PHYS704: Assignment 5

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Attractive shell potential

1.a

$$
\begin{aligned}
B_2 &= -\frac{1}{2}\int d^3q(e^{-\beta\mathcal{V}(q)}-1) \\
&= -\frac{1}{2}[\int_0^a 4\pi r^2 dr(e^{-\beta\mathcal{V}(r)}-1) + \int_a^b 4\pi r^2 dr(e^{-\beta\mathcal{V}(r)}-1) + \int_b^\infty 4\pi r^2 dr(e^{-\beta\mathcal{V}(r)}-1)] \\
&= -\frac{1}{2}[-\int_0^a 4\pi r^2 dr + \int_a^b 4\pi r^2 dr(e^{\beta\epsilon}-1)] \\
&= \frac{2\pi a^3}{3} - (e^{\frac{\epsilon}{k_BT}}-1)\frac{2\pi(b^3-a^3)}{3} \\
&= \frac{2\pi b^3}{3} - e^{\frac{\epsilon}{k_BT}}\frac{2\pi(b^3-a^3)}{3}
\end{aligned}
$$

1.b

at high temperature, we have

$$
\begin{aligned}
&\frac{2\pi b^3}{3} - e^{\frac{\epsilon}{k_BT}}\frac{2\pi(b^3-a^3)}{3} \approx \frac{2\pi b^3}{3} - (1+\frac{\epsilon}{k_BT})\frac{2\pi(b^3-a^3)}{3} \\
&= \frac{2\pi a^3}{3} - \frac{\epsilon}{k_BT}\frac{2\pi(b^3-a^3)}{3}
\end{aligned}
$$

at low temperature $\beta >> 1$, the attractive component takes over, and

$$
B_2 \approx -e^{\frac{\epsilon}{k_BT}}\frac{2\pi(b^3-a^3)}{3} < 0
$$

1.c

From the expansion

$$
\frac{P}{k_BT} = \frac{N}{V} + B(T)\frac{N^2}{V^2}
$$

for constant T and N, we have

$$
\begin{aligned}
\frac{1}{k_BT} &= -\frac{N}{V^2}\frac{\partial V}{\partial P} - 2B_2(T)\frac{N^2}{V^3}\frac{\partial V}{\partial P} \\
\frac{1}{k_BT} &= (-\frac{N}{V} - 2B_2(T)\frac{N^2}{V^2})\frac{1}{V}\frac{\partial V}{\partial P} \\
\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} &= \frac{V}{Nk_BT}\frac{1}{1+2B_2(T)\frac{N}{V}} \approx \frac{V}{Nk_BT}(1 - \frac{2B_2(T)N}{V})
\end{aligned}
$$

1.d

using the high temperature limit, we have

$$
\begin{aligned}
\frac{P}{k_BT} &= n + (\frac{2\pi a^3}{3} - \frac{\epsilon}{k_BT}\frac{2\pi(b^3-a^3)}{3})n^2 \\
P &= k_BTn + k_BT(\frac{2\pi a^3}{3} - \frac{\epsilon}{k_BT}\frac{2\pi(b^3-a^3)}{3})n^2 \\
P + \epsilon\frac{2\pi(b^3-a^3)}{3}n^2 &= k_BTn(1+\frac{2\pi a^3}{3}n) \approx k_BTn(1-\frac{2\pi a^3}{3}n)^{-1} \\
(P + \epsilon\frac{2\pi(b^3-a^3)}{3}n^2)(1-\frac{2\pi a^3}{3}n) &= k_BTn \\
(P + \epsilon\frac{2\pi(b^3-a^3)}{3}\frac{N}{V}^2)(V-\frac{2\pi a^3}{3}N) &= Nk_BT
\end{aligned}
$$

thus the *van der Waals* parameters are $a = \epsilon\frac{2\pi(b^3-a^3)}{3}$ and $b = \frac{2\pi a^3}{3}$

