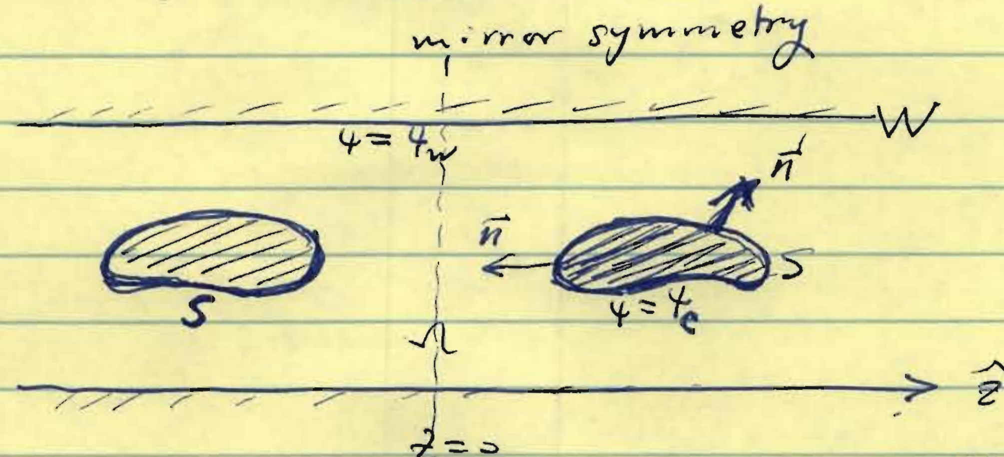
The PB theory does not predict the wall-mediated like-charge attraction



Assume:
- symmetry
- constant bdry data ψ_w, ψ_c

$$\begin{cases} \Delta\psi - B'(\psi) = 0 & \Omega \\ \psi = \psi_w & \text{on walls } W \\ \psi = \psi_c & \text{on bdry of colloidal bodies } S \\ \psi(\infty) = 0 & \end{cases}$$

$-B'(\psi) = \sum_1^M c_i^\infty z_i e^{-z_i \psi}$ (in reduced units)

$B(\psi) = \sum c_i^\infty e^{-z_i\psi}$

Force acting on a colloidal surface

$$\vec{F} = \frac{1}{2}\int_S \left(\frac{\partial\psi}{\partial n}\right)^2 \hat{n} \, \cancel{ds} \, da$$

$\vec{F}\cdot\hat{z} < 0$ attraction

$\vec{F}\cdot\hat{z} > 0$ repulsion.

Let $T = \nabla\psi \otimes \nabla\psi - f I$

where $f = \frac{1}{2}|\nabla\psi|^2 + B(\psi)$.

(I) $$\vec{F} = \frac{1}{2}\int_S \left(\frac{\partial\psi}{\partial n}\right)^2 n \, da = \int_S T n \, da$$

Verify. $Tn = (\nabla\psi \otimes \nabla\psi)n - (fI)n$

$$= (\nabla\psi \cdot n)\nabla\psi - fn$$

$$= (\nabla\psi \cdot n)\nabla\psi - \tfrac{1}{2}|\nabla\psi|^2 n - B(\psi)n$$

$$\int_S Tn\,da = \int_S \left[\frac{\partial\psi}{\partial n}\nabla\psi - \tfrac{1}{2}|\nabla\psi|^2 n - B(\psi)n\right]da$$

on S: $\psi = \psi_c = \text{const.}$ $\quad B(\psi) = B(\psi_c)$.

$\int_S n\,da = \vec{0}$. $\qquad \int_S n_j\,da = -\int_\omega \frac{\partial 1}{\partial x_j}\,dv = 0$.

$\nabla\psi = \frac{\partial\psi}{\partial n}n + \frac{\partial\psi}{\partial\tau_1}\tau_1 + \frac{\partial\psi}{\partial\tau_2}\tau_2 \qquad (n, \tau_1, \tau_2)$ orthonormal

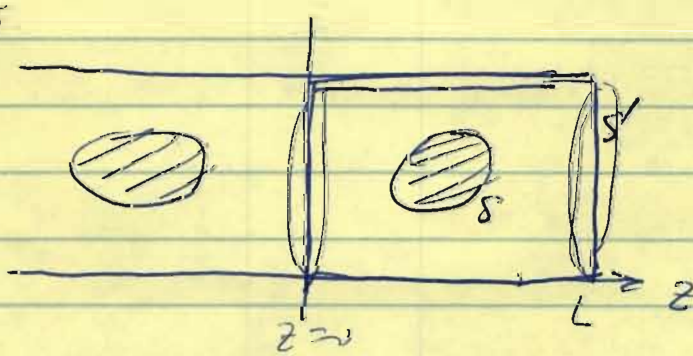
τ_1, τ_2: tangential direction.

