Electrostatics in ~~the~~ water.

Note: this is a mean field approach (see E3 etc.)

Charge q in water + salt:

ion conc.
$$\begin{cases} n_+(r) = c_\infty e^{-q_e\phi/kT} \\ n_-(r) = c_\infty e^{q_e\phi/kT} \end{cases} \qquad \boxed{q_e > 0}$$

$$c_\infty = [NaCl]$$

$$\rho(r) = q_e n_+ - q_e n_- + q\,\delta(r)$$

$$\nabla^2\phi = -4\pi\rho = -4\pi q_e c_\infty \left(e^{-q_e\phi/kT} - e^{q_e\phi/kT}\right) - 4\pi q\,\delta(r)$$

P-B equation.

Introduce finite size of the ion (and charges):
(a "distance of closest approach")

then $\nabla^2\phi = -4\pi q_e c_\infty (\quad)$ for $r > a$

b.c.: $\displaystyle\int_{r=a} \vec{E}\cdot\vec{n}\,ds = 4\pi q$ (Gauss)

P-B in dimensionless form: $\tilde{\phi} = \phi/kT/q_e$, $\tilde{r} = r/\delta$
with $\delta = \sqrt{\dfrac{kT}{8\pi q_e^2 c_\infty}}$ Debye length

$\rightarrow$ P-B: $\tilde{\nabla}^2\tilde{\phi} = -\left(e^{-\tilde{\phi}} - e^{\tilde{\phi}}\right)\frac{1}{2}$, $\tilde{r} > \frac{a}{\delta}$.

for $c_\infty = 0.1\,M$, $\delta \simeq 1$ nm.

Linearized (Debye-Hückel): $q_e\phi/kT \ll 1$

in dimensionless var.: $\nabla^2 \phi = \phi$

solution $\phi \sim \frac{e^{-r}}{r}$ $\longrightarrow$

i.e. in dimensional var.: $\phi(r) = A \frac{e^{-r/\delta}}{r}$

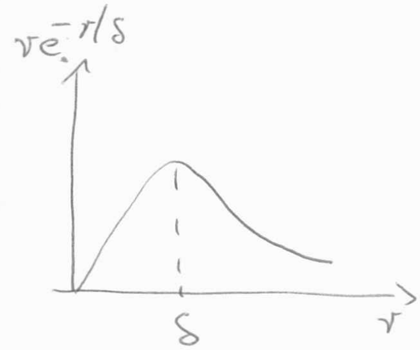
b.c.: $E_r = A\left[\frac{e^{-r/\delta}}{r^2} + \frac{1}{\delta}\frac{e^{-r/\delta}}{r}\right]$ $\quad 4\pi a^2 E_r(a) = 4\pi q$

$\Rightarrow A\, e^{-a/\delta}\left(1+\frac{a}{\delta}\right) = q \Rightarrow A = \frac{q\, e^{a/\delta}}{1+a/\delta}$

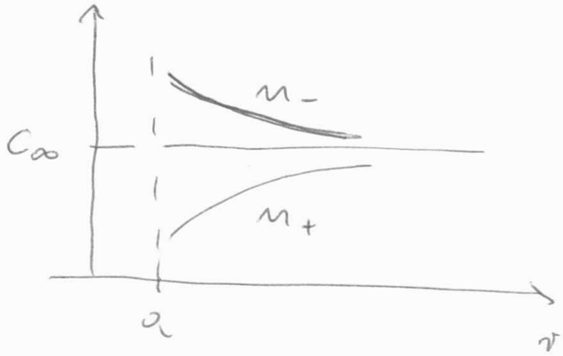
$\Rightarrow \phi(r) = q \frac{e^{a/\delta}}{1+a/\delta}\frac{e^{-r/\delta}}{r} \qquad (r > a)$.