Surfactant condensation

2.a

$$
\begin{aligned}
Z &= \frac{1}{N!}\int\prod_i^N \frac{d^2q d^2p}{h^2}\exp[-\beta(\sum_i \frac{\vec{p}_i^2}{2m} + \frac{1}{2}\sum_{ij}\mathcal{V}(\vec{q}_i - \vec{q}_j))] \\
&= \frac{1}{N!}\int\frac{d^2q}{h^2}\exp[-\frac{\beta}{2}\sum_{ij}\mathcal{V}(\vec{q}_i-\vec{q}_j)](\int d^2p\exp[-\beta\frac{\vec{p}^2}{2m}])^N \\
&= (\frac{2\pi m}{\beta})^N\frac{1}{N!h^{2N}}\int\prod_i^N d^2q_i\exp[-\frac{\beta}{2}\sum_{ij}\mathcal{V}(\vec{q}_i-\vec{q}_j)] \\
&= \frac{1}{\lambda^{2N}N!}\int\prod_i^N d^2q_i\exp[-\frac{\beta}{2}\sum_{ij}\mathcal{V}(\vec{q}_i-\vec{q}_j)]
\end{aligned}
$$

2.b

Denote the area of a molecule as $\Omega = \pi a^2$, the first molecule can occupy A, the 2nd $A - \Omega$,

$$
\begin{aligned}
S_N = \int \frac{\prod_i d^3 q_i}{N!} &= \frac{1}{N!} A(A-\Omega)(A-2\Omega)\cdots(A-(N-1)\Omega) \\
&= \frac{1}{N!}(A - \frac{N\Omega}{2})^N
\end{aligned}
$$

2.c

the total potential energy can be calculated with following

$$
\begin{aligned}
U &= \frac{1}{2}\int d^2r_1 d^2r_2 n_1 n_2 \mathcal{V}(r_1 - r_2) \\
&= \frac{1}{2}(\frac{N}{A})^2 \int d^2r_1 d^2r_2 \mathcal{V}(r_1 - r_2) \\
&= \frac{1}{2}(\frac{N}{A})^2 A \int 2\pi r dr \mathcal{V}(r) \\
&= \frac{1}{2}(\frac{N}{A})^2 A - u_0 \\
&= -\frac{1}{2}\frac{N^2 u_0}{A}
\end{aligned}
$$

thus the partition function can be written as

$$
\begin{aligned}
Z &= \frac{1}{\lambda^{2N}}\frac{1}{N!}(A - \frac{N\Omega}{2})^N \exp[-\beta\overline{U}] \\
&= \frac{(A - \frac{N\Omega}{2})^N}{N!\lambda^{2N}} \exp[\frac{\beta N^2 u_0}{2A}]
\end{aligned}
$$

2.d

The work done by surface tension is σdA, thus we have free energy

$$dG = -SdT + \sigma dA + \mu dN$$

thus

$$
\begin{aligned}
\sigma &= \left.\frac{\partial G}{\partial A}\right|_{T,n} \\
&= -k_B T \frac{\partial \ln(Z)}{\partial A} \\
&= -k_B T \frac{\partial}{\partial A}[N \ln(A - \frac{N\Omega}{2}) - \ln(N!\lambda^{2N}) + \frac{\beta N^2 u_0}{2A}] \\
&= \frac{-Nk_B T}{A - \frac{N\Omega}{2}} + \frac{N^2 u_0}{2A^2} \\
&= \frac{-k_B T}{n - \frac{\Omega}{2}} + \frac{u_0}{2n^2}
\end{aligned}
$$

2.e

since the first and second derivative of σ of A is zero at critical point T_c, we have

$$
\begin{aligned}
\left.\frac{\partial \sigma}{\partial A}\right|_{T_c} &= \frac{Nk_B T_c}{(A - \frac{N\Omega}{2})^2} - \frac{N^2 u_0}{A^3} = 0 \\
T_c &= \frac{Nu_0(A - \frac{N\Omega}{2})^2}{k_B A^3} \\
\left.\frac{\partial^2 \sigma}{\partial A^2}\right|_{T_c} &= \frac{-2Nk_B T_c}{(A - \frac{N\Omega}{2})^3} + \frac{3N^2 u_0}{A^4} = 0 \\
T_c &= \frac{3Nu_0(A - \frac{N\Omega}{2})^3}{2k_B A^4}
\end{aligned}
$$

