Lecture 8: Charged systems

Charges are abundant in classical systems!

$$\text{Solvent} + \text{ions}\ (\underbrace{Na^+, H^+, Mg^{2+}, Ca^{2+}}_{\text{cations}}, \overbrace{Cl^-, Br^-, \dots}^{\text{anions}}) \quad NaCl \quad MgCl_2$$

dissociates because of competition U vs S.

Instead of explicitly including solvent $\epsilon_0 \longrightarrow \epsilon$ (dielectric continuum)

For example, only two species of ions:

$$H(\vec{r}_\pm^{\,N}, \vec{p}_\pm^{\,N}) = \sum_{\alpha=\pm} \sum_{i=1}^{N_\alpha} \frac{\vec{p}_{i\alpha}^{\,2}}{2m_\alpha} + \underbrace{\Phi_{\text{non-electrostatic}}(\vec{r}_\pm^{\,N})}_{\text{VdW, hard-core etc}} + \Phi_{elec}(\vec{r}_\pm^{\,N})$$

$$\Phi_{ele}(\vec{r}_\pm^{\,N}) = \sum_{i<j} \sum_{\alpha} \phi^c_{\alpha\alpha}(|\vec{r}_{i\alpha} - \vec{r}_{j\alpha}|) + \frac{1}{2} \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} \phi^c_{+-}(|\vec{r}_{i,+} - \vec{r}_{j,-}|)$$

With Coulomb potential: $\phi^c_{\alpha\beta}(r) = z_\alpha z_\beta \dfrac{e^2}{4\pi\epsilon_0\epsilon_r r}$.

z_α: valence of an ion.

E.g. $z_{Na^+} = +1$

$z_{Cl^-} = -1$

ϵ_r : relative dielectric permittivity.

e.g. water: $\epsilon_r = 80$.

oil: $\epsilon_r = 2-8$.

e: elementary charge unit.

For simplicity: $\beta\phi^c_{\alpha\beta}(r) = z_\alpha z_\beta \dfrac{\beta e^2}{4\pi\epsilon_0\epsilon_r r} =: z_\alpha z_\beta \dfrac{l_B}{r}$

l_B: Bjerrum length: Seperation between two equal point charges for which the Coulomb potential equals $k_B T$.

Observe $\epsilon_r \uparrow$ $l_B \downarrow$: Easier to seperate charges with thermal fluctuations!

e.g water $T = 300\,K$: $l_B = 7.2\,\text{Å}$

vacuum: $l_B = 54\,nm$

Objective: Thermodynamic properties of an ionic solution.

Problem: Virial expansion $B_2^{\alpha\beta}(T) = \frac{1}{2}\int d\vec{r}\left[e^{-\beta\phi^c_{\alpha\beta}(r)} - 1\right]$

is divergent: Virial expansion is not good method!

Instead, we use the caloric route to thermodynamics.

Recall: $\frac{\mathcal{U}}{N} = \frac{3}{2}k_B T + \frac{\rho}{2}\int d\vec{r}\, g(r)\, v(r)$

Generalisation to multicomponent mixture:

$$\frac{\mathcal{U}}{N} = \frac{3}{2}k_B T + \frac{\rho}{2}\sum_{\alpha,\beta} x_\alpha x_\beta \int d\vec{r}\, v_{\alpha\beta}(r)\, g_{\alpha\beta}(r) \qquad x_\alpha = \frac{N_\alpha}{N}$$

Radial distribution function $g_{\alpha\beta}(r) = g_{\beta\alpha}(r)$

Particle in centre of type α ; $\propto$ probability to find particle of type β in spherical shell of thickness dr.

Or particle of type β in center and then probability to find particle of type α

We have the constraint $N_+ + N_- = N$

but in charged systems, we have $\sum_\alpha z_\alpha N_\alpha = 0$ (global charge neutrality).

For simplicity, take $z_\pm = \pm 1$

and defining $\phi_C(r) = \frac{k_B T l_B}{r}$, we find for the excess internal energy:

$$\frac{U_{ex}}{N} = \frac{1}{2}\int d\vec{r}\, \phi_C(r)\rho_s\left[g_{++}(r) + g_{--}(r) - 2g_{+-}(r)\right].$$

$$\rho_s = \frac{N_+}{V} = \frac{N_-}{V}$$

If we take moreover same hardcore diameter σ : $g_{++}(r) = g_{--}(r)$

(restricted primitive model)

$\int d\vec{r} \to \int_{r>\sigma} d\vec{r}$.

