

The Random Phase Approximation:

Electrolytes, Polymer Solutions and Polyelectrolytes

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II. Electrolyte solutions

A. Poisson-Boltzmann equation

Let $\Phi(\vec{r}) =$ electrostatic potential at \vec{r}

$$\nabla^2 \Phi(r) = -\frac{4\pi}{\epsilon} e \rho(\vec{r}) \quad \text{Poisson}$$

where $\rho(\vec{r}) = z_+ n_+(\vec{r}) - z_- n_-(\vec{r})$

valency \nearrow
of + charges # density of - charges \uparrow

But $n_+(\vec{r}) = n_+^0 e^{-\beta z_+ e \Phi(\vec{r})}$

$n_-(\vec{r}) = n_-^0 e^{\beta z_- e \Phi(\vec{r})}$ Boltzmann (mean field approximation)

So

$$\rho(\vec{r}) = z_+ n_+^0 e^{-\beta z_+ e \Phi(\vec{r})} - z_- n_-^0 e^{\beta z_- e \Phi(\vec{r})}$$

P-B eqn

$$\nabla^2 \Phi = -\frac{4\pi}{\epsilon} e \left\{ z_+ n_+^0 e^{-\beta z_+ e \Phi(\vec{r})} - z_- n_-^0 e^{\beta z_- e \Phi(\vec{r})} \right\}$$

B. Debye-Hückel equation

Linearize the Poisson-Boltzmann equation (assume electrostatic energy is weak compared to kT)

$$\nabla^2 \Phi = -\frac{4\pi}{\epsilon} e \left\{ z_+ n_+^0 e^{-\beta z_+ e \Phi(\vec{r})} - z_- n_-^0 \left(1 + e^{\beta z_- e \Phi(\vec{r})} \right) \right\}$$

$$\nabla^2 \Phi = -\frac{4\pi}{\epsilon} e \left\{ \left(z_+ n_+^0 - z_- n_-^0 \right) - \beta e \left(z_+^2 n_+^0 + z_-^2 n_-^0 \right) \Phi(\vec{r}) + \dots \right\}$$

but $z_+ n_+^0 - z_- n_-^0 = 0$ due to electroneutrality, so

$$\nabla^2 \Phi = -\frac{4\pi e^2}{\epsilon kT} \left(z_+^2 n_+^0 + z_-^2 n_-^0 \right) \Phi$$

Let $\frac{e^2}{\epsilon kT} = \ell_B$ Bjerrum length

Then $\nabla^2 \Phi = 4\pi \ell_B \underbrace{\left(z_+^2 n_+^0 + z_-^2 n_-^0 \right)}_{\kappa^2} \Phi$

Where $\kappa^{-1} =$ Debye screening length---multivalent ions screen more effectively.

Thus, we have

$$\boxed{\nabla^2 \Phi = \kappa^2 \Phi}$$

Debye-Hückel equation

1. Free energy of Debye-Hückel equation

Consider hard spheres of diameter a with charges z_{\pm} . What is potential around a sphere of charge q_0 whose center is at the origin?

$$\nabla^2 \Phi = \kappa^2 \Phi \quad r < a$$

$$\nabla^2 \Phi = 0 \quad r \leq a$$

B.C.'s: $\Phi(r = \infty) = 0$

$\Phi(r)$ is continuous at $r = a$

$\epsilon \frac{\partial \Phi}{\partial r}$ is continuous at $r = a$ (electric field)

$$\text{Solution: } \Phi(r) = \begin{cases} \frac{q}{\epsilon r} - \frac{q\kappa}{\epsilon(1+\kappa a)} & r \leq a \\ \frac{q\epsilon^{-\kappa(r-a)}}{\epsilon r(1+\kappa a)} & r > a \\ \text{Yukawa} \end{cases}$$

Exclude the self-energy term $\frac{q}{\epsilon r}$. Then $\phi(0)$ due to all the other charges is

$$\psi(r=0) = \frac{q\kappa}{\epsilon r(1+\kappa a)}$$

The electrostatic free energy satisfies

$$dF_{el} = \sum_i \psi_i dq_i$$

where ψ_i = potential acting on charge q_i due to all the other charges, because ψ_i and q_i are thermodynamic conjugates.

$$\left(\frac{\partial F_{el}}{\partial q_i} \right)_{N,V,T} = \psi_i$$

$$\text{So } F_{el} = \sum_i \int_0^1 \psi_i(\lambda) d(\lambda q_i)$$

potential on ion i when all ions have charges λq_i .