thus we have

$$
\begin{aligned}
\frac{Nu_0(A - \frac{N\Omega}{2})^2}{k_B A^3} &= \frac{3Nu_0(A - \frac{N\Omega}{2})^3}{2k_B A^4} \\
1 &= \frac{3(A - \frac{N\Omega}{2})}{2A} \\
A &= \frac{3N\Omega}{2}
\end{aligned}
$$

thus

$$
\begin{aligned}
T_c &= \frac{Nu_0(A - \frac{N\Omega}{2})^2}{k_B A^3} = \frac{Nu_0(N\Omega)^2}{k_B(\frac{3N\Omega}{2})^3} \\
&= \frac{8u_0}{27k_B\Omega}
\end{aligned}
$$

At low temperature there is a phase transition thus it doesn't satisfy the original equation anymore.

2.f

$$C_A = \left.\frac{dQ}{dT}\right|_A = \left.\frac{\partial E}{\partial T}\right|_A$$

since

$$\begin{aligned}
E &= -\frac{\partial \ln(Z)}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta}\{N\ln(A - \frac{N\Omega}{2}) - \ln(N!h^{2N}) + N\ln(2\pi m) - N\ln(\beta) + \frac{\beta N^2 u_0}{2A}\} \\
&= \frac{N}{\beta} - \frac{N^2 u_0}{2A} \\
&= Nk_B T - \frac{N^2 u_0}{2A}
\end{aligned}$$

thus $C_A = Nk_B$

$$C_\sigma = \left.\frac{dQ}{dT}\right|_\sigma = \frac{dE - \sigma dA}{dT} = C_A - \sigma \left.\frac{\partial A}{\partial T}\right|_\sigma$$

Critical point behavior

3.a

$$\begin{aligned}
P &= -\left.\frac{\partial F}{\partial V}\right|_{T,N} \\
&= k_B T\frac{\partial}{\partial V}\{\ln(Z_{ideal}) + \frac{\beta b N^2}{2V} - \frac{\beta c N^3}{6V^2}\} \\
&= k_B T\{\frac{N}{V} - \frac{\beta b N^2}{2V^2} + \frac{\beta c N^3}{3V^3}\} \\
&= nk_B T - \frac{b}{2}n^2 + \frac{c}{3}n^3
\end{aligned}$$

3.b

the stability condition $-\delta P\delta V \leq 0$ implies that $\delta P\delta n \geq 0$, thus we have

$$\left.\frac{\partial P(T = T_c)}{\partial n}\right|_{T,V} = k_B T - bn + cn^2 = 0$$
$$\left.\frac{\partial^2 P(T = T_c)}{\partial n^2}\right|_{T,V} = -b + 2cn = 0$$

thus

$$
\begin{aligned}
n_c &= \frac{b}{2c} \\
T_c &= \frac{bn_c - cn_c^2}{k_B} = \frac{\frac{b^2}{2c} - \frac{b^2}{4c}}{k_B} \\
&= \frac{b^2}{k_B}(\frac{1}{2c} - \frac{1}{4c}) = \frac{b^2}{4ck_B}
\end{aligned}
$$

3.c

$$
\begin{aligned}
P(T_c, n_c) &= k_B T_c n_c - \frac{b}{2} n_c^2 + \frac{c}{3} n_c^3 \\
&= k_B \frac{b^2}{4ck_B} \frac{b}{2c} - \frac{b}{2} \frac{b^2}{4c^2} + \frac{c}{3} \frac{b^3}{8c^3} \\
&= \frac{b^3}{24c^2}
\end{aligned}
$$

thus $k_B T_c n_c / P_c = k_B \frac{b^2}{4ck_B} \frac{b}{2c} / \frac{b^3}{24c^2} = 24/8 = 3$