$\frac{\partial\psi}{\partial\tau_1} = 0 \quad \frac{\partial\psi}{\partial\tau_2} = 0$ along S. since $\psi = \psi_c = \text{const}$.

$$\int_S Tn\,da = \int_S \left[\left(\frac{\partial\psi}{\partial n}\right)^2 n - \frac{1}{2}\left(\frac{\partial\psi}{\partial n}\right)^2 n\right]da$$

$$= \int_S \frac{1}{2}\left(\frac{\partial\psi}{\partial n}\right)^2 n\,da.$$

Let $\hat{z}$ be the unit vector in the positive direction of the z-axis



(II) $\qquad \hat{z}\cdot\vec{F} = \int_S \hat{z}\cdot Tn\,da = \int_{S'} \hat{z}\cdot Tn\,da$.

Since T is divergence free.

[illegible]

Check $T = \nabla\psi \otimes \nabla\psi - \frac{1}{2}|\nabla\psi|^2 I - B(\psi) I$

$$\nabla\cdot T = 2\Delta\psi\,\Delta\psi - \Delta\psi\,\nabla\psi - B'(\psi)\nabla\psi$$
$$= [\Delta\psi - B'(\psi)]\,\nabla\psi = \vec{0}.$$

$$\int_{\text{boundary}} Tn\,da = \int_{\text{volume}} \nabla\cdot T\,dV = 0.$$

boundary $= S + S'$. different directions of n.

(IV) Calculate $\hat{z}\cdot\vec{F} = \int_{S'} \hat{z}\cdot Tn\,da$

on the ~~base of the~~ cylinder section, $\psi = \text{const.} = \psi_w$

$$\hat{z}\cdot Tn = 0$$
$$\hat{z}\cdot Tn = \hat{z}\cdot\left[\left(\frac{\partial\psi}{\partial n}\nabla\psi\right) - \frac{1}{2}|\nabla\psi|^2 n - B(\psi)n\right]$$
$$= \frac{\partial\psi}{\partial n}\cdot\underbrace{\frac{\partial\psi}{\partial\hat{z}}}_{=0} - \frac{1}{2}|\nabla\psi|^2\underbrace{(n\cdot\hat{z})}_{=0} - B(\psi_w)\underbrace{(n\cdot\hat{z})}_{=0}$$
$$= 0.$$

on $z = L$: $\hat{z}\cdot Tn = \left(\frac{\partial\psi}{\partial z}\right)^2(y,L) - f(y,L).$
$\vec{n} = \hat{z}$

on $z = 0$. $n = -\hat{z}$

$$\hat{z}\cdot T\hat{n} = \cancel{f(y,0)} - \left(\frac{\partial\psi}{\partial z}(y,0)\right)^2 + f(y,0)$$
$$= -f(y,0)$$

$\boxed{\left.\frac{\partial\psi}{\partial z}\right|_{z=0} = 0}$ Due to mirror symmetry.

$$\hat{z}\cdot\vec{F} = \int_{S'} \hat{z}\cdot T\hat{n}\,da$$
$$= \int_D \left[\left(\frac{\partial\psi}{\partial z}\right)^2(y,L) + f(y,0) - f(y,L)\right]dy$$
$$\geq \int_D \left[f(y,0) - f(y,L)\right]dy$$

cross section of cylinder

$$\hat{z}\cdot\vec{F} \geq \lim_{L\to+\infty} \int_D \left[f(y,0)-f(y,L)\right]dy .$$

Assume $\psi(y,L) \longrightarrow \Phi(y)$ in D.

2 dim. $$\begin{cases} \Delta\Phi - V'(\Phi) = 0 & \text{in } D \\ \Phi = u_w & \text{on } \partial D \end{cases}$$

$$\hat{z}\cdot\vec{F} \geq \cancel{\int_D \tfrac{1}{2}|\nabla\Phi|} \int_D \left[f(y,0)-f(y,L)\right]dy$$

$$= \int_D \left[\frac{1}{2}\left|\nabla\psi(y,z=0)\right|^2 + B(\underbrace{\psi(y,z=0)}_{\psi^{(0)}})\right]dy$$

$$-\int_D \left[\frac{1}{2}\left|\nabla\psi(y,z=+\infty)\right|^2 + B(\psi(y,z=\infty))\right]dy$$

Let $G[h] = \int_D \left[\frac{1}{2}|\nabla h|^2 + B(h)\right]dy$.

$$\hat{z}\cdot\vec{F} \geq G[\psi^{(0)}] - G[\Phi] \geq 0.$$

Since Φ is ~~the~~ global minimum of $G[\psi^{(0)}]$. $\square$