$$\text{So } \psi_i(\lambda) = \frac{q_{i\lambda} \kappa \lambda}{\epsilon(1+\kappa \lambda a)}$$

$$F_{el} = \sum_i \frac{q_i^2 \kappa}{\epsilon} \int_0^1 d\lambda \frac{\lambda^2}{1+\kappa a \lambda}$$

$$\begin{aligned} \text{But: } \sum_i \frac{q_i^2}{\epsilon} &= \frac{1}{\epsilon} (e^2 z_+^2 n_+^0 V + e^2 z_-^2 n_-^0 V) \\ &= V \frac{e^2}{\epsilon} (z_+^2 n_+^0 + z_-^2 n_-^0) \end{aligned}$$

$$\text{recall that } \kappa^2 = \frac{4\pi e^2}{\epsilon kT} (z_+^2 n_+^0 + z_-^2 n_-^0)$$

$$\Rightarrow \sum_i \frac{q_i^2}{\epsilon} = \frac{kT}{4\pi} \kappa^2 V$$

$$f_{el} = \frac{F_{el}}{kTV} = \frac{\kappa^3}{4\pi} \int_0^1 d\lambda \frac{\lambda^2}{1+\kappa a \lambda}$$

So we have

$$f_{el} = -\frac{\kappa^3}{12\pi} f(\kappa a)$$

where

$$f(\kappa a) = \frac{3}{\kappa^3 a^3} \left\{ \ln(1+\kappa a) - \kappa a + \frac{1}{2} \kappa^2 a^2 \right\}$$

Note that $f(\kappa a) \rightarrow 1$ as $\kappa a \rightarrow 0$.

So, for dilute solutions

$$f_{el} = -\frac{\kappa^3}{12\pi}$$

This is **negative**: attractive interactions between opposite charges predominate.

Osmotic pressure: $\beta p = n_+^0 + n_-^0 - \frac{\kappa^3}{24\pi}$

Note that there is no second virial coefficient due to long-ranged interaction.

2. Correlations in Debye-Hückel theory: Poor Person's version.

Look at charge distribution around a central ion q_i

$$\begin{aligned} -\frac{4\pi}{\epsilon} \rho(r) &= \nabla^2 \phi(r) && \text{Poisson} \\ &= \kappa^2 \phi(r) \end{aligned}$$

$$\begin{aligned} \text{So } \rho(r) &= -\frac{\epsilon}{4\pi} \kappa^2 \phi(r) \\ &= -\frac{\epsilon}{4\pi} \kappa^2 q_i \frac{e^{-\kappa(r-a)}}{\epsilon r(1+\kappa a)} \end{aligned}$$

So the charge q_i is surrounded by a screening cloud of opposite sign that decays exponentially and monotonically with screening length.

III. Polymer Solutions – the random phase approximation

Suppose we have N chains, each M monomers long, in a box of volume V .

Define the number density of monomers:

$$n(\vec{r}) = \sum_{i=1}^N \int_0^M ds \delta(\vec{r} - \vec{r}_{is})$$

A. What are the interactions?

1. There are interactions that hold the chain together.

$$\beta H_0 = + \frac{3}{2b^2} \int_0^M ds \left(\frac{\partial \vec{r}}{\partial s} \right)^2$$

This is a continuous version of

$$\beta H_0 = + \frac{3}{2b^2} \sum_{s=1}^M (\vec{r}_s - \vec{r}_{s-1})^2$$

So, this corresponds to a bead-spring model of a chain:



This has an average bond length

$$\langle \vec{r}^2 \rangle = b^2.$$

2. In addition, we can include a short-ranged interaction between monomers:

$$\beta H_2 = + \frac{1}{2} v \int d\vec{r} (\rho(r))^2 \quad \begin{array}{l} \text{for good solvent} \\ v > 0 \end{array}$$

3. Finally, allow for a chemical potential $\mu(\vec{r})$ (in units of kT). This will allow us to examine the average density and density correlations.

$$\beta H_1 = - \int d\vec{r} \mu(\vec{r}) \rho(\vec{r}).$$

B. The partition function is

$$Z = \frac{1}{N!} \int D\vec{r}_{is} e^{-\beta_2 H_0(\{\vec{r}_{is}\})} e^{-\beta H_1} e^{-\beta H_2}$$

this is the hard one because it is a two-body interaction term.

