Midterm exam SCMT April 12, 9:00-12:00 -model answers

Friday, 12 April 2019 14:34

1) a) First law $dU = TdS - pdV + \mu dN$ (given)

so $dG = d(U - TS + pV) =$

$= -SdT + Vdp + \mu dN$ 1 (*) has T, p, N as independent variables 1

so $G = G(T, p, N)$ is appropriate

Extensivity: $G(N, p, T) = \mu(p, T)N$ 1

so $dG = \mu dN + N d\mu$ 1

Combine with (*): $dG = -SdT + Vdp + \mu dN$

gives $N d\mu = -SdT + Vdp$ 1

so Gibbs-Duhem:

$d\mu = -s\,dT + v\,dp$ 1 with $s = \frac{S}{N}$, $v = \frac{V}{N}$

b) $N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T,A}$ 1

$= V\left(\frac{\partial p}{\partial \mu}\right)_T - A\left(\frac{\partial \gamma}{\partial \mu}\right)_T$ 1

$= A\int dz\, \rho(\bar{r})$ 1 $= \rho_b V + A\int dz(\rho(z) - \rho_b)$ 1

Since $\left(\frac{\partial p}{\partial T}\right)_T \overset{!}{=} \rho_b$ we have

$\left(\frac{\partial \gamma}{\partial \mu}\right)_T \overset{!}{=} -\int_0^\infty dz(\rho(z) - \rho_b)$

2) a) $q(z) = \rho_+(z) - 2\rho_-(z)$ 1

$\rho_+(z) = \rho_s e^{-\beta e\psi(z)}$ 1 ; $\rho_-(z) = \left(\frac{\rho_s}{2}\right) e^{+2\beta e\psi(z)}$ 2

Poisson: $\Rightarrow \beta e\psi''(z) = -4\pi\lambda_B\rho_s\left[e^{-\beta e\psi(z)} - \underbrace{2\cdot\tfrac{1}{2}}_{=1} e^{+2\beta e\psi(z)}\right]$ PB

BC's: $\psi(\infty) = 0$ 1

$\psi(0) = \psi_0$ 1

b) $\psi_0 \ll 10$ mV so $\beta e \psi_0 \ll \frac{10}{25} < 1$ so linearisation is OK. 1 1

$$\beta e \psi''(z) = -4\pi \lambda_B \rho_s \left[1 - \beta e \psi(z) - (1 + 2\beta e \psi(z)) + \cancel{O(\psi^2)}\right] \quad 1$$

$$= \beta e \, 4\pi \lambda_B \cdot 3\rho_s \, \psi(z) \quad 1$$

$$\Rightarrow \psi''(z) = \kappa^2 \psi(z) \text{ with } \kappa^2 = 12\pi \lambda_B \rho_s \quad 2$$

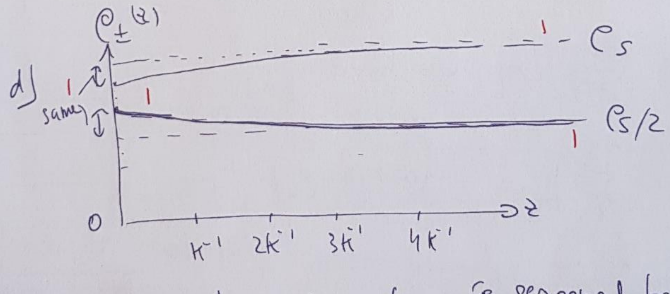
$$\text{so } \kappa^{-1} = \frac{1}{\sqrt{12\pi \lambda_B \rho_s}}$$

c) $\psi(z) \overset{1}{=} \underset{\substack{\| \\ 0 \\ (\text{BC at } \infty)}}{A} e^{+\kappa z} + \underset{\substack{\| \\ \psi_0 \\ (\text{BC at } z=0)}}{B} e^{-\kappa z} = \psi_0 e^{-\kappa z}$ 2

Gauss: $\underset{\substack{\| \\ -\kappa\psi_0}}{\beta e \psi'(0^+)} \overset{1}{=} -4\pi \lambda_B \sigma$ 1

$$\Rightarrow e\sigma = e \frac{\kappa \psi_0}{4\pi \lambda_B} \quad 1$$

d) 1 1 1 1



$(\psi_0 > 0)$

The positive surface charge is screened by the net negative cloud of ions, of thickness $\sim \kappa^{-1}$ 1 1

e) (i) $\lambda_B = 0.7$ nm 2 (anything ~1 nm is fine)

(ii) $\kappa^{-1} \simeq 10\,nm$ at $\rho_s \simeq 1\,mM$ (actually a factor $\frac{\sqrt{3}}{2}$ smaller

2

$\kappa^{-1} \simeq 8\,nm$

(iii) $\rho_s \times nm^3 = 10^{-3} \cdot (0.6) \cdot 10^{24} \frac{nm^3}{10^{-3}\,m^3}$

