Homework #2 . Interfaces and membranes :
self-organization, mechanical energy.

Corrections

Ex I

1 - Self organization of q free molecules into 1 micelle :
- decreases (interaction) energy with the solvent
- but also decreases configurational entropy (posit° of the q molecules are bounds)

2 - $N_{tot} = N + q n$

3 - $F_{part}(N_{tot}, V, T ; N)$: partial free energy corresponding to configs with N free molecules (among N_{tot} molecules)

$$= -k_B T \ln Z_{part}(N_{tot}, V, T ; N) \qquad \text{with} \quad Z_{part}(N_{tot}, V, T; N) = \sum_{\substack{\{\text{configs } \ell \\ \to N \text{ free molecules}\}}} e^{-\beta \epsilon_\ell}$$

Probability to ~~have a configuration~~ have N free molecules :

$$P(N) = \frac{Z_{part}(N_{tot}, V, T; N)}{Z(N_{tot}, V, T)} = \frac{e^{-\beta F_{part}(N_{tot}, V, T; N)}}{e^{-\beta F(N_{tot}, V, T)}}$$

$$Z(N_{tot}, V, T) = \sum_{\{\text{configs } \ell\}} e^{-\beta \epsilon_\ell}$$

$\Rightarrow$ $P(N)$ is max when $F_{part}(N_{tot}, V, T; N)$ is min

Let N^* the value of N that maximizes $F(N_{tot}, V, T; N)$

Moreover, in the thermodynamic limit :

$$P(N) \simeq \begin{cases} 1 & \text{if } N \simeq N^* \\ 0 & \text{otherwise} \end{cases}$$

$$\Rightarrow \boxed{F_{part}(N_{tot}, V, T ; N^*) \simeq F(N_{tot}, V, T)} \quad \text{and} \quad \boxed{N^* \simeq \langle N \rangle}$$

4/ μ : chemical potential of free molecule

$$= \frac{\partial F_{mol}}{\partial N}(N,V,T)$$

μ_{mic} : chemical potential of micelles

$$= \frac{\partial F_{mic}}{\partial n}(n,V,T)$$

$\mu_{\in mic}$: chemical potential of a molecule in a micelle

$$= \cancel{q}\ \mu_{mic}/q$$

N^{eq} satisfies $\frac{\partial F_{part}}{\partial N} = 0 \iff \frac{\partial F_{mol}}{\partial N} + \frac{\partial F_{mic}}{\partial N} = 0$

$$\iff \frac{\partial F_{mol}}{\partial N} + \frac{\partial F_{mic}}{\partial n} \cdot \frac{\partial n}{\partial N} = 0$$

$$\iff \mu + \mu_{mic} \cdot \left(-\frac{1}{q}\right) = 0$$

$$\iff \boxed{\mu_{mic} = q\mu}$$

5/ $\mu_{mic} = q\,(\varepsilon - \Delta\varepsilon) - k_B T \ln\left(\frac{n}{V}\lambda^3_{(qm)}\right)$ $\qquad \lambda^*_{(qm)} = \frac{1}{q^{1/2}}\lambda_m$

$$\boxed{\mu_{mic} = q\,(\varepsilon - \Delta\varepsilon) - k_B T \ln\left(\frac{N'}{V}\frac{\lambda_m^3}{q^{5/2}}\right)}$$ $\qquad N' = qn$

6/ $\phi = \lambda_m \frac{N}{V}$, $\phi' = \lambda_m \frac{N'}{V}$, $\phi_{tot} = \lambda_m \frac{N_{tot}}{V} = \phi + \phi'$

note here N is the extremum value N^{eq}

$$\mu_{mic} = q\mu \iff \ln\phi = \underbrace{-\frac{\Delta\varepsilon}{k_B T} - \frac{5}{2}\frac{\ln q}{q}}_{\hat{=}\, -\delta} + \frac{1}{q}\ln\phi'$$

$$\Rightarrow \phi' = \left(e^{\delta}\phi\right)^q$$

7/ $\phi_c = \phi = \phi'$

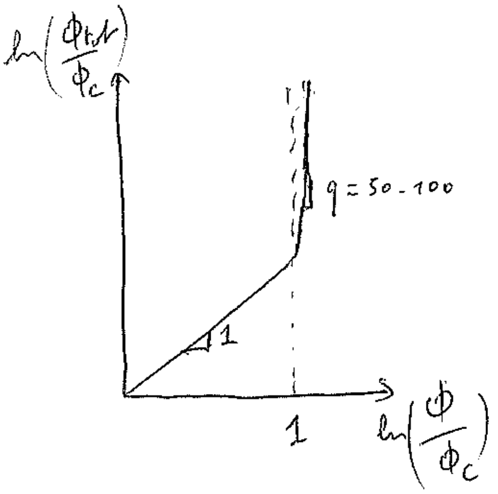
Thus : $\phi_c = \left(e^{\delta}\phi_c\right)^q \Rightarrow \boxed{\dfrac{\phi_{tot}}{\phi_c} = \dfrac{\phi}{\phi_c} + \left(\dfrac{\phi}{\phi_c}\right)^q}$