$\rho_{ions} = q_e n_+ - q_e n_- \propto \phi \propto \frac{e^{-r/\delta}}{r}$

$dq = 4\pi r^2 dr\, \rho(r) \sim r e^{-r/\delta} dr$



Debye length $\delta \sim$ thickness of ion cloud around q.



e.g. in spherical coord.: $\nabla^2 \longrightarrow \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)$

$\hookrightarrow \left(\frac{1}{r}\frac{d^2}{dr^2}r\right)$

set $\phi(r) = \frac{u(r)}{r}$ $\Rightarrow$ $\nabla^2\phi = \frac{u''}{r}$

so $(\nabla^2 - 1)\phi = 0 \longrightarrow u'' - u = 0$ $(r > 0)$

$\Rightarrow$ $u = Ae^{r} + Be^{-r}$ and the physical sol. is

e^{-r} so $\phi(r) \sim \frac{e^{-r}}{r}$.

So what is approximate in the PB eq. ?

Alternative derivation :

consider an ion Q surrounded by cloud of counterions, number density $n(\vec{x})$:

$$\nabla^2 \phi = -4\pi\rho \, , \quad \rho = q_e n$$ counterions charge density

$$G = \int d^3x \left\{ kT\, n \left(\ln \frac{n}{n_0} - 1 \right) + \frac{1}{2} \rho \phi \right\}$$

($\frac{\partial G}{\partial n} = \mu(\vec{x}) = \mu_0 + kT \ln n(\vec{x})$, $\mu_0 = -kT \ln n_0$

i.e. the dilution term is the entropy of mixing of the ideal gas ; other terms (involving $(\nabla n)^2$?) missing)

Eq.: $\delta G = 0$ under
$$n \to n + \delta n$$
$$\phi \to \phi + \delta\phi$$

under the constraint of the Poisson eq. i.e. δn & $\delta\phi$ <u>not</u> indep. !

$$\delta G = \int d^3x \left\{ kT \, (n+\delta n)\left[\ln \frac{n+\delta n}{n_0} - 1\right] + \frac{1}{2}(n+\delta n) q_e (\phi + \delta\phi) \right\}$$

$$- \int d^3x \left\{ kT \, n \left(\ln \frac{n}{n_0} - 1\right) + \frac{1}{2} n q_e \phi \right\}$$

$\longrightarrow$

$$\ln \frac{n}{n_0}\left(1 + \frac{\delta n}{n}\right) \simeq \ln \frac{n}{n_0} + \frac{\delta n}{n} \qquad \text{so} \quad :$$

$$\delta G = \int d^3x \left\{ kT \, \delta n \ln \frac{n}{n_0} + \frac{1}{2} q_e \, \delta n \, \phi + \frac{1}{2} q_e n \, \delta\phi \right\}$$

integrate last term by parts =

$$\int d^3x \; n \, \delta\phi = -\frac{1}{4\pi q_e} \int \nabla^2\phi \, \delta\phi = \frac{1}{4\pi q_e} \int \nabla\phi \, \nabla\delta\phi$$

$$= -\frac{1}{4\pi q_e} \int d^3x \, \phi \, \nabla^2 \delta\phi = \int d^3x \, \phi \, \delta n$$

$$\Rightarrow \delta G = \int d^3x \left\{ kT \ln \frac{n}{n_0} + q_e \phi \right\} \delta n = 0$$

$$\Rightarrow kT \ln \frac{n}{n_0} + q_e \phi = 0 \Rightarrow n = n_0 e^{-\frac{q_e \phi}{kT}}$$

$$\text{so} \quad \nabla^2 \phi = -4\pi q_e n_0 e^{-\frac{q_e\phi}{kT}}$$

B.C.: for $r \to 0$

$\phi \sim \frac{Q}{r}$ etc.

Excursus on <u>mean field</u> (see Ma, Stat. Mech.).

E.g. Ising model

$$H = -\frac{1}{2} \sum_{\substack{i,j \\ n.n.}} J s_i s_j - h \sum_i s_i \quad ; \quad s_i = \pm 1$$

J coupling const.; h magnetic field. Any dimension.