$= (0.6) \cdot 10^{-3}$

so volume per ion in nm^3

$v/nm^3 = \frac{1}{\rho_s\, nm^3} = \frac{10^3}{0.6}$ 2

3) a) $\phi(r) \equiv 0$: ideal gas

$Z = \frac{V^N}{N!\,\Lambda^{3N}}$ with $\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

1

$\left(\text{or } Z = \frac{1}{N!\,h^{3N}} \int_V d\bar{r}^N \int d\bar{p}\; e^{-\beta K} = \ldots \right)$

$U = \langle H \rangle = \langle K \rangle = \frac{3}{2} N k_B T$ 2

equipartition

$p = -\frac{\partial}{\partial V}\left(-k_B T \ln Z\right) = \frac{N k_B T}{V}$ 1

$S = \frac{-F + U}{T} = \frac{k_B T \ln Z + U}{T}$ 1 with Z and U as above

$\mu = \partial F / \partial N = k_B T \ln(N\Lambda^3/V)$ 1

(b) fluid is isotropic & homogeneous 1

so $\rho^{(2)}(\bar{r}, \bar{r}')$ only depends on $|\bar{r} - \bar{r}'|$ 1

$\langle \Phi \rangle = \langle \sum_{i<j} \phi(r_{ij}) \rangle =$

$= \frac{1}{2} \langle \sum_{i}^{N} \sum_{j}^{N} \int d\bar{r}\, d\bar{r}'\, \delta(\bar{r} - \bar{r}_i)\, \delta(\bar{r}' - \bar{r}_j)\, \phi(|\bar{r} - \bar{r}'|) \rangle$

$$= \frac{1}{2}\left\langle \sum_{i=1}^{N} \sum_{j\neq i}^{N} \int d\bar{r}\, d\bar{r}'\, \delta(\bar{r}-\bar{r}')\,\delta(\bar{r}'-\bar{r}_j)\; \phi(|\bar{r}-\bar{r}'|) \right\rangle \quad 1$$

$$= \frac{1}{2}\int d\bar{r}\, d\bar{r}'\, \rho^{(2)}(\bar{r},\bar{r}')\, \phi(|\bar{r}-\bar{r}'|) = \quad 1$$

$$= \frac{1}{2}\rho^2 V \int d\bar{r}_{12}\, g(r_{12})\, \phi(r_{12}) \quad 1$$

$$= \frac{1}{2}\rho^2 V\, 4\pi \int_0^\infty dr\, r^2\, g(r)\, \phi(r) \quad 1$$

c)

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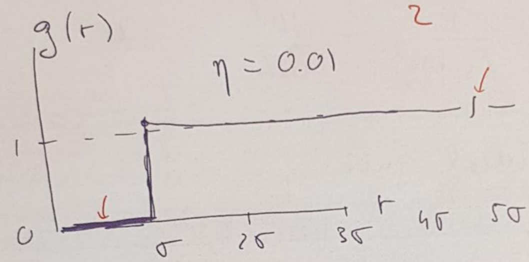

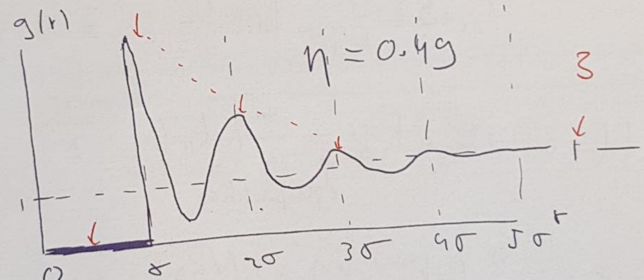

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In both cases $\langle \Phi \rangle = 0$ because

either $g(r) = 0 \quad (r<\sigma)$ 1

or $\phi(r) = 0 \quad (r>\sigma)$

d) $$B_2 = \frac{1}{2}\int d\bar{r}\left(1 - e^{-\beta\phi(r)}\right) \quad 2$$

$$= \frac{1}{2}\, 4\pi\left(\int_0^\sigma dr\, r^2 + \int_\sigma^{2\sigma} dr\, r^2\left(1 - e^{+\beta\varepsilon}\right)\right) \quad 2$$

$$= \frac{2\pi}{3}\sigma^3 + \frac{2\pi}{3}(1-e^{\beta\varepsilon})\sigma^3(8-1)$$

$$= \frac{2\pi}{3}\sigma^3 + \frac{14}{3}\sigma^3(1-e^{\beta\varepsilon}) \quad 2$$

e) $H_\lambda = H_0 + \lambda \Phi_1$ 1 ; $H_0 = K + \sum_{i<j} \phi_0$ 1 ; $\Phi_1 = \sum_{i<j} \phi_1(r_{ij})$

$$\phi_1(r) = \begin{cases} -\varepsilon & \sigma < r < 2\sigma \\ 0 & \text{otherwise} \end{cases}$$ 1

