Final solutions

2024

(1.) (a) $\langle (N_A - \langle N_A \rangle)^2 \rangle = \langle N_A^2 \rangle - \langle N_A \rangle^2 =$

$$= \sum_{i,j=1}^{N} \left[\langle n_{Ai} n_{Aj} \rangle - \langle n_{Ai} \rangle \langle n_{Aj} \rangle \right],$$

where

$$n_{Ai} = \begin{cases} 1 & \text{if molecule } i \text{ is in state A} \\ 0 & \text{otherwise} \end{cases}$$

$$\sum_{i=1}^{N} n_{Ai} = N_A$$

Next, $\langle (N_A - \langle N_A \rangle)^2 \rangle =$

$$= \sum_{i=1}^{N} [\langle \underbrace{n_{Ai}^2}_{= n_{Ai}} \rangle - \langle n_{Ai} \rangle^2] +$$

$$+ \sum_{\substack{i,j=1 \\ i \neq j}}^{N} [\underbrace{\langle n_{Ai} n_{Aj} \rangle}_{= \langle n_{Ai} \rangle \langle n_{Aj} \rangle \text{, no correlations}} - \langle n_{Ai} \rangle \langle n_{Aj} \rangle] =$$

$$= N \langle n_{A1} \rangle (1 - \langle n_{A1} \rangle) = N x_A (1 - x_A) = N x_A x_B.$$

all molecules equivalent

$$\sum_{i=1}^{N} \langle n_{Ai} \rangle = N \langle n_{A1} \rangle = \langle N_A \rangle,$$

or $\langle n_{A1} \rangle = \dfrac{\langle N_A \rangle}{N}$.

(b) Clearly,

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{g_A e^{-E_A/k_BT}}{g_B e^{-E_B/k_BT}} = \frac{g_A}{g_B} e^{-\beta \Delta E} . \qquad \beta = \frac{1}{k_BT}$$

For an ideal mixture,

$$Z = \frac{q_A^{N_A}}{N_A!} \frac{q_B^{N_B}}{N_B!} , \quad \text{where } \begin{cases} q_A = g_A e^{-\beta E_A} , \\ q_B = g_B e^{-\beta E_B} \end{cases}$$

Recall that

$$\begin{cases} -\beta \mu_A = \left(\frac{\partial \log Z}{\partial N_A} \right)_{\beta, V, N_B} \\ -\beta \mu_B = \left(\frac{\partial \log Z}{\partial N_B} \right)_{\beta, V, N_A} \end{cases}$$

Now, $\log Z = N_A \log q_A - \log N_A! +$

$$+ N_B \log q_B - \log N_B! \simeq$$

$$\simeq N_A \log q_A - N_A \log N_A + N_A +$$

$$+ N_B \log q_B - N_B \log N_B + N_B .$$

Then

$\mu_A = \mu_B$ yields

$$\log q_A - \log N_A = \log q_B - \log N_B, \quad \text{or}$$

$$\underbrace{\frac{N_A}{N_B}}_{\frac{\langle N_A \rangle}{\langle N_B \rangle}} = \frac{q_A}{q_B} = \frac{g_A}{g_B} e^{-\beta \Delta E}$$ as before.

$\boxed{\text{QED}}$

(2.) (a) $$Z = \sum_{\{ABC\}} e^{-\beta(E_0+E_A+E_B+E_C)} =$$

$$= e^{-\beta E_0}\left(\sum_{\{A\}} e^{-\beta E_A}\right)\left(\sum_{\{B\}} e^{-\beta E_B}\right)\left(\sum_{\{C\}} e^{-\beta E_C}\right) \equiv$$

$$\equiv e^{-\beta E_0}\, q_A q_B q_C .$$

Then $$\langle E\rangle = \frac{\partial \log Z}{\partial(-\beta)} = E_0 + \frac{\partial \log q_A}{\partial(-\beta)} +$$

$$+ \frac{\partial \log q_B}{\partial(-\beta)} + \frac{\partial \log q_C}{\partial(-\beta)} .$$