Simple approximation (Debye, Hückel, 1920)

$$g_{+\pm}(r) = e^{-\beta e \psi(r)} \qquad (r>\sigma)$$

$\uparrow$ average electrostatic potential s.t. another ion with charge $\pm e$ has electrostatic energy $\pm e\psi(r)$

It is convenient to introduce a dimensionless electrostatic potential $\varphi(r) := \beta e \psi(r)$

Then average charge density $eQ(r)$ around a cation in the origin is given by:

$$Q(r) = \rho_s\left[g_{++}(r) - g_{+-}(r)\right] = -2\rho_s \sinh[\varphi(r)]$$

Second approximation $\varphi(r) \ll 1 \Rightarrow Q(r) \approx -2\rho_s \varphi(r)$

Two unknowns: $\varphi(r)$ and $Q(r)$. Additional relation comes from Poisson eqn:

$$\nabla^2 \varphi(r) = -4\pi l_B\left[Q(r) + \delta(\vec{r})\right]$$

$$\Rightarrow \nabla^2 \varphi(r) = \begin{cases} 4\pi l_B \delta(\vec{r}) & r < \sigma \\ \kappa^2 \varphi(r) & r > \sigma \end{cases} \qquad \kappa^2 = 8\pi l_B \rho_s$$

$\kappa^{-1} = l_D$ Debye length.

$$\varphi(r) = \begin{cases} \dfrac{l_B}{r} + a_1 & (r < \sigma) \\ a_2 \dfrac{e^{-\kappa r}}{r} & (r > \sigma) \end{cases}$$

Impose. • $\varphi(r) \to 0 \quad (r \to \infty)$

• $\varphi(r)$ continuous at $r = \sigma$. (no dielectric constant jump)

So we find: $\varphi(r) = \dfrac{l_B \exp(\kappa\sigma)}{1+\kappa\sigma} \, \dfrac{\exp(-\kappa r)}{r} \quad (r > \sigma)$

Screened electrostatic potential.
with Debye length being the characteristic
decay length.

Note that: $\displaystyle\int_{r>\sigma} d\vec{r}\, Q(r) = -1$

$\Rightarrow$ central charge is on average surrounded by an opposite charge $-e$

and one finds $Q(r) \propto \exp(-\kappa r)/r$.

Charge cloud "screens" central charge $\Rightarrow \varphi(r) \propto \frac{1}{r} \to \varphi(r) \propto \frac{e^{-\kappa r}}{r}$

We find: $\frac{U^{ex}}{Nk_BT} = \frac{-\kappa l_B}{2}\,\frac{1}{1+\kappa\sigma}$

Note: • $U^{ex} < 0$: central ion is on average surrounded by an ion cloud of the opposite charge

• $\frac{U^{ex}}{Nk_BT} \propto \rho_s^{1/2}$ Different from e.g. LJ particles where $\frac{U^{ex}}{Nk_BT} \propto \rho$

independent of σ! $(\kappa\sigma \ll 1)$

first correction always depends on σ.

Hallmark of long-range character of Coulomb interactions.

Recall: $U = \left(\frac{\partial \beta F}{\partial \beta}\right)_{N,V,T}$ $\beta = 0$ (high T limit is HS)

$$\Rightarrow \beta F = \beta F_{HS} + \int_0^\beta d\beta' \, U(\beta')$$

So we can use a coupling parameter integration to find:

$$\frac{F - F_{HS}}{Vk_BT} = \frac{-\kappa^3}{8\pi}\int_0^1 d\lambda \frac{\sqrt{\lambda}}{1+\sqrt{\lambda}\,\kappa\sigma} = -\frac{\kappa^3}{8\pi}\,\frac{2\log(1+\kappa\sigma) - 2\kappa\sigma + (\kappa\sigma)^2}{(\kappa\sigma)^3}$$

In low-density limit or equivalently $\sigma \to 0$

$\frac{F - F_{HS}}{Vk_BT} = -\frac{\kappa^3}{12\pi}. \propto -\rho_s^{3/2}$. However, F_{HS} first order correction $\propto \rho_s^2$ (virial expansion)

$\Rightarrow \frac{F - F_{id}}{Vk_BT} \overset{\rho_s \to 0}{=} -\frac{\kappa^3}{12\pi} \propto -\rho_s^{3/2}$. (Limiting law).