$$\frac{\partial F_\lambda}{\partial \lambda} = \langle \Phi_1 \rangle_\lambda$$

So $F_{\lambda=1} \equiv F$

$$\overset{\shortparallel}{F_{\lambda=0}} + \int_0^1 d\lambda \, \langle \Phi_1 \rangle_\lambda = \quad 1$$

$$= F_{HS} + \int_0^1 d\lambda \, \frac{1}{2}\rho^2 V \int_0^\infty dr \, 4\pi r^2 \phi_1(r) g_\lambda(r) \quad 1$$

$$= F_{HS} + \frac{1}{2}\rho^2 V 4\pi \int_\sigma^{2\sigma} dr\, r^2(-\varepsilon) \int_0^1 d\lambda \, g_\lambda(r) \quad 1$$

f) 1st order perturbation theory: $g_\lambda(r) \simeq g_0(r)$ 2

so $a = 2\pi\varepsilon \int_\sigma^{2\sigma} dr\, r^2 g_0(r)$ 1

$\rho\sigma^3 = 0.4$: no crystallisation but
at low enough $T < T_c$ a VdW loop develops in 1
free energy → Gas - Liquid transition 1
→ system is NOT stable at all T. 1.

4) ... ... $^{1/2}$ > D ... R_n is swollen

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$R_g \simeq bN^{3/5} \sim$ ... compared to ideal chain. 2 1

(ii) monomer volume fraction inside single chain is 1

$$\phi^* = \frac{Nb^3}{R_g^3} = \frac{N}{N^{3\cdot 3/5}} = N^{-4/5}$$ 2

b) Virial expansion:

$$\beta\Pi b^3 = b^3\left[\frac{M}{V} + B_2\left(\frac{M}{V}\right)^2 + \dots\right]$$ 1

with $B_2 = c\,R_g^3 =$ 1

$$\frac{Mb^3}{V} = \phi/N$$

so $\beta\Pi b^3 = \phi/N + cR_g^3 b^3 (\phi/Nb^3)^2$ 1

$= (\phi/N)\left(1 + c(\phi/\phi^*) + \dots\right)$

so $f(x) = 1 + cx$ if $x \ll 1$

De Gennes: $x \gg 1$ then Π should be independent of N, 1

so $(\phi/N)(N^{4/5}\phi)^m$ ind of N 1

$\Rightarrow m = 5/4$

and $\Pi \sim \phi^{9/4}$ 1

c) $\langle x^2 \rangle = 2Dt$ with $D = \dfrac{k_BT}{6\pi\eta a}$ (SE) 1 2

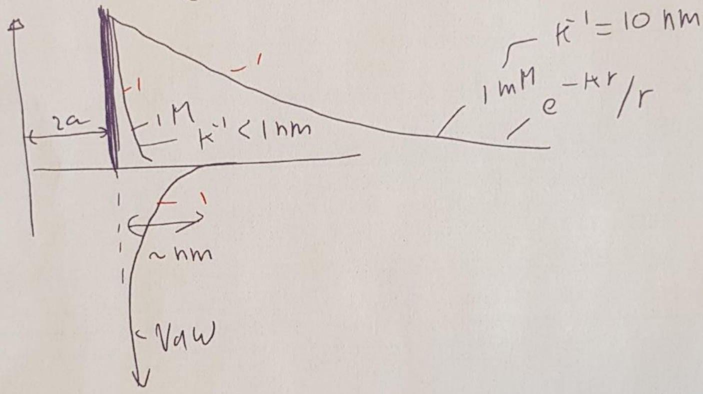
so $t_D = \dfrac{a^2}{2D} = \dfrac{12\pi\eta a^3}{k_BT} \sim a^3$ 1

exp techniques: – confocal microscopy 1

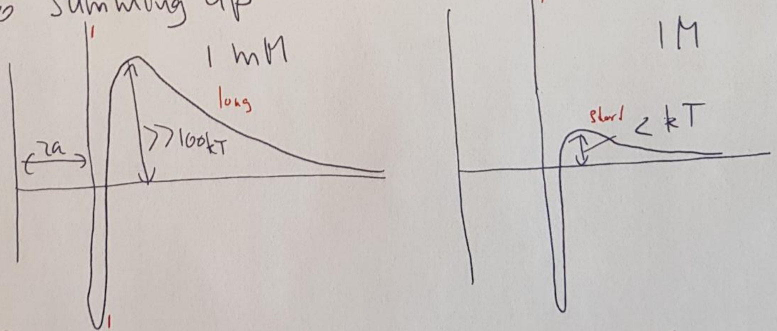
..

for $a = 1\mu m$ — light scattering 1
— (video tracking)
— ...

d) 3 ingredients of DLVO:
— steric "hard-core" repulsions 1
— VdW "dispersion" attractions 1
— Screened-Coulomb repulsions due to charged surfaces & ionic screening 1



So summing up



total 3 points