3.d

since we have

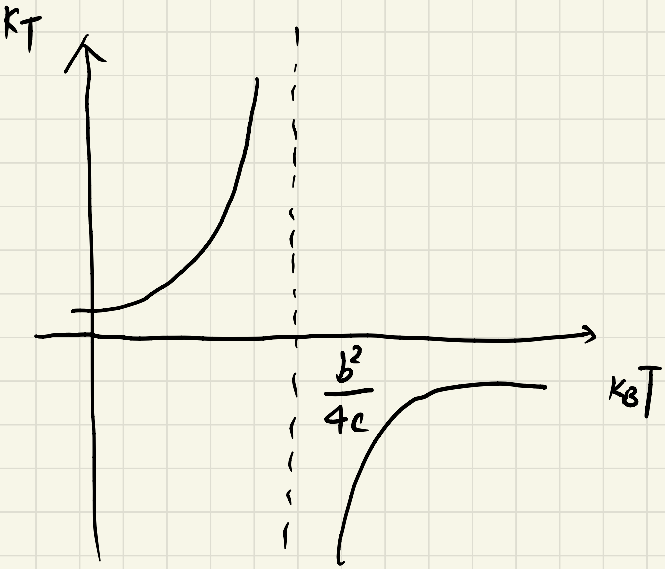
$$
\begin{aligned}
\partial_P P &= k_B T \partial_P \{ \frac{N}{V} - \frac{\beta b N^2}{2V^2} + \frac{\beta c N^3}{3V^3} \} \\
1 &= k_B T \{ -\frac{N}{V^2} + \frac{\beta b N^2}{V^3} - \frac{\beta c N^3}{V^4} \} \frac{\partial V}{\partial P}
\end{aligned}
$$

thus

$$
\begin{aligned}
\kappa_T &= -\left. \frac{1}{V} \frac{\partial V}{\partial P} \right|_T \\
&= \frac{1}{k_B T} \frac{1}{-\frac{N}{V} + \frac{\beta b N^2}{V^2} - \frac{\beta c N^3}{V^3}} \\
&= -\frac{1}{n k_B T - b n^2 + c n^3}
\end{aligned}
$$

at $n = n_c = \frac{b}{2c}$ we have

$$
\begin{aligned}
\kappa_T &= -\frac{1}{k_B T \frac{b}{2c} - \frac{b^3}{4c^2} + \frac{b^3}{8c^2}} \\
&= -\frac{1}{k_B T \frac{b}{2c} - \frac{b^3}{8c^2}} \\
&= -n_c \frac{1}{k_B T - \frac{b^2}{4c}}
\end{aligned}
$$



κ_T
$\frac{b^2}{4c}$
$k_B T$

3.e

$$
\begin{aligned}
P - P_c &= nk_BT - \frac{b}{2}n^2 + \frac{c}{3}n^3 - \frac{b^3}{24c^2} \\
&= \frac{b^2}{4c}n - \frac{b}{2}n^2 + \frac{c}{3}n^3 - \frac{b^3}{24c^2} \\
&= \frac{c}{3}[3n_c^2 n - 3n_c n^2 + n^3 - n_c^3] \\
&= \frac{c}{3}(n - n_c)^3
\end{aligned}
$$

3.f

the chemical potential of two phases are equal at critical point, which implies

$$
\begin{aligned}
&0 = \mu_+ - \mu_- = \int_{n_-}^{n^+} \frac{dP}{n} \\
&= \int_{n_-}^{n_+} \frac{1}{n}(k_BT - bn + cn^2)dn \\
&= k_BT \ln(\frac{n_+}{n_-}) - b(n_+ - n_-) + \frac{1}{2}c(n_+^2 - n_-^2) \\
&= k_BT \ln(\frac{1+\delta}{1-\delta}) - 2bn_c\delta + 2cn_c^2\delta \\
&(2bn_c - 2cn_c^2)\delta = k_BT \ln(\frac{1+\delta}{1-\delta}) \\
&\frac{b^2}{2c}\delta = k_BT \ln(\frac{1+\delta}{1-\delta}) \\
&\delta = \frac{T}{2T_c}[\ln(1+\delta) - \ln(1-\delta)] \approx \frac{T}{T_c}[\delta - \delta^3], \quad \delta \to 0 \\
&\delta = \sqrt{1 - \frac{T_c}{T}}
\end{aligned}
$$