Hubbard-Stratanovich transformation (complete the square)

Note that

$$-\frac{1}{2}v \int d\bar{r} (\rho(\bar{r}))^2 = \frac{1}{2v} \int d\bar{r} [J(\bar{r}) - iv\rho(\bar{r})]^2 - \frac{1}{2v} \int d\bar{r} (J(\bar{r}))^2 + i \int d\bar{r} J(\bar{r})\rho(\bar{r})$$

So

$$\int DJ e^{-\frac{1}{2}v \int d\bar{r} \rho(\bar{r})^2} e^{\frac{1}{2v} \int d\bar{r} [J(\bar{r}) - iv\rho(\bar{r})]^2} = \int DJ e^{-\frac{1}{2}v \int d\bar{r} (J(\bar{r}))^2} e^{i \int d\bar{r} J(\bar{r})\rho(\bar{r})}$$

or

$$e^{-\frac{1}{2}v \int d\bar{r} \rho(\bar{r})^2} = \frac{\int DJ e^{i \int d\bar{r} J(\bar{r})\rho(\bar{r}) - \frac{1}{2v} \int d\bar{r} J^2}}{\int DJ e^{-\frac{1}{2v} \int d\bar{r} (J(\bar{r}))^2}}$$

So, the partition function is

$$Z = \frac{1}{N!} \frac{1}{Q_J} \int DJ e^{-\frac{1}{2v} \int d\bar{r} (J(\bar{r}))^2} \int D\bar{r}_{is} e^{-\rho_i H_0^{(i)}} e^{\int d\bar{r} [\mu(\bar{r}) + iJ(\bar{r})]\rho(\bar{r})}$$

$$\text{where } Q_J = \int DJ e^{-\frac{1}{2v} \int d\bar{r} (J(\bar{r}))^2}$$

The advantage of the Hubbard-Stratanovich transformation is that we have replaced a two-body interaction with a one-body interaction with a chemical potential $iJ(\mathbf{r})$. This reduces the problem to one of non-interacting chains in a spatially varying chemical potential.

$$\text{Note that } \rho(\bar{r}) = \sum_i \rho_i(\bar{r})$$

$$\text{Where } \rho_i(\bar{r}) = \int ds \delta(\bar{r} - \bar{r}_{is})$$

So, we can rewrite Z:

$$Z = \frac{1}{N!} \frac{1}{Q_J} \int DJ (Z_1[\mu + iJ])^N e^{-\frac{1}{2v} \int d\bar{r} (J(\bar{r}))^2}$$

where $Z_1[\mu + iJ]$ is the partition function of a single chain in chemical potential $\mu(\mathbf{r}) + iJ(\mathbf{r})$.

Let $\tilde{\mu} = \mu + iJ$. Then we have

$$Z_1[\tilde{\mu}] = \int D\tilde{r}_s e^{-\beta H_0} e^{\int d\tilde{r} \tilde{\mu}(\tilde{r}) \rho(\tilde{r})}.$$

*Digression on Fourier transformations:

I will use the convention

$$\tilde{f}_k = \int d\tilde{r} e^{ik \cdot \tilde{r}} f(\tilde{r})$$

$$f(\tilde{r}) = \frac{1}{V} \sum_k e^{-ik \cdot \tilde{r}} \tilde{f}_k$$

$$\delta(\tilde{r} - \tilde{r}') = \frac{1}{V} \sum_k e^{-ik \cdot (\tilde{r} - \tilde{r}')} \tilde{f}_k$$

$$\delta_{k,k'} = \frac{1}{V} \int d\tilde{r} e^{+i(k-k') \cdot \tilde{r}}$$

$$\text{So } \int d\tilde{r} \tilde{\mu}(\tilde{r}) \rho(\tilde{r}) = \frac{1}{V} \sum_k \tilde{\mu}_k \rho_{-k}.$$

Note: we are fixing $\rho_{k=0}$ so $\mu_{k=0} = 0$. Also, $\langle \rho_k \rangle = 0$ for $k \neq 0$.

Now expand the exponential in Z_1 .

$$e^{\frac{1}{V} \sum_k \tilde{\mu}_k \rho_{-k}} = 1 + \frac{1}{V} \sum_k \tilde{\mu}_k \rho_{-k} + \frac{1}{2V^2} \sum_{kk'} \tilde{\mu}_k \tilde{\mu}_{k'} \rho_{-k} \rho_{-k'} + \dots$$

$$Z_1[\tilde{\mu}] = Z_1^0 \left[1 + \frac{1}{2V^2} \sum_k \tilde{\mu}_k \tilde{\mu}_{-k} \langle \rho_k \rho_{-k} \rangle + \dots \right]$$

Define $Mg_k = \langle \rho_k \rho_{-k} \rangle$. This is the form factor of the chain.

Re-exponentiate:

$$Z_1[\tilde{\mu}] = Z_1^0 e^{\frac{M}{2V^2} \sum_k g_k \tilde{\mu}_k \tilde{\mu}_{-k} + \dots}$$

Substitute back into Z : let $c = \frac{NM}{V}$ be the monomer density.

