potential functions. We thus look for ways of rendering convex known, accurate functionals. Our main tool in this effort will be the Legendre transform in a form presented in [10] as a reciprocal principle for variational calculations. We denote the Legendre transform of a convex function $g(x)$ as

$$\tilde{g}(\xi) = \mathcal{L}(g)[\xi] = \sup_x (x\xi - g(x)). \quad (7)$$

In the following calculations the way that the energy $\epsilon(\nabla \phi)^2/2$ is transformed into an equivalent form $\mathbf{D}^2/2\epsilon$ will remind the reader of the transformation of the kinetic energy in a Lagrangian, $m\dot{x}^2/2$ into the Hamiltonian equivalent, $p^2/2m$.

We now show how to transform Poisson-Boltzmann functionals expressed in terms of electrostatic potentials ϕ into those based on the displacement field, \mathbf{D} . Start with the electrostatic energy density

$$u = \rho_f \phi - \epsilon \frac{(\nabla \phi)^2}{2}. \quad (8)$$

Introduce now $\mathbf{E} = -\nabla \phi$ using a Lagrange multiplier \mathbf{D} to find the constrained functional

$$u = \rho_f \phi - \epsilon \frac{\mathbf{E}^2}{2} + \mathbf{D} \cdot (\mathbf{E} + \nabla \phi). \quad (9)$$

The advantage of this form is that we can perform independent variations in all variables. Integrate by parts and regroup:

$$u = -\epsilon \frac{\mathbf{E}^2}{2} + \mathbf{D} \cdot \mathbf{E} - \phi(\text{div } \mathbf{D} - \rho_f). \quad (10)$$

We now eliminate \mathbf{E} and see the equivalence of eq. (10) to

$$u = \frac{\mathbf{D}^2}{2\epsilon} - \phi(\text{div } \mathbf{D} - \rho_f). \quad (11)$$

We now re-interpret the field ϕ as a Lagrange multiplier [10] imposing Gauss' law and find the starting point of our previous papers [11] on constrained statistical mechanics in electrostatics.

We can now write eq. (2) in the form [11–14]

$$f = \frac{\mathbf{D}^2}{2\epsilon} + k_B T \sum_j (c_j \ln(c_j/c_{j0}) - c_j) \quad (12)$$

with

$$\text{div } \mathbf{D} - \rho = 0. \quad (13)$$

For a one-component plasma one trivially eliminates [15–17] the density degree of freedom to find

$$f = \frac{\mathbf{D}^2}{2\epsilon} + k_B T s((\text{div } \mathbf{D} - \rho_f)/q), \quad (14)$$

$$s(z) = z \ln(z/c_0) - z. \quad (15)$$

The functional equation (14) is now an unconstrained functional of the field \mathbf{D} . It can be discretized as in [11] where the vector field \mathbf{D} is associated to the links of a cubic lattice, while scalar quantities such as $(\text{div } \mathbf{D})$ and ρ_f are associated with the vertexes of the lattice. Equation (14) has the advantage of being both convex and local.

Let us now generalize this approach to Poisson-Boltzmann functionals expressed in terms of the potential rather than the density

$$f = \rho_f \phi - \epsilon \frac{(\nabla \phi)^2}{2} - g(\phi). \quad (16)$$

The transformation of eqs. (8)–(11) still goes through and we find

$$f = \frac{\mathbf{D}^2}{2\epsilon} + \phi(\rho_f - \text{div } \mathbf{D}) - g(\phi). \quad (17)$$

Further variations with respect to ϕ give simply the Legendre transform, eq. (7), of the function $g(\phi)$, where the transform variable is $\xi = (\rho_f - \text{div } \mathbf{D})$. Thus

$$F = \int \left\{ \frac{\mathbf{D}^2}{2\epsilon(\mathbf{r})} + \mathcal{L}(g)[\rho_f - \text{div } \mathbf{D}] \right\} d^3 \mathbf{r}. \quad (18)$$

This demonstrates the principle result of the present paper. Starting from a concave functional expressed in terms of the potential we have found a convex functional of the vector field \mathbf{D} . The critical points of the two functionals are, however, numerically identical.