Typically, $q = 50-100$

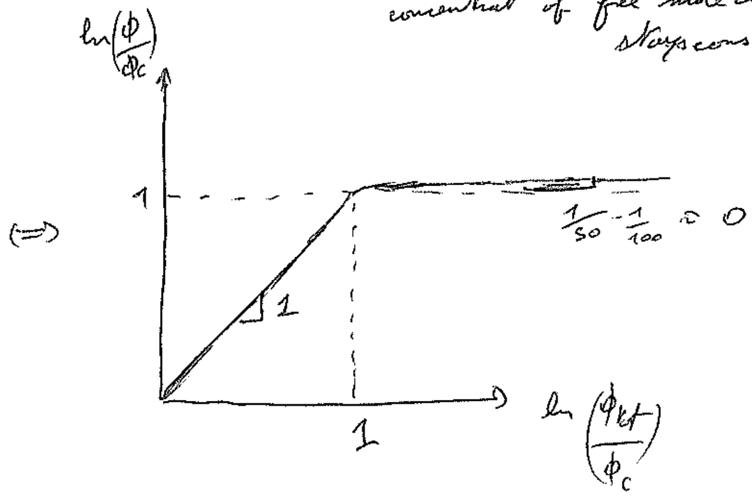
↳ As long as $\dfrac{\phi}{\phi_c} < 1 \Rightarrow \dfrac{\phi'}{\phi_c} = \left(\dfrac{\phi}{\phi_c}\right)^q \simeq 0 \Rightarrow \boxed{\phi_{tot} \simeq \phi}$

$\left(\text{e.g. } (0{,}9)^{50} = 5.10^{-3} \ ; \ (0{,}9)^{100} \simeq 2{,}5.10^{-5}\right)$

↳ As soon as $\dfrac{\phi}{\phi_c} \geq 1$, $\dfrac{\phi_{tot}}{\phi_c} \simeq \left(\dfrac{\phi}{\phi_c}\right)^q \rightarrow$ all added molecules go to creation of new micelles
concentrat° of free molecules stays constant.



$\Leftrightarrow$



8/ $\phi_c = \left(e^{\delta}\phi_c\right)^q \Leftrightarrow \phi_c = e^{-\frac{q\delta}{q-1}} \underset{q \gg 1}{\simeq} e^{-\delta}$

with $\delta = \dfrac{\Delta\varepsilon}{k_B T} + \dfrac{5}{2}\dfrac{\ln q}{q} \underset{q\gg 1}{\simeq} \dfrac{\Delta \varepsilon}{k_B T}$

$$\Rightarrow \boxed{C_{CMC} = \frac{\phi_c}{\lambda_m^3} = \left(\frac{m\, k_B T}{2\pi \hbar^2}\right)^{3/2} e^{-\frac{\Delta\varepsilon}{k_B T}}}$$

$C_{CMC} \nearrow$ when $T \nearrow$ or $\Delta\varepsilon \searrow$

Higher temperature favorizes free molecule in agreement with $F = U - TS$ min $\Leftrightarrow S_{max}$ when entropic term dominates.

Ex 2

1/ $\boxed{E_{flat} = \lambda \times 2\pi R}$

2/ Surface area : $S = 4\pi R_s^2 = \pi R^2 \iff \boxed{R_s = \frac{R}{2}}$

$$E_{sph} = \iint \left(\frac{\kappa_b}{2} H^2 + \kappa_G G \right) d^2S$$

$$H^2 = \left(\frac{1}{R_s} + \frac{1}{R_s} \right)^2 = \frac{4}{R_s^2} \quad = cst$$

$$G = \frac{1}{R_s^2} = cst.$$

$$\hookrightarrow E_{sph} = \frac{(2\kappa_b + \kappa_G)}{R_s^2} \times S = \boxed{4\pi (2\kappa_b + \kappa_G) = E_{sph}}$$

3/ $E_{flat} < E_{sph} \iff \lambda 2\pi R < 4\pi (2\kappa_b + \kappa_G)$

$$\iff \boxed{R < \frac{2(2\kappa_b + \kappa_G)}{\lambda} \hat{=} R_c}$$

If $R < R_c$ flat bilayer with boundary favorized

If $R > R_c$ spherical vesicle with no boundary (but bending energy) favorized