Then the partition function for the many-chain system is

$$Z = \frac{(Z_1^0)^N}{N!} \frac{1}{Q_J} \int DJ e^{\frac{1}{2} \frac{1}{V} \sum_k c g_k (\mu_k + iJ_k)^2 + \dots} e^{-\frac{1}{2} \frac{1}{V} \sum_k |J_k|^2}$$

Z

$$Z = \frac{(Z_1^0)^N}{N!} \frac{1}{Q_J} e^{\frac{1}{2} \frac{1}{V} \sum_k c g_k \mu_k \mu_{-k}} \int \mathcal{D}J e^{\frac{i}{V} \sum_k c g_k \mu_k J_{-k} - \frac{1}{2} \frac{1}{V} \sum_k \left(c g_k + \frac{1}{v} \right) J_k J_{-k}}$$

Solve by saddlepoint approximation:

argument of exponential has zero derivative when

$$i c g_k \mu_k = \left(c g_k + \frac{1}{v} \right) J_k$$

$$\Rightarrow J_k = i \frac{c g_k}{c g_k + \frac{1}{v}} \mu_k$$

Evaluate argument at saddlepoint:

$$-\frac{1}{V} \sum_k \frac{c^2 g_k^2}{c g_k + 1/v} \mu_k \mu_{-k} + \frac{1}{2} \frac{1}{V} \sum_k \frac{c^2 g_k^2}{c g_k + \frac{1}{v}} \mu_k \mu_{-k} = -\frac{1}{2} \frac{1}{V} \sum_k \frac{c^2 g_k^2}{c g_k + \frac{1}{v}} \mu_k \mu_{-k}$$

$$Z = \frac{(Z_1^0)^N}{N!} \frac{1}{Q_J} e^{\frac{1}{2} \frac{1}{V} \sum_k c g_k \left(1 - \frac{c g_k}{c g_k + \frac{1}{v}} \right) \mu_k \mu_{-k}} = \frac{(Z_1^0)^N}{N!} \frac{1}{Q_J} e^{\frac{1}{2} \frac{1}{V} \sum_k \left(\frac{c g_k}{1 + v c g_k} \right) \mu_k \mu_{-k}}$$

The free energy is

$$\beta W = -\ln Z = \text{stuff} - \frac{1}{2} \frac{1}{V} \sum_k \frac{c g_k}{1 + v c g_k} \mu_k \mu_{-k}$$

The correlations functions satisfy

$$\langle \rho_k \rho_{-k} \rangle = -\frac{\partial^2 \beta W}{\partial \mu_k \partial \mu_{-k}} = \frac{c g_k}{1 + v c g_k}$$

So we have

$$\boxed{\langle \rho_k \rho_{-k} \rangle = \frac{1}{v + \frac{1}{c g_k}}}$$

This is the RPA result for the correlation function.

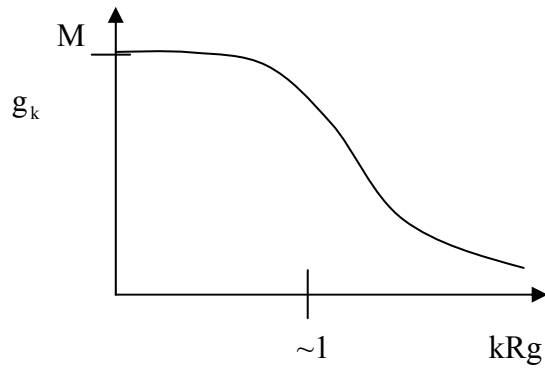
Recall that $M g_k = \langle \rho_k \rho_{-k} \rangle$ for a single chain, where g_k is the form factor.

$$g_k = M f(k^2 M b^2 / 6) = M f(k^2 R g^2)$$

where $f(x) = \frac{2}{x^2} (e^{-x} - 1 + x)$ is the Debye function (see Doi & Edwards, pp. 22-23).

$$f(x) \approx 1 - \frac{1}{3}x \quad x \rightarrow 0$$

$$\approx 2/x \quad x \rightarrow \infty$$



Increasing ν just flattens the curve out.

RPA is a good way to derive mean-field free energies and correlation functions.

IV. Field theoretical derivation of Debye-Hückel theory.

Consider $\left. \begin{array}{l} N_+ \text{ ions of valency } Z_+ \\ N_- \text{ ions of valency } Z_- \end{array} \right\} \begin{array}{l} N_+ Z_+ = N_- Z_- \\ \text{by electroneutrality} \end{array}$

Let $n_{\pm}^0 = \frac{N_{\pm}}{V}$ average density of each species

$$n_{\pm}(\vec{r}) = \sum_{i=1}^{N_{\pm}} \delta(\vec{r} - \vec{r}_i) \quad \text{local density of each species}$$

$$\rho(\vec{r}) = z_+ n_+(\vec{r}) - z_- n_-(\vec{r})$$

$$\text{and } \beta H_{el} = \frac{1}{2} \ell_B \int d\vec{r} \int d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

where $\ell_B = \frac{e^2}{\epsilon kT}$ is the Bjerrum length.