We continue with the explicit example of the symmetric electrolyte for which

$$g(\phi) = 2k_B T c_0 \cosh(\beta q \phi). \quad (19)$$

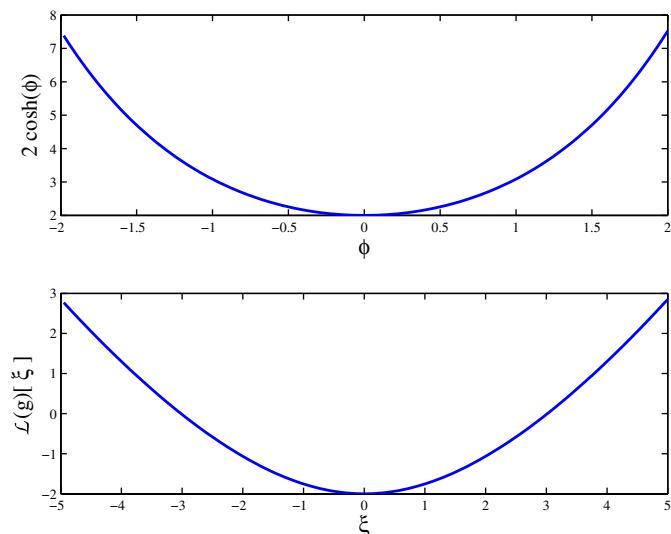


Fig. 1: (Colour on-line) Ionic contribution to the free energy density eq. (19) and its Legendre transform eq. (20) for $c_0 = q = k_B T = 1$.

The reciprocal free energy density that we require is

$$\tilde{g}(\xi) = \frac{k_B T \xi}{q} \sinh^{-1}(\xi/2qc_0) - k_B T \sqrt{4c_0^2 + \xi^2/q^2}. \quad (20)$$

We plot the function $\tilde{g}(\xi)$ in fig. 1.

When there are no ions within a region—for instance within a macromolecule—the Legendre transform requires some care in its definition: We take $g(\phi) = \eta\phi^2/2$ with η small. Then $\tilde{g} = \xi^2/(2\eta)$. The limit $\eta \rightarrow 0$ imposes a delta-function constraint on Gauss' law. Experience with local Monte Carlo algorithms based on the electric field [11,12, 14,18] implies that relaxation of longitudinal and transverse degrees of freedom via link, and plaquette updates is the most efficient manner to sample the above functionals.

In recent years theoretical methods have been introduced to generalize the application of Poisson-Boltzmann equations to a larger range of systems [19,20]. All these methods are based on the Hubbard-Stratonovich transformation to break pair interactions into one-body potentials. They have shown their power in producing functionals that include the finite volume of ions as well as mobile dipoles. A typical example of such a function for both symmetric ions and dipoles is [21–23]

$$f = \rho_f \phi - \epsilon_0 \frac{(\nabla\phi)^2}{2} - \left(2\lambda_{ion} \cosh(\beta q \phi) + \lambda_{dip} \frac{\sinh(\beta p_0 |\nabla\phi|)}{\beta p_0 |\nabla\phi|} \right), \quad (21)$$

where λ_{ion} and λ_{dip} are fugacities of the ions and the dipoles, p_0 is a dipole moment. $\epsilon(\mathbf{r}) = \epsilon_0$, since dielectric effects are generated dynamically.

We now consider the transformation of the functional equation (21). In this case we find a contribution of the

form

$$f_{\mathbf{E}} = -\epsilon_0 \frac{\mathbf{E}^2}{2} - \lambda_d \frac{\sinh(\beta p_0 |\mathbf{E}|)}{\beta p_0 |\mathbf{E}|} + \mathbf{D} \cdot \mathbf{E}. \quad (22)$$

Again if we consider the extremal equation for \mathbf{E} we recognize the Legendre transform, this time for the electric field, rather than for the potential.