For water at room temperature, limiting law is accurate up to $\rho_s < 100$ mM!

Very large regime where linear screening theory is accurate.

Furthermore, note that limiting law implies the presence of a gas-liquid phase transition!

$$\beta p \simeq 2\rho_s\Big(\underset{\substack{\uparrow\\ \text{van 't Hoff}\\ \text{law}}}{1} - \overset{\swarrow\ \text{corrections from limiting law.}}{\frac{\kappa l_B}{6}} + \ldots\Big)$$

cohesive nature of Coulomb forces.

⇒ Gas-liquid phase transition ($\underset{\sim}{F}$ can develop concave part).

Introduce quantity $T^* = \frac{\sigma}{l_B}$

For DH free energy, we find $T_c^* \approx 0.06$ (MC of RPM has $T_c^* \approx 0.05$)

For water at room temperature with NaCl $T^* \approx 0.3 > T_c^*$.

(not expected to observe phase transition).

Candidate systems:
- Ionic oils ($\epsilon \approx 8$) $l_B > 7.2$ nm (Bjerrum pairs though).
- Multivalent ions

Inhomogeneous charged systems.

Assume pair-wise additive: $\Phi(\vec{r}^N) = \sum_{i<j} v(\vec{r}_i, \vec{r}_j)$

then: $$\rho^{(2)}(\vec{r}, \vec{r}\,') = 2\,\frac{\delta \Omega}{\delta v(\vec{r}, \vec{r}\,')}$$

Define: $v_\lambda(\vec{r}, \vec{r}\,') = v_0(\vec{r}, \vec{r}\,') + \lambda\, v_1(\vec{r}, \vec{r}\,')$.

Functional integration:

$$\mathcal{F}_{ex}[\rho] = \mathcal{F}_{ex}^{ref}[\rho] + \frac{1}{2}\int d\vec{r} \int d\vec{r}\,' \rho(\vec{r})\rho(\vec{r}\,') v_1(\vec{r}, \vec{r}\,') + \mathcal{F}_{corr}[\rho].$$

$$\mathcal{F}_{corr}[\rho] = \frac{1}{2}\int_0^1 d\lambda \int d\vec{r} \int d\vec{r}\,' \rho(\vec{r})\rho(\vec{r}\,') h(\vec{r}, \vec{r}\,'; \lambda) v_1(\vec{r}, \vec{r}\,').$$

Let us neglect correlations. Take an s-component electrolyte with density profiles $\{\rho_\alpha(\vec{r})\}$ and valencies z_α $(\alpha=1,\dots,s)$ in a structureless medium of dielectric constant $\epsilon=\epsilon_0\epsilon_r$. We also include the presence of non-Coulombic external potentials $V_\alpha^{ext}(\vec{r})$ $(\alpha=1,\dots,s)$ and electrostatic external potentials characterised by the external electric potential $\psi_{ext.}(\vec{r})$.

Within the mean-field approximation we find for the intrinsic Helmholtz functional:

$$\mathcal{F}[\{\rho_\alpha\}]=\underbrace{\frac{1}{2}\sum_{\alpha,\beta}\int d\vec{r}\int d\vec{r}\,'\,\frac{\rho_\alpha(\vec{r})\rho_\beta(\vec{r}\,')z_\alpha z_\beta e^2}{4\pi\epsilon_0\epsilon_r|\vec{r}-\vec{r}\,'|}}_{\text{mean-field electrostatic}}+\underbrace{\mathcal{G}[\{\rho_\alpha\}]}_{\text{non-Coulombic contributions.}}$$

Note that $\mathcal{F}$ is unique functional of $\{\rho_\alpha(\vec{r})\}$ $\Rightarrow$ so is $\mathcal{G}$.