Rewrite this in matrix form:

$$\text{let } \mathbf{n}(\vec{r}) = \begin{pmatrix} n_+(\vec{r}) \\ n_-(\vec{r}) \end{pmatrix}$$

$$V(\vec{r} - \vec{r}') = \frac{\ell_B}{|\vec{r} - \vec{r}'|} \begin{pmatrix} z_+^2 & -z_+ z_- \\ -z_+ z_- & z_-^2 \end{pmatrix}$$

Then

$$\frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} = \mathbf{n}(\vec{r}) \cdot V(\vec{r} - \vec{r}') \cdot \mathbf{n}(\vec{r}')$$

$$\beta H_{el} = \frac{1}{2} \int d\vec{r} \int d\vec{r}' \mathbf{n}(\vec{r}) \cdot V(\vec{r} - \vec{r}') \cdot \mathbf{n}(\vec{r}')$$

In Fourier space:

$$\beta H_{el} = \frac{1}{2} \frac{1}{V} \sum_k \mathbf{n}_k \cdot V_k \cdot \mathbf{n}_{-k}$$

$$\text{where } V_k = \frac{4\pi\ell_B}{k^2} \begin{pmatrix} z_+^2 & -z_+ z_- \\ -z_+ z_- & z_-^2 \end{pmatrix}$$

In addition, we can introduce $\mu(r) = \begin{pmatrix} \mu_+(r) \\ \mu_-(r) \end{pmatrix}$ and $\beta H_1 = - \int d\bar{r} \mu(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r})$ in order to calculate correlation functions.

The partition function is then given by

$$Z = \frac{1}{N_+! N_-!} \int D r_+ \int D r_- e^{-\beta H_1} e^{-\beta H_{el}}$$

Carry out the Hubbard-Stratanovich transformation:

$$e^{-\frac{1}{2} \int n \cdot v \cdot n} = \frac{\int D J_+ \int D J_- e^{i \int n \cdot J} e^{-\frac{1}{2} \int J \cdot V^{-1} \cdot J}}{\int D J_+ \int D J_- e^{-\frac{1}{2} \int J \cdot V^{-1} \cdot J}}$$

where $J(r) = \begin{pmatrix} J_+(r) \\ J_-(r) \end{pmatrix}$

Note that $i J_{\pm}(\mathbf{r})$ is like $\pm \beta e \Phi(\mathbf{r})$

↖
potential acting at \mathbf{r} due to other charges

As before,

$$Z = \frac{1}{N_+! N_-!} \int D J_{\pm} e^{-\frac{1}{2} \int J \cdot V^{-1} \cdot J} \underbrace{\int D r_{\pm} e^{-\frac{1}{2} \int (\mu+iJ) \cdot n}}_{(Z_1[\mu+iJ_{\pm}])^{N_{\pm}}}$$

where

$$Z_1[\mu + iJ_{\pm}] = \int D r_{\pm} e^{\int \mu_{\pm} n_{\pm}} \quad \text{for a +/- ion.}$$

Again, define $\tilde{\mu} = \mu + iJ$ and examine the single particle partition function.

$$Z_1[\mu_{\pm}] = Z_{\pm} e^{-\frac{1}{2} \frac{1}{V^2} \sum_k \tilde{\mu}_{\pm}(k) g_{\pm}(k) \tilde{\mu}_{\pm}(-k) + H.O.T}$$

↖ where $g_{\pm}(k)$ is the form factor of the +/- ion.

truncate in Debye-Hückel theory. This is equivalent to assuming electrostatic energy is weak compared to kT .

$$(Z_1[\mu_{\pm}])^{N_{\pm}} = Z_{\pm}^{N_{\pm}} e^{-\frac{1}{2} \frac{N_{\pm}}{V} \sum_k \tilde{\mu}_{\pm} g_{\pm} \tilde{\mu}_{\pm}}$$

So, $(Z_+[\tilde{\mu}_+])^{N_+} (Z_-[\tilde{\mu}_-])^{N_-} = Z_+^{N_+} Z_-^{N_-} e^{-\frac{1}{2V} \sum_k \tilde{\mu} \cdot G \cdot \tilde{\mu}}$

where $G = \begin{pmatrix} \mathbf{n}_+^0 \mathbf{g}_+ & 0 \\ 0 & \mathbf{n}_-^0 \mathbf{g}_- \end{pmatrix}$.