E.g. 1-D: $$H = -\left(\tfrac{1}{2}\right) \sum_{i=1}^{N} J s_i s_{i+1} - h \sum_i s_i$$

$(s_{N+1} = s_1)$ can be solved exactly

(transfer matrix or partition points method, see later).

Mean field approach (any dimension):

$$H = \sum_i \left(\tfrac{1}{2}\right) \Big(\underbrace{-J \sum_{\substack{j \\ n.n.\ of\ i}} s_j}_{\text{replace by } -J\nu\langle s\rangle} - h \Big) s_i$$

replace by $-J \nu \langle s \rangle$, ν # of n.n.

with $h' = h + J\nu\langle s\rangle$ you just have spins in an effective magn. field h', i.e.

$$H = -\sum_{i=1}^{N} h' s_i$$

Solution: $$Z = z_1^N \ , \quad z_1 = \sum_{s=\pm 1} e^{h's/T}$$

(spins are indep.)

$$\left[\quad Z = \sum_{\substack{s_1 = \pm 1 \\ s_2 = \pm 1 \\ \vdots}} e^{\sum_{i=1}^{N} h' s_i / T} = \sum_{\text{states}} \prod_{i=1}^{N} e^{h' s_i / T} \right.$$

$$\left. = \prod_{i=1}^{N} \sum_{s_i = \pm 1} e^{h' s_i / T} = \left(\sum_{s = \pm 1} e^{h' s / T} \right)^N \quad \right]$$

So $\quad Z = \left(e^{h'/T} + e^{-h'/T} \right)^N \quad$ in this case

Now $\quad E = -N h' \langle s \rangle \quad$ and $\quad E = -\dfrac{\partial \ln Z}{\partial \beta}$

$$= -\frac{\partial \ln Z}{\partial (1/T)}$$

$$\Rightarrow \quad E = -N h' \frac{e^{h'/T} - e^{-h'/T}}{e^{h'/T} + e^{-h'/T}}$$

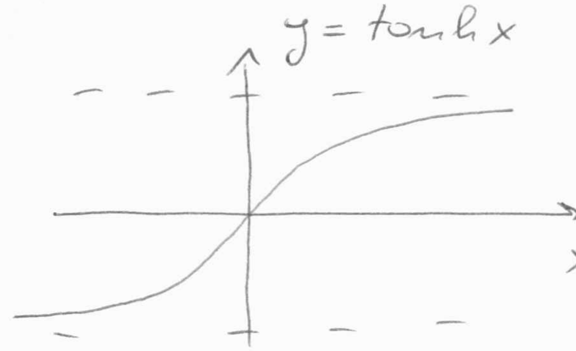
$$\Rightarrow \quad \langle s \rangle = \frac{M}{N} = m = \frac{e^{h'/T} - e^{-h'/T}}{e^{h'/T} + e^{-h'/T}} = \tanh\left(\frac{h'}{T}\right)$$

so the mean field solution of the Ising model is :

$$\left. \begin{aligned} \langle s \rangle = m &= \tanh\left[\frac{h + J\nu m}{T} \right] \\ \text{or} \quad h &= T \tanh^{-1}(m) - J \nu m \end{aligned} \right\}$$

<u>Note</u> : this is fantastic because the Ising model in 2D is already very hard to solve exactly and in 3D

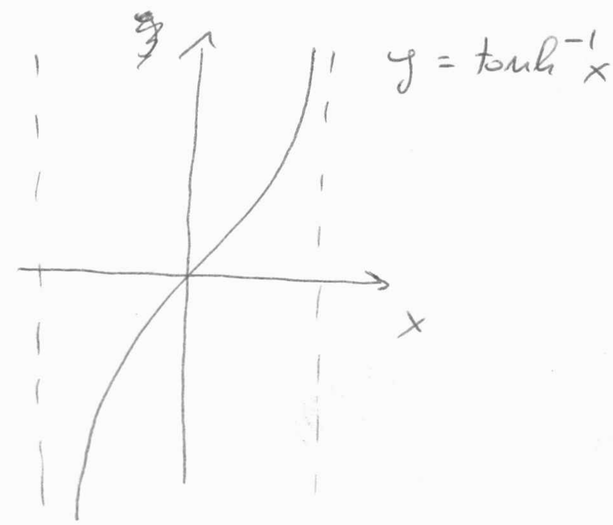
it is impossible! But, ---



$$\frac{\partial m}{\partial h} = \frac{1}{\cosh^2(\ )} \frac{1}{T} \left(1 + J\nu \frac{\partial m}{\partial h}\right)$$

