Coulomb Systems

charge density

Potential energy: $U = \frac{1}{2}\int d^d r \int d^d r' \, \rho(\vec{r})\, u(\vec{r}-\vec{r}')\, \rho(\vec{r}')$

where

$$\nabla^2 u(\vec{r}-\vec{r}') = -4\pi\,\delta(\vec{r}-\vec{r}')$$

This leads to

$$u(\vec{r}) = \begin{cases} -2\pi|x-x'|, & d=1 \\ -2\log|\vec{r}-\vec{r}'|, & d=2 \\ \dfrac{1}{|\vec{r}-\vec{r}'|}, & d=3 \end{cases}$$

Point particles: $\rho(\vec{r}) = \sum_{i=1}^{N} q_i\, \delta(\vec{r}-\vec{x}_i)$

where q_i is the charge of the i^{th} particle.

Assume two possible values for q_i: $\pm e$

Electric potential:

$$\phi(\vec{r}) = \int d^d r'\, u(\vec{r}-\vec{r}')\, \rho(\vec{r}')$$

$$= \sum_i q_i\, u(\vec{r}-\vec{x}_i)$$

Then $U = \frac{1}{2}\int d^d r\, \phi(\vec{r})\, n(\vec{r}) = \frac{1}{2}\sum_i q_i \phi(\vec{x}_i)$

$$= \sum_{i<j} q_i q_j\, u(\vec{x}_i - \vec{x}_j)$$

where we drop "diagonal" terms with $i=j$ corresponding to self-interactions.

Debye-Hückel Mean Field Theory

Work in GCE, where

$$\Xi(T,V,\mu_+,\mu_-) = \sum_{N_+=0}^{\infty}\sum_{N_-=0}^{\infty} \frac{1}{N_+!} e^{\beta\mu_+ N_+} \lambda_+^{-dN_+}$$

$$\times \frac{1}{N_-!} e^{\beta\mu_- N_-} \lambda_-^{-dN_-} \times \int d^d x_1 \cdots d^d x_N\, e^{-\beta U(\vec{x}_1,\dots,\vec{x}_N)}$$

with $N = N_+ + N_-$ and

$$U(\vec{x}_1,\dots,\vec{x}_N) = \sum_{i<j} q_i q_j\, u(\vec{x}_i - \vec{x}_j)$$

We write

$$\rho(\vec{r}) = \bar{\rho}(\vec{r}) + \delta\rho(\vec{r})$$

$$\phi(\vec{r}) = \bar{\phi}(\vec{r}) + \delta\phi(\vec{r})$$

with $\nabla^2\bar{\phi} = -4\pi\bar{\rho}$, $\nabla^2\delta\phi = -4\pi\delta\rho$

Here $\bar{\rho}(\vec{r})$ is the thermodynamic average of the charge density at $\vec{r}$, and $\bar{\phi}(\vec{r})$ the thermodynamic average electric potential. We assume that the fluctuations $\delta\rho$ and $\delta\phi$ relative to these averages are small in some sense -- small enough that in the energy

$$U = \frac{1}{2}\int d^d r\, [\bar{\rho}(\vec{r}) + \delta\rho(\vec{r})][\bar{\phi}(\vec{r}) + \delta\phi(\vec{r})]$$

$$= -\frac{1}{2}\int d^d r\, \bar{\phi}(\vec{r})\bar{\rho}(\vec{r}) + \int d^d r\, \bar{\phi}(\vec{r})\rho(\vec{r})$$

$$+ \frac{1}{2}\int d^d r\, \delta\phi(\vec{r})\,\delta\rho(\vec{r})$$

we may neglect the last term. Then

$$U = -U_0 + \sum_i q_i\, \bar{\phi}(\vec{x}_i)$$

with $U_0 = \frac{1}{2}\int d^d r\, \bar{\phi}(\vec{r})\bar{\rho}(\vec{r})$. We now have

$$\Xi = e^{U_0/k_B T} \prod_{\sigma=\pm} \left(z_\sigma \lambda_\sigma^{-d} \int d^d r\, e^{-\sigma e \bar{\phi}(\vec{r})/k_B T} \right)$$

$$\Omega = -U_0 - k_B T \sum_{\sigma=\pm} z_\sigma \lambda_\sigma^{-d} \int d^d r\, e^{-\sigma e \bar{\phi}(\vec{r})/k_B T}$$

We now demand

$$\frac{\delta\Omega}{\delta\bar{\phi}(\vec{r})} = -\bar{\rho}(\vec{r}) + e\sum_{\sigma=\pm}\sigma z_\sigma \lambda_\sigma^{-d}\, e^{-\sigma e\bar{\phi}(\vec{r})/k_BT}$$

local potential

As $r\to\infty$ we must have charge neutrality or the energy will blow up. Thus

$$n_+(\infty) = z_+\lambda_+^{-d} = n_-(\infty) = z_-\lambda_-^{-d} \equiv n_\infty$$

I.e. n_∞ is the number density of either species at infinity. So

$$\frac{z_+}{z_-} = e^{\beta(\mu_+-\mu_-)} = \left(\frac{\lambda_+}{\lambda_-}\right)^d = \left(\frac{m_-}{m_+}\right)^{d/2}$$

$$\Rightarrow \mu_+ - \mu_- = \frac{d}{2}k_BT\log\left(\frac{m_-}{m_+}\right)$$

Thus, and dropping the bars,

$$\rho(\vec{r}) = -2en_\infty\sinh\left(\frac{e\phi(\vec{r})}{k_BT}\right)$$

Next we invoke Poisson's eqn:

$$\nabla^2\phi = 8\pi e\, n_\infty \sinh\left(\frac{e\phi}{k_BT}\right) - 4\pi\rho_{ext}$$

where $\rho_{ext}(\vec{r})$ is the external charge density. If $|e\phi| << k_B T$, then

$$\nabla^2 \phi = K_D^2 \phi - 4\pi \rho_{ext}$$

where

$$K_D = \left(\frac{8\pi n_\infty e^2}{k_B T} \right)^{1/2}, \quad \lambda_D = \frac{1}{K_D} = \text{Debye length}$$

Suppose $\rho_{ext}(r) = Q\,\delta(r)$. Then

$$\phi(\vec{r}) = \frac{Q}{r} e^{-K_D r} \quad \text{(Yukawa potential)}$$

$$\rho(\vec{r}) = Q\,\delta(\vec{r}) - Q K_D^2 \frac{e^{-K_D r}}{4\pi r}$$

Note from Poisson eqn

$$-\vec{q}^{\,2} \hat{\phi}(\vec{q}) = K_D^2 \hat{\phi}(\vec{q}) \overbrace{- 4\pi \hat{\rho}_{ext}(\vec{q})}^{-4\pi Q} \Rightarrow$$

$$\hat{\phi}(\vec{q}) = \frac{4\pi Q}{K_D^2 + \vec{q}^{\,2}}, \quad \hat{\rho}(\vec{q}) = \frac{Q \vec{q}^{\,2}}{K_D^2 + \vec{q}^{\,2}}$$

and $\int d^3r\, \rho(\vec{r}) = \hat{\rho}(0) = 0 \rightarrow$ perfect screening.