Substitute back into Z:

$$Z \cong \frac{Z_+^{N_+} Z_-^{N_-}}{N_+! N_-!} \frac{\int \mathcal{D}J_{\pm} e^{\frac{1}{2} \frac{1}{V} \sum_k (\mu+iJ) G (\mu+iJ)} e^{-\frac{1}{2} \frac{1}{V} \sum_k J \cdot V^{-1} \cdot J}}{\int \mathcal{D}J_{\pm} e^{-\frac{1}{2} \frac{1}{V} \sum_k J \cdot V^{-1} \cdot J}}$$

Carry out the Gaussian integrals (see Doi and Edwards appendix 2.I)

Denominator: $\int \mathcal{D}J_{\pm} e^{-\frac{1}{2} \frac{1}{V} \sum_k J \cdot V^{-1} \cdot J} = \pi^{\frac{1}{2}f} \prod_k |V^{-1}|^{-\frac{1}{2}}$

Numerator: $\int \mathcal{D}J_{\pm} e^{\frac{i}{V} \sum_k \mu \cdot G \cdot J} e^{-\frac{1}{2} \frac{1}{V} \sum_k J (G+V^{-1}) J}$
 $= \int \mathcal{D}J_{\pm} e^{-\frac{1}{2V} \sum_k \mu \cdot G \cdot (G+V^{-1})^{-1} \cdot G \cdot \mu} \cdot \pi^{\frac{1}{2}f} \prod_k |G+V^{-1}|^{-\frac{1}{2}}$

So $Z \cong \frac{Z_+^{N_+} Z_-^{N_-}}{N_+! N_-!} e^{\frac{1}{2} \frac{1}{V} \sum_k \mu \tilde{G} \cdot \mu} \prod_k |G+V^{-1}|^{-\frac{1}{2}} |V^{-1}|^{\frac{1}{2}}$

where $\tilde{G} = G \cdot (1 - (G+V^{-1})^{-1} \cdot G) = G \cdot (1 + V \cdot G)^{-1}$

or equivalently,

$$Z = \frac{(Z_+)^{N_+} (Z_-)^{N_-}}{N_+! N_-!} e^{\frac{1}{2} \frac{1}{V} \sum_k \mu \tilde{G} \cdot \mu} \prod_k |1 + V \cdot G|^{-1/2}$$

For point particles, $Z_{\pm} = V$, $g_{\pm}(k) = 1$.

So

$$Z = \frac{V^{N_+} V^{N_-}}{N_+! N_-!} \prod_k |1 + V \cdot G|^{-\frac{1}{2}} e^{\frac{1}{2} \frac{1}{V} \sum_k \mu \tilde{G} \cdot \mu}$$

To get the free energy, we can set $\mu_k \equiv 0$.

$$\beta f = \beta \frac{F}{V} = -\frac{\ln Z}{V} = n_+^0 \ln n_+^0 + n_-^0 \ln n_-^0 + \frac{1}{2} \frac{1}{V} \sum_k \ln |1 + V \cdot G|$$


Now take the thermodynamic limit:

$$\beta f = n_+^0 \ln n_+^0 + n_-^0 \ln n_-^0 + \frac{1}{2} \int \frac{d\bar{k}}{(2\pi)^3} \ln |1 + V \cdot G|$$

$$\begin{aligned} |1 + V \cdot G| &= \det \begin{pmatrix} 1 + \frac{4\pi\ell_B}{k^2} n_+^0 z_+^2 & -n_-^0 z_+ z_- \frac{4\pi\ell_B}{k^2} \\ -n_+^0 z_+ z_- \frac{4\pi\ell_B}{k^2} & 1 + \frac{4\pi\ell_B}{k^2} n_-^0 z_-^2 \end{pmatrix} \\ &= 1 + \frac{4\pi\ell_B}{k^2} (n_+^0 z_+^2 + n_-^0 z_-^2) \\ &= 1 + \frac{\kappa^2}{k^2}. \end{aligned}$$

So for point particles,

$$\beta f = n_+^0 \ln n_+^0 + n_-^0 \ln n_-^0 + \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \left[\ln \left(1 + \frac{\kappa^2}{k^2} \right) - \frac{\kappa^2}{k^2} \right]$$

subtract self-energy 

let $x^2 = \frac{k^2}{\kappa^2}$

$$\beta f = n_+^0 \ln n_+^0 + n_-^0 \ln n_-^0 + \frac{1}{2} \kappa^3 \underbrace{\int \frac{d^3 x}{(2\pi)^3} \left[\ln \left(1 + \frac{1}{x^2} \right) - \frac{1}{x^2} \right]}_{-\frac{1}{6\pi}}$$

So the final answer is:

$$\beta f = n_+^0 \ln n_+^0 + n_-^0 \ln n_-^0 - \frac{\kappa^3}{12\pi}$$

Same answer as before from standard approach!