Thus, the fully transformed functional in the presence of both ions and dipoles is

$$f = \mathcal{L} \left(\epsilon_0 \frac{\mathbf{E}^2}{2} + \lambda_{dip} \frac{\sinh(\beta p_0 |\mathbf{E}|)}{\beta p_0 |\mathbf{E}|} \right) [\mathbf{D}] + 2\lambda_{ion} \mathcal{L}(\cosh(\beta e \phi)) [\text{div } \mathbf{D} - \rho_f]. \quad (23)$$

For small fields, \mathbf{E} , we expand the first line of eq. (23). The modification of the curvature of the function is a manifestation of the electric susceptibility the dipoles.

In general it is impossible to analytically transform the functions needed in the dual formulation. However, in a given ionic system the Legendre transformed functionals are uniform in space. For the most general problem we require the two-dimensional transform with respect to the variables (ϕ, \mathbf{E}) . Fast numerical methods [24] are available for performing these transforms, and the result can be tabulated for a given application. Forces can be evaluated as well as energies, for instance in eq. (20), $d\tilde{g}(\xi)d\xi = \phi$ —a general property of the transform [25], thus the force on a test particle with charge e_j is just

$$\mathbf{F}_j = -e_j \nabla \phi = e_j \mathbf{E}. \quad (24)$$

We now show that the theory of Legendre transforms gives a direct route from the free energy expressed in terms of densities to that expressed in terms of the displacement field. The theorem that we require is that [26]

$$\mathcal{L}(\tilde{g} + \tilde{d})[x] = \inf_y [g(y) + d(x - y)], \quad (25)$$

defining the operation of *infimal convolution*.

Consider an electrolyte with charges, $q_j = \pm 1$ and with reference concentrations $c_0 = 1$. We study the minimum of the total ionic entropy $s(c_1) + s(c_2)$ under the constraint of Gauss' law. We use a Lagrange multiplier ϕ and study the variational form

$$t(c_1, c_2) = s(c_1) + s(c_2) + \phi(\xi - c_1 + c_2), \quad (26)$$

where $\xi = (\text{div } \mathbf{D} - \rho_f)$. The variation with respect to c_j gives

$$\tilde{t}(\phi) = -\tilde{s}(-\phi) - \tilde{s}(\phi) + \phi \xi. \quad (27)$$

The Legendre transformation of the entropy function $s(z)$ of eq. (15) is the Boltzmann factor $\mathcal{L}(s)[\xi] = c_0 e^\xi$ appearing in eq. (4). We now see that the extremal over ϕ corresponds to a second Legendre transform which we evaluate using eq. (25)

$$\mathcal{L}(\tilde{t}) = \inf_y [y \ln(y) - y + (y - \xi) \ln(y - \xi) - (y - \xi)]. \quad (28)$$

We find the stationary point of the entropy sums by taking the derivative and find $y = (\xi + \sqrt{4 + \xi^2})/2$. The action for the symmetric electrolyte eq. (20) is found with the help of the identity $\sinh^{-1}(\xi/2) = \ln((\xi + \sqrt{4 + \xi^2})/2)$.

We now return to the full field theoretical formulation of the Poisson-Boltzmann equation after Hubbard-Stratonovich transformation of the action, now denoted h , but before the saddle point evaluation [19,20]:

$$h = \epsilon \frac{(\nabla\phi)^2}{2} + g(i\phi) - i\rho_f\phi. \quad (29)$$

We now consider transformation in the philosophy of our above reciprocal formulation, but replacing Lagrange multipliers by complex integral representations of the delta-function. We do not neglect fluctuations in the fields and do not make any approximation in the statistical mechanics of the ionic system. Following very closely the logic described above we find the following succession of transformations of the action:

$$h = \epsilon \frac{(\nabla\phi)^2}{2} + g(i\phi) - i\rho_f\phi \quad (30)$$

$$\rightarrow \epsilon \frac{\mathbf{E}^2}{2} + g(i\phi) - i\mathbf{D} \cdot (\nabla\phi + \mathbf{E}) - i\rho_f\phi \quad (31)$$

$$\rightarrow \epsilon \frac{\mathbf{E}^2}{2} + g(i\phi) - i\mathbf{D} \cdot \mathbf{E} + i\phi(\text{div } \mathbf{D} - \rho_f) \quad (32)$$

$$\rightarrow \frac{\mathbf{D}^2}{2\epsilon} + g(i\phi) + i\phi(\text{div } \mathbf{D} - \rho_f). \quad (33)$$