Electron spin

4.a

if B is along the z axis, then we have

$$
\rho = \frac{1}{Z}\exp[-\beta H] = \frac{1}{Z}\exp[\beta\mu_B B_z \sigma_z] = \frac{1}{Z}\begin{pmatrix} \exp(\beta\mu_B B_z) & 0 \\ 0 & \exp(-\beta\mu_B B_z) \end{pmatrix}
$$

the normalization condition will be $tr(\rho) = 1$, thus

$$
Z = \exp(\beta\mu_B B_z) + \exp(-\beta\mu_B B_z) = 2\cosh(\beta\mu_B B)
$$

4.b

if B is along the x axis, then we have

$$\begin{aligned}
\rho &= \frac{1}{Z}\exp[-\beta H] = \frac{1}{Z}\exp[\beta\mu_B B_x \sigma_x] \\
&= \frac{1}{Z}[\sum_{n=0}^{\infty}\frac{1}{n!}(\beta\mu_B B_x\sigma_x)^n] \\
&= \frac{1}{Z}[\sum_{k=0}^{\infty}\frac{1}{(2k)!}(\beta\mu_B B_x)^{2k} I + \sum_{k=0}^{\infty}\frac{1}{(2k+1)!}(\beta\mu_B B_x)^{2k+1}\sigma_x] \\
&= \frac{1}{Z}[\cosh(\beta\mu_B B_x)\mathbf{I} + \sinh(\beta\mu_B B_x)\sigma_x]
\end{aligned}$$

the normalization condition will be $tr(\rho) = 1$, thus

$$Z = 2\cosh(\beta\mu_B B_x)$$

4.c

along z axis

$$\begin{aligned}
\langle E\rangle = tr(\rho H) &= \frac{-\mu_B B_z}{Z} tr[\begin{pmatrix} \exp(\beta\mu_B B_z) & 0 \\ 0 & \exp(-\beta\mu_B B_z) \end{pmatrix}\sigma_z] \\
&= \frac{-\mu_B B_z}{Z} 2\sinh(\beta\mu_B B_z) \\
&= -\mu_B B_z \tanh(\beta\mu_B B_z)
\end{aligned}$$

along x axis

$$\begin{aligned}
\langle E\rangle = tr(\rho H) &= \frac{-\mu_B B_x}{Z} tr[[\cosh(\beta\mu_B B_x)\mathbf{I} + \sinh(\beta\mu_B B_x)\sigma_x]\sigma_x] \\
&= \frac{-\mu_B B_x}{Z} tr[\cosh(\beta\mu_B B_x)\sigma_x + \sinh(\beta\mu_B B_x) I] \\
&= -\mu_B B_x 2\sinh(\beta\mu_B B_x) \\
&= -\mu_B B_z \tanh(\beta\mu_B B_z)
\end{aligned}$$

Quantum mechanical entropy

5.a

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho]$$

and we have

$$
\begin{aligned}
\frac{dS(t)}{dt} &= -\frac{d}{dt} tr[\rho(t)\ln(\rho(t))] \\
&= -tr[\frac{d}{dt}\rho(t)\ln(\rho(t))] \\
&= -tr[\frac{d\rho(t)}{dt}\ln(\rho(t)) + \rho(t)\frac{d}{dt}\ln(\rho(t))] \\
&= -tr[\frac{d\rho(t)}{dt}\ln(\rho(t)) + \frac{d\rho(t)}{dt}] \\
&= \frac{i}{\hbar} tr[(\ln(\rho(t))+1)[H,\rho]] \\
&= \frac{i}{\hbar}[tr((\ln(\rho(t))+1)H\rho) - tr((\ln(\rho(t))+1)\rho H)] \quad = 0
\end{aligned}
$$