Grand potential functional is given by:

$$\Omega_V[\{\rho_\alpha\}]=\mathcal{F}[\{\rho_\alpha\}]-\sum_\alpha\int d\vec{r}\,\Big[\underbrace{\mu_\alpha}_{\substack{\text{chemical}\\\text{potential}\\\text{of species }\alpha}}-\underbrace{V_\alpha^{ext}(\vec{r})}_{\substack{\text{external}\\\text{non-Coulombic}}}-\underbrace{z_\alpha e\,\psi_{ext}(\vec{r})}_{\substack{\text{external}\\\text{electric}}}\Big]\rho_\alpha(\vec{r})$$

Euler-Lagrange equations:

$$\frac{\delta\Omega_V[\{\rho_\alpha\}]}{\delta\rho_\alpha(\vec{r})}=0\quad\Rightarrow\quad 0=-\mu_\alpha+V_\alpha^{ext}(\vec{r})+z_\alpha e\,\psi(\vec{r})+\frac{\delta\mathcal{G}}{\delta\rho_\alpha(\vec{r})}$$

with $$\psi(\vec{r})=\psi_{ext}(\vec{r})+\sum_\beta\int d\vec{r}\,'\,\frac{\rho_\beta(\vec{r}\,')z_\beta e}{4\pi\epsilon_0\epsilon_r|\vec{r}-\vec{r}\,'|}$$

Let us write:

$$\psi_{ext}(\vec{r})=\int d\vec{r}\,'\,\frac{q_{ext}(\vec{r}\,')}{4\pi\epsilon_0\epsilon_r|\vec{r}-\vec{r}\,'|}\;\longleftarrow\;\text{external charge distribution.}$$

Therefore, $\psi(\vec r) = \int d\vec r' \, \frac{q_{ext}(\vec r') + \sum_\beta z_\beta e \rho_\beta(\vec r')}{4\pi\epsilon_0\epsilon_r|\vec r - \vec r'|}$

Using that: $\nabla^2 |\vec r - \vec r'| = -4\pi\delta(\vec r - \vec r')$, we find:

$$\boxed{\begin{aligned} &\nabla^2\psi(\vec r) = -\frac{1}{\epsilon_0\epsilon_r}\left[q_{ext}(\vec r) + \sum_\beta z_\beta e \rho_\beta(\vec r')\right] \quad \text{(Poisson equation)} \\ &\mu_\alpha = V_\alpha^{ext}(\vec r) + z_\alpha e\psi(\vec r) + \frac{\delta G}{\delta\rho_\alpha(\vec r)} \quad \text{(constancy of chemical potentials).} \end{aligned}}$$

Simplest approximation:

$$G[\{\rho_\alpha\}] = k_B T \sum_\alpha \int d\vec r \, \rho_\alpha(\vec r)\left[\ln\left(\rho_\alpha(\vec r)\Lambda_\alpha^3\right) - 1\right]$$

→ thermal de Broglie wavelength of species α.

⇝ Poisson-Boltzmann theory.

Constancy of chemical potentials yield, using $\frac{\delta G}{\delta\rho_\alpha(\vec r)} = k_B T \ln[\rho_\alpha(\vec r)\Lambda_\alpha^3]$:

$$\mu_\alpha = V_\alpha^{ext}(\vec r) + z_\alpha e\psi(\vec r) + k_B T \ln[\rho_\alpha(\vec r)\Lambda_\alpha^3].$$

Assume $r \to \infty \Rightarrow \rho_\alpha(\vec r) \to \rho_\alpha^b \quad \alpha = 1, \ldots, S.$

← bulk ion density.

$$\mu_\alpha = V_\alpha^{ext}(\infty) + z_\alpha e\psi(\infty) + k_B T \ln(\rho_\alpha^b \Lambda^3)$$

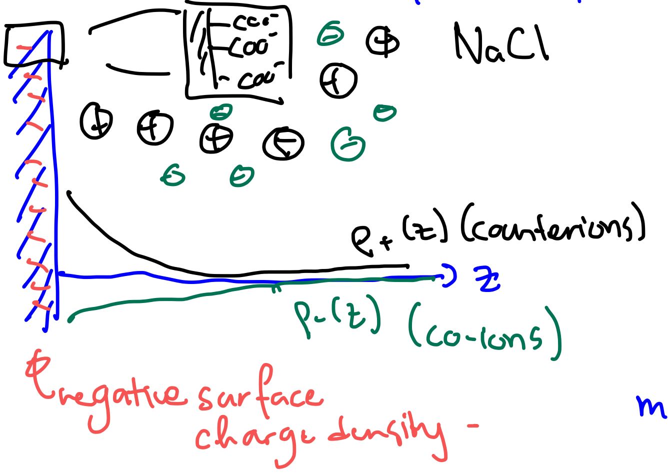
$$\Rightarrow \frac{\rho_\alpha(\vec r)}{\rho_\alpha^b} = \exp\left(-\beta\left\{\underbrace{[V_\alpha^{ext}(\vec r) - V_\alpha^{ext}(\infty)]}_{\text{external}} + \underbrace{z_\alpha e[\psi(\vec r) - \psi(\infty)]}_{\text{electrostatic.}}\right\}\right)$$