Look at correlations:

$$\langle n_+(k) n_-(k) \rangle = - \left. \frac{\delta \beta f}{\delta \mu_k^+ \delta \mu_k^-} \right|_{\mu_k=0}$$

The free energy contribution from $\mu_k \neq 0$ terms is $-\frac{1}{2} \frac{1}{V} \sum_k \mu_k \cdot \tilde{G} \cdot \mu_{-k}$

where $\tilde{G} = G \cdot (1 + V \cdot G)^{-1}$.

The advantage of this approach is that we can now write down the Debye-Hückel free energy for particles of arbitrary structure.

Recall

$$\beta f = n_+^0 \ln n_+^0 + n_-^0 \ln n_-^0 + \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \ln(1 + V \cdot G)$$

where

$$|1 + V \cdot G| = \det \begin{pmatrix} 1 + \frac{4\pi\ell_B}{k^2} n_+^0 z_+^2 g_+(k) & -n_-^0 z_+ z_- \frac{4\pi\ell_B}{k^2} g_-(k) \\ -n_+^0 z_+ z_- \frac{4\pi\ell_B}{k^2} g_+(k) & 1 + \frac{4\pi\ell_B}{k^2} n_-^0 z_-^2 g_-(k) \end{pmatrix}$$

$$|1 + V \cdot G| = 1 + \frac{\kappa^2(k)}{k^2}$$

where $\kappa^2(k) = 4\pi\ell_B (n_+^0 z_+^2 g_+(k) + n_-^0 z_-^2 g_-(k))$

For example, suppose the ions are spheres of diameter a .

Then $\kappa^2(k) = \kappa^2 g_k$

where $g_k = 3 \frac{\sin ka - ka \cos ka}{(ka)^3}$

is the form factor of a sphere.

So a more general expression for the free energy is

$$\beta f = n_+^0 \ln n_+^0 + n_-^0 \ln n_-^0 + \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \left[\ln \left(1 + \frac{\kappa^2(k)}{k^2} \right) - \frac{\kappa^2(k)}{k^2} \right]$$

For the general case, the FT of the charge correlation function is

$$\langle \rho_k \rho_{-k} \rangle = \frac{k^2}{k^2 + \kappa^2(k)} [n_+^0 g_+(k) + n_-^0 g_-(k)]$$

V. Field-theoretical derivation of Poisson-Boltzmann theory

Suppose there are fixed charges with some distribution $\sigma(\mathbf{r}) < 0$.

Assume that the N counterions are point charges of valency z .

Then the partition function is

$$Z_N = \frac{1}{N!} \int D\bar{r}_i e^{-\beta H}$$

where

$$\begin{aligned} \beta H &= \frac{1}{2} \ell_B z^2 \int dr \int dr' n(r) V(r-r') n(r) + z \ell_B \int dr \int dr' n(r) V(r-r') \sigma(r) \\ &+ \frac{1}{2} \ell_B \int dr \int dr' \sigma(r) V(r-r') \sigma(r) - \int dr n(r) \mu(r) \\ &= \frac{1}{2} \ell_B \int dr \int dr' [zn(r) + \sigma(r)] V(r-r') [zn(r') + \sigma(r')] - \int n(r) \mu(r) dr. \end{aligned}$$

let $\tilde{n}(\mathbf{r}) = zn(\mathbf{r}) + \sigma(\mathbf{r})$.

then

$$\beta H = \frac{1}{2} \ell_B \int dr \int dr' \tilde{n}(r) V(r-r') \tilde{n}(r') - \int dr n(r) \mu(r)$$

Introduce the Hubbard-Stratanovich transformation:

$$e^{-\frac{1}{2} \ell_B \int \tilde{n} V \tilde{n}} = \frac{\int D J e^{i \int \tilde{n} J} e^{-\frac{1}{2 \ell_B} \int J V^{-1} J}}{\int D J e^{-\frac{1}{2 \ell_B} \int J V^{-1} J}}$$

So

$$\begin{aligned} Z &= \frac{1}{N!} \int D r_i \frac{1}{Q_J} \int D J e^{i \int \tilde{n} J} e^{\int n \mu} e^{-\frac{1}{2 \ell_B} \int J V^{-1} J} \\ &= \frac{1}{N!} \frac{1}{Q_J} \int D J e^{-\frac{1}{2 \ell_B} \int J V^{-1} J} \int D \bar{r}_i e^{\int i(zn + \sigma) J + n \mu} \\ &= \frac{1}{N!} \frac{1}{Q_J} \int D J e^{-\frac{1}{2 \ell_B} \int J V^{-1} J} e^{i \int \sigma J} \int D \bar{r}_i e^{\int n \tilde{\mu}} \end{aligned}$$

where $\tilde{\mu}(r) = \mu(r) + i z J(r)$.