The only thing that remains is the integral over ϕ . This we recognize as a Fourier transform with variable $\xi = (\text{div } \mathbf{D} - \rho_f)$. Thus the action expressed in terms of \mathbf{D} is

$$h = \frac{\mathbf{D}^2}{2\epsilon} - \ln\{\mathcal{F}(e^{-g(i\phi)})\}[\text{div } \mathbf{D} - \rho_f] \quad (34)$$

with \mathcal{F} the Fourier transform.

This action should be integrated over to find the partition sum

$$Z = \int d\mathbf{D} e^{-\beta \int h d^3\mathbf{r}}. \quad (35)$$

When the fluctuations at the saddle point are neglected the Fourier transform reduces to the Legendre transform as above, and the infimal convolution is a simple echo of the standard convolution of statistical weights occurring at the saddle point. If the Fourier transform becomes negative then the action becomes complex, or one must at least sample functions which are non-positive.

To conclude, we have introduced a duality transformation for Poisson-Boltzmann functionals which allows us to find a local minimizing principle for both electrostatic and conformation degrees of freedom in a simulation. This opens the perspective of simpler annealing

and dynamic relaxation in molecular simulation, including local Car-Parrinello evolution of ionic degrees of freedom [12] for complex molecules; for one-off solutions of the Poisson-Boltzmann equation standard methods based on the potential will remain the most efficient [17]. Clearly the interpolation of source charges to a grid requires control of their self-energy in a manner which is familiar in molecular dynamics simulations [27–29].

The functionals are designed to *exactly* conserve the saddle point. This is only true in practice if the numerical discretization is strictly equivalent. The final formulation requires a discretized divergence for Gauss' law in eq. (17), “Div”. This divergence operator is adjoint to the “–Grad” from eq. (9). Finally the Laplacian in the potential formulation must obey $\nabla^2 = \text{Div Grad}$. If this is not true discretization errors differ between the formulations. The form of the discretized that is natural is close to that used in the simulation of Maxwell's equations [30]. As stated in [10] the potential and field formulations can be used together to give upper and lower bounds for the mean field free energy.

A footnote on classical mechanics: let us now go back to variational principles in mechanics and develop the analogy to the above formulation of the Poisson-Boltzmann equation. Particle motion is deduced by studying the stationary points of a Lagrangian

$$L = m \frac{\dot{x}^2}{2} - V(x). \quad (36)$$

This variational problem can be simplified by introducing $v = \dot{x}$ and then studying the constrained problem

$$L = m \frac{v^2}{2} - V(x) - p(v - \dot{x}), \quad (37)$$

where p is a Lagrange multiplier. We can now consider the variational equation for v and deduce $p = mv$. Substituting for v we find that

$$L = -\frac{p^2}{2m} - V(x) + p\dot{x} \rightarrow -x\dot{p} - H(x, p) \quad (38)$$

is stationary, where H is the Hamiltonian, and we have integrated once by parts in the action principle to transfer the derivative from x to p . In classical mechanics we normally stop at this point and write down the Hamiltonian equations of motion. However, one can also recognize that a further variation with respect to x generates the Legendre transform of $V(x)$ (if it is convex). As a concrete example consider a particle in the potential $V(x) = |x|^s/s$, $s > 1$. The double transformed variational problem is

$$L = -\frac{p^2}{2m} + \frac{|\dot{p}|^r}{r} \quad (39)$$

with $1/s + 1/r = 1$. We thus find a Lagrangian expressed in terms of the momentum and its time derivative. For this non-linear oscillator it is easy to check that the equations of motion are equivalent in terms of the variable x or p .

Our transformation of the Poisson-Boltzmann equation introduces a similar double transformation, the Hamiltonian form eq. (38) corresponds to eq. (17). We have the translation $x \rightarrow \phi$, $v \rightarrow \mathbf{E}$ and $p \rightarrow \mathbf{D}$.

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