This is a Boltzmann distribution! Substitution in Poisson equation gives

$$\nabla^2\psi(\vec r) = -\frac{1}{\epsilon_0\epsilon_r}\sum_{\alpha=1}^{S} z_\alpha e \rho_\alpha^b \exp(\ldots)$$

Poisson-Boltzmann equation

Let us consider a simple example.



$$q_{ext}(\vec r) = \sigma\,\delta(z) \qquad \sigma < 0.$$

{ constant surface charge density.

$$V_\alpha^{ext}(z) = \begin{cases}\infty & z<0\\ 0 & z>0.\end{cases}$$

monovalent salt: $z_+ = -z_- = 1$,

$$\rho_+^b = \rho_-^b = \rho_b$$

$$\Rightarrow \rho_\pm(\vec r) = \begin{cases}\rho_b \exp[\mp \beta e\psi(z)] & z>0\\ 0 & z<0.\end{cases}$$

PB eqn becomes: $\frac{d^2\psi}{dz^2} = \frac{2e\rho_b}{\epsilon_0\epsilon_r}\sinh[\beta e\psi(z)]$ $(z>0)$

B.C.: $\psi(z)\to 0$ for $z\to\infty$ (Global charge neutrality).

Analytically soluable problem! $\left.\frac{d\psi}{dz}\right|_{z=0^+} = -\frac{\sigma}{\epsilon_0\epsilon_r}$.

(no image charges).

Effective interactions

Suppose in addition we have a set of charged surfaces/particles which do not have a fixed position in an electrolyte solution. (simplicity monovalent)

From lecture 11:

$$e^{-\beta\Phi_{eff}(\vec R^N;\mu,T)} = \underset{\uparrow}{e^{-\beta\Phi_{bare}(\vec R^N)}}\, e^{-\beta W(\vec R^N;\mu_\pm,V,T)}$$

e.g. hard-core etc.

{ grand potential of inhomogeneous ionic fluid in fixed configuration of particles $\{\vec R^N\}$.

$$\Rightarrow W^{(\vec R^N,\mu_\pm,V,T)} = \min_{\rho_\pm}\Omega_V[\rho_\pm;\vec R^N]$$

Because charges on particles are often of ionic nature, it is convenient to include the electrostatic piece of the particle-particle interaction in $\Omega_V[\rho_\pm;\vec{R}^N]$.

That is, we arrive at the Poisson-Bolzmann functional (non-electrostatic part is ideal gas)

$$\Omega_V[\rho_\pm;\vec{R}^N] = \frac{1}{2}\int d\vec{r}\int d\vec{r}\,' \frac{[Q(\vec{r})+\underline{q}(\vec{r})][Q(\vec{r}\,')+\underline{q}(\vec{r}\,')]}{4\pi\epsilon_0\epsilon_r|\vec{r}-\vec{r}\,'|}$$

Mean-field electrostatic.

$$+k_BT\sum_\alpha\int d\vec{r}\,\rho_\alpha(\vec{r})\left[\ln(\rho_\alpha(\vec{r})\Lambda_\alpha^3)-1\right]$$

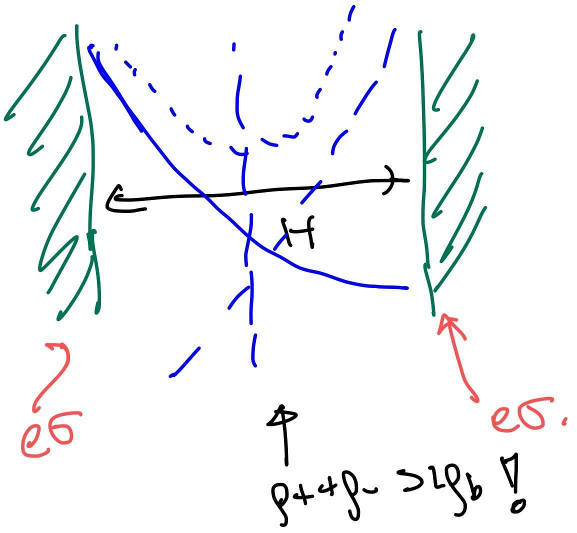
non-electrostatic ideal gas contribution.