5.b

$$
\begin{aligned}
L &= S(t) + \alpha(tr(\rho\mathcal{H}) - E) + \beta(tr(\rho) - 1) \\
&= -tr[\rho(t)\ln(\rho(t))] + \alpha(E - tr(\rho\mathcal{H})) + \beta(tr(\rho) - 1) \\
&= tr[\rho\{-\ln(\rho) - \alpha\mathcal{H} - \beta\}] + \alpha E + \beta
\end{aligned}
$$

thus we have

$$
\begin{aligned}
\frac{\partial L}{\partial \rho} &= -\ln(\rho) - 1 - \alpha\mathcal{H} - \beta = 0 \\
\frac{\partial L}{\partial \alpha} &= E - \rho\mathcal{H} = 0 \\
\frac{\partial L}{\partial \beta} &= 1 - \rho = 0
\end{aligned}
$$

the density can be written as

$$
\rho = \exp(-(\beta+1)) tr(\exp(-\alpha\mathcal{H}))
$$

and the factors should have the following equations

$$
\begin{aligned}
\exp(\beta+1) &= tr(\exp(-\alpha\mathcal{H})) \\
tr(\exp(-\alpha\mathcal{H})\mathcal{H}) &= E\exp(\beta+1) \\
\exp(-\alpha\mathcal{H})(\mathcal{H} - E) &= 0
\end{aligned}
$$

where α and β can be solved from above matrix equation.

5.c

the density in 5.b is stationary, since $\mathcal{H}$ and $\exp[-\alpha\mathcal{H}]$ commute, because

$$
\begin{aligned}
\mathcal{H}\exp[-\alpha\mathcal{H}] &= -\alpha\mathcal{H}^2 + \alpha\mathcal{H}^3/2 + \cdots \\
\exp[-\alpha\mathcal{H}]\mathcal{H} &= -\alpha\mathcal{H}^2 + \alpha\mathcal{H}^3/2 + \cdots \\
\frac{\partial\rho}{\partial t} &= 0
\end{aligned}
$$

van Leeuwens theorem

the partition function is

$$Z = \frac{1}{N!}\int\prod_i^N \frac{d^3pd^3q}{h^3}\exp[-\beta\mathcal{H}] = \frac{1}{N!}\int\prod_i^N \frac{d^3pd^3q}{h^3}\exp(-\beta[\sum_i \frac{(\vec{p}_i - e\vec{A})^2}{2m} + U])$$
$$= \frac{1}{N!}\int\prod_i^N d^3q\exp[-\beta U]\int\prod_i^N \frac{d^3p}{h^3}\exp(-\beta\sum_i \frac{(\vec{p}_i - e\vec{A})^2}{2m})$$
$$= \frac{1}{N!h^{3N}}\int\prod_i^N d^3q\exp[-\beta U](\int d^3p\exp[-\beta\frac{(\vec{p}_i - e\vec{A})^2}{2m}])^N$$
$$= \frac{1}{N!h^{3N}}\int\prod_i^N d^3q\exp[-\beta U]\sqrt{\frac{2\pi m}{\beta}}$$

the derivative of B is then just zero.

The binary alloy

7.a

The minimum energy configuration has as little A-B bonds as possible, thus the zero temperature we have the minimum bonds when A B sperates.

7.b

$$E = N_{bonds} * (-Jp_A^2 - Jp_B^2 + Jp_Ap_B)$$
$$= -3JN(\frac{N_A - N_B}{N})^2$$

7.c

The entropy is

$$S = k_B\ln(\frac{N!}{N_A!N_B!})$$
$$= k_B(N\ln(N) - N_A\ln(N_A) - N_B\ln(N_B)) = -Nk_B(p_A\ln(p_A) + p_B\ln(p_B))$$

7.d

$$F = E - TS$$
$$= -3JNx^2 + Nk_BT(\frac{N_A}{N}\ln(\frac{N_A}{N}) + \frac{N_B}{N}\ln(\frac{N_B}{N}))$$

and since $\frac{1+x}{2} = \frac{N_A}{N}$, $\frac{1-x}{2} = \frac{N_B}{N}$

$$F = -3JNx^2 + Nk_BT(\frac{1+x}{2}\ln(\frac{1+x}{2}) + \frac{1-x}{2}\ln(\frac{1-x}{2}))$$

expand F to fourth order of x, we have

$$F = -Nk_BT\ln(2) + N(\frac{k_BT}{2} - 3J)x^2 + \frac{Nk_BT}{12}x^4$$

where the second order should be zero at T_c, gives

$$T_c = \frac{6J}{k_B}$$