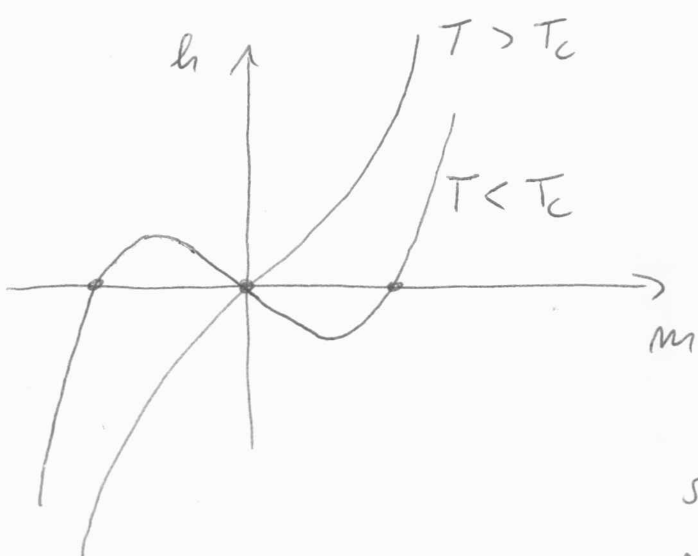
$$\Rightarrow \frac{\partial m}{\partial h} \left[\cosh^2(\ ) - \frac{J\nu}{T}\right] = \frac{1}{T}$$

i.e. $\frac{\partial m}{\partial h} > 0$ for $\frac{J\nu}{T} < 1$



or $T > T_c = J\nu$

whereas for $T < T_c$ there is a region around $m = 0$ where $\frac{\partial m}{\partial h} < 0$:



So for $T > T_c$, for $h = 0$ there is only one solution : $m = 0$

But for $T < T_c$, for $h = 0$ there is one $m = 0$ solution and two more solutions $m = \pm m_0(T)$

($\rightarrow$ spontaneous magnetization)

E.g. for $T \simeq T_c$ (then $m \ll 1$) and $h = 0$

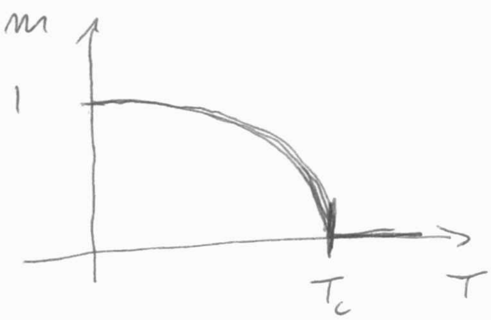
developing $\tanh x \simeq x - \frac{1}{3}x^3$ $(x \ll 1)$

you get $$m \simeq \frac{T_c}{T} m - \frac{1}{3}\left(\frac{T_c}{T} m\right)^3$$

$$\Rightarrow \quad m \simeq \sqrt{3}\left(\frac{T_c}{T} - 1\right)^{1/2} \quad \text{or} \quad m \simeq \sqrt{3}\left(1 - \frac{T}{T_c}\right)^{1/2}$$

valid for $T \leq T_c$ and $\frac{T_c - T}{T_c} \ll 1$.

The m vs. T curve for $h = 0$ looks like this:



(you can also find easily the behavior for $T \to 0$).

Exact solution in 2-D (Onsager): $T_c = 2.269\, J$

(mean field: $T_c = 4J$, square lattice).

Also, $m \propto (T_c - T)^{1/8}$ while mean field exponent is $1/2$.

I.e. critical exponents are generally wrong in the mean field approach.