$$-\int d\vec{r}\sum_\alpha\left[\mu_\alpha - V_\alpha^{ext}(\vec{r})\right]\rho_\alpha(\vec{r}),$$

External potential.

$Q(\vec{r})$: external charge distribution.

$q(\vec{r}) = \sum_\alpha z_\alpha e\rho_\alpha(\vec{r})$: ionic charge distribution.



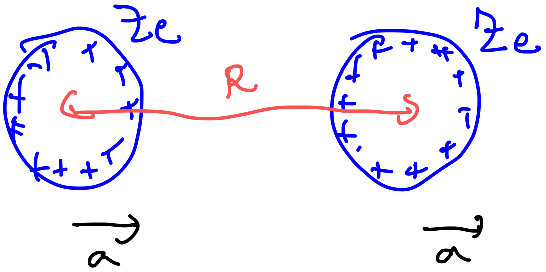
With above formalism one can compute

$\Phi_{eff}(H;\mu_\pm,T)$.

two charged walls repel each other in an electrolyte due to osmotic pressure!

Disjoining pressure: $\Pi(H) \propto e^{-\kappa H}$ $(\kappa H \gg 1)$

$$\boxed{\Pi = -\frac{\partial \Phi_{eff}}{\partial H}}$$



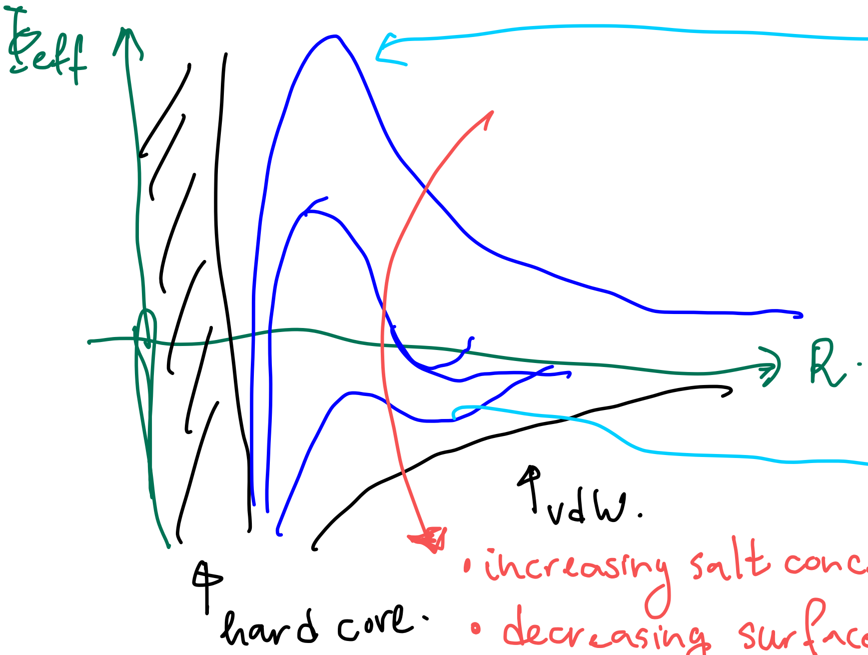
Two charged "macro ions"

$$\beta\Phi_{eff}(R) = Z^2\ell_B\left(\frac{e^{\kappa a}}{1+\kappa a}\right)^2\frac{e^{-\kappa R}}{R} \quad (R>2a)$$

$$= \infty \quad (R<2a)$$

low surface potential, linear superposition approximation

Charge stabilisation of colloidal suspensions !



potential barrier prevents particles getting into each others primary minimum.

secondary minimum.

- increasing salt concentration. (salting out)
- decreasing surface charge density.

Charge stabilisation is kinetic, not thermodynamic !