Free-energy functionals of the electrostatic potential for Poisson-Boltzmann theory

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In simulating charged systems, the numerically intensive task of solving the PB equation at each step of the simulation can be bypassed using variational methods that promote the electrostatic potential to a dynamical variable. But such approaches require access to a free-energy functional of potential: a functional that not only provides the correct solution of the PB equation at the stationary point, but also evaluates to the true free energy of the system at its minimum. We present a variational formulation with a local free-energy functional of the potential which aside from shedding new light on the PB theory, provides an ideal platform for dynamical minimization methods.

$$\mathcal{K}_{\mathrm{L}}[\psi] = \int \left[\frac{\epsilon\,|\nabla\psi|^2}{8\pi} - \frac{1}{\beta}\sum_{j=1}^{N} C_j e^{-\beta q_j \psi}(\beta q_j \psi + 1) \right] d\mathbf{r} + \int \Psi_{\mathrm{L}} \left[\nabla\cdot\frac{\epsilon}{4\pi}\nabla\psi + \rho_f + h(\psi) \right] d\mathbf{r},$$

$$\Psi_{\mathrm{L}} = h^{-1}\left(-\nabla\cdot\frac{\epsilon}{4\pi}\nabla\psi - \rho_f \right).$$

Local free-energy PB functional of potential

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