Note that $V^{-1}(r-r') = -\frac{1}{4\pi} \nabla^2 \delta(r-r')$

Is the inverse operator for the Coulomb interaction. Why?

By definition, the inverse operator satisfies

$$\int d r' V^{-1}(r-r') V(r-r') = \delta(r-r'')$$

From Poisson's equation

$$\frac{1}{\varepsilon} \nabla^2 V(r) = -\frac{4\pi}{\varepsilon} \delta(r)$$

$$\Rightarrow -\frac{1}{4\pi} \nabla^2 V(r-r'') = \delta(r-r'')$$

$$\text{So } \int d r' V^{-1}(r-r') V(r-r'') = -\frac{1}{4\pi} \nabla^2 V(r-r'')$$

$$\text{So } V^{-1}(r-r') = -\frac{1}{4\pi} \nabla^2 \delta(r-r')$$

Now look at

$$\begin{aligned} Z_1[\tilde{\mu}] &= \int d\tilde{r}_1 e^{\int n(r) \tilde{\mu}(r) dr} \\ &= \int d\tilde{r}_1 e^{\int dr \delta(r-r_1) \tilde{\mu}(r)} \\ &= \int d\tilde{r}_1 e^{\tilde{\mu}(r_1)} \end{aligned}$$

so we have

$$Z_N = \frac{1}{N!} \frac{1}{Q_J} \int D J e^{-\frac{1}{2\ell_B} \int J V^{-1} J} e^{i \int \sigma(r) J(r) dr} \left[\int d\tilde{r} e^{\mu(r) + i z J(r)} \right]^N$$

Now look at the grand canonical partition function:

$$\begin{aligned} \Xi &= \sum_N \lambda^N Z_N[\tilde{\mu}] \\ &= \frac{1}{Q_J} \int D J e^{-\frac{1}{2\ell_B} \int J V^{-1} J} e^{i \int \sigma J} \sum_N \frac{1}{N!} \lambda^N (Z_1[\mu + i z J])^N \end{aligned}$$

$$\Xi = \frac{1}{Q_J} \int \mathcal{D}J e^{-\frac{1}{2\ell_B} \int J V^{-1} J + i \int \sigma J} e^{\lambda \int e^{\mu + iz} J dr}$$

Look at

$$\begin{aligned} \int J V^{-1} J &= \int dr \int dr' J(r) \left(-\frac{1}{4\pi} \nabla^2 \right) \delta(r-r') J(r') \\ &= -\frac{1}{4\pi} \int dr J(r) \nabla^2 J(r) \\ &= +\frac{1}{4\pi} \int dr (\nabla J(r))^2 \end{aligned}$$

So the grand canonical partition function is

$$\Xi = \frac{1}{Q_J} \int \mathcal{D}J e^{-\frac{1}{2} \frac{1}{4\pi\ell_B} \int (\nabla J)^2 + i \int \sigma J + \lambda \int e^{\mu + iz} J}$$

From the partition function, we can find the average local density:

$$\begin{aligned} \langle n(r) \rangle &= \left. \frac{\delta \ln \Xi}{\delta \mu(r)} \right|_{\mu=0} \\ &= \lambda \langle e^{iz J(r)} \rangle \end{aligned}$$

Now carry out the saddle point approximation for the integral over J. (set $\mu = 0$)

$$\text{let } F = \frac{1}{8\pi\ell_B} (\nabla J)^2 - i \sigma(r) J(r) - \lambda e^{iz J(r)}$$

Then we have

$$\Xi = \frac{1}{Q_J} \int \mathcal{D}J e^{-\int F dr}$$

The argument of the exponential is extremized when

$$\frac{\delta F}{\delta J} = 0 \Rightarrow \frac{\partial F}{\partial J} - \nabla \frac{\partial F}{\partial (\nabla J)} = 0$$

$$\Rightarrow -i \sigma(r) - iz \lambda e^{+iz J(r)} = \frac{1}{4\pi\ell_B} \nabla^2 J.$$

$$\nabla^2 J = 4\pi\ell_B [-i \sigma(r) - iz \lambda e^{iz J(r)}] = 4\pi\ell_B [-i \sigma(r) - iz \langle n(r) \rangle]$$

But recall that $\psi(r)$ is the effective electrostatic potential due to all of the other charges.

$$\Rightarrow \psi = + \beta e \Phi$$

$$\Rightarrow \nabla^2 \Phi = - \frac{4 \pi e}{\epsilon} [\sigma(r) + z n(r)]$$

$$= - \frac{4 \pi e}{\epsilon} [\sigma(r) + z \langle n(r) \rangle]$$

This is the Poisson-Boltzmann equation.