Finally,

$$C_V = -k_B\beta^2 \left.\frac{\partial\langle E\rangle}{\partial\beta}\right|_{V=\text{const}} = k_B\beta^2\left(\left.\frac{\partial^2\log q_A}{\partial\beta^2}\right|_V +\right.$$

$$\left.+ \left.\frac{\partial^2\log q_B}{\partial\beta^2}\right|_V + \left.\frac{\partial^2\log q_C}{\partial\beta^2}\right|_V\right) = C_V^A + C_V^B + C_V^C .$$

It is clearly indep. of E_0. $\Leftarrow$ only energy fluctuations produce C_V

(b) Now,

$$q_A = g_0 e^{-\beta\varepsilon_0} + g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2} .$$

Set $\epsilon_0 = \varepsilon_0 - \varepsilon_0 = 0$, $\epsilon_1 = \varepsilon_1 - \varepsilon_0$, $\epsilon_2 = \varepsilon_2 - \varepsilon_0$.

Then $q_{\theta A} = g_0 + g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2}$, and

$$C_V^A = + k_B \beta^2 \left(\frac{\partial^2 \log q_{\theta A}}{\partial \beta^2} \right)_V =$$

$$= k_B \beta^2 \frac{\partial}{\partial\beta} \left[\frac{1}{q_{\theta A}} \left(-g_1 \epsilon_1 e^{-\beta\epsilon_1} - g_2 \epsilon_2 e^{-\beta\epsilon_2} \right) \right] =$$

$$= k_B \beta^2 \left[-\frac{1}{q_{\theta A}^2} \left(g_1 \epsilon_1 e^{-\beta\epsilon_1} + g_2 \epsilon_2 e^{-\beta\epsilon_2} \right)^2 + \right.$$

$$\left. + \frac{1}{q_{\theta A}} \left(g_1 \epsilon_1^2 e^{-\beta\epsilon_1} + g_2 \epsilon_2^2 e^{-\beta\epsilon_2} \right) \right].$$

(3.) Use

$$\bar{f}(t,h) = b^{-d}\bar{f}(b^{y_1}t,\ b^{y_2}h),$$

where b is the scaling factor.

Then $M \sim \left(\dfrac{\partial \bar{f}}{\partial h}\right)_t \underset{\underset{h=0}{\uparrow}}{=} b^{y_2-d}\,\underset{\underset{\text{derivative wrt } h}{\uparrow}}{\bar{f}_h}(b^{y_1}t, 0)$.

Choose $b^{y_1}|t| = 1$:

$$b = |t|^{-\frac{1}{y_1}}, \quad \text{and}$$

$$M \sim |t|^{\frac{d-y_2}{y_1}} \underbrace{\bar{f}_h(\pm 1, 0)}_{\text{const}} \Rightarrow \beta = \frac{d-y_2}{y_1}.$$

Next, consider

$$M(t,h) \sim b^{y_2-d} M(b^{y_1}t,\ b^{y_2}h).$$

Use $b^{y_2}|h| = 1 \Rightarrow b = |h|^{-\frac{1}{y_2}}$

Then $M(t,h) \sim |h|^{\frac{d-y_2}{y_2}} M(\underbrace{t|h|^{-\frac{y_1}{y_2}}}_{=\,0\ @\ T=T_c}, \pm 1)$.

So, $\delta = \dfrac{y_2}{d-y_2}$. $\Leftarrow |M| \sim |h|^{1/\delta}$

Note that $\beta\delta = \dfrac{y_2}{y_1}$.

(4.) The master equation is given by

$$\partial_t p(n,t) = \lambda [\underbrace{p(n-1,t)}_{\text{gain}} - \underbrace{p(n,t)}_{\text{loss}}].$$

IC: $p(n,0) = \delta_{n,0}$

Introduce $p(s,t) = \sum_{n=0}^{\infty} s^n p(n,t)$:

$$p(s,0) = s^0 = 1.$$

Then $\partial_t p(s,t) = \lambda [\sum_{n=0}^{\infty} s^n p(n-1,t) -$

$$- \sum_{n=0}^{\infty} s^n p(n,t)] =$$

$$= \lambda [s \underbrace{\sum_{n=0}^{\infty} s^{n-1} p(n-1,t)}_{p(s,t)} - p(s,t)] \ominus$$

$$[p(\underset{n}{\underset{\shortparallel}{-1}},t) = 0, \forall t]$$

$\ominus$ $\lambda(s-1)\, p(s,t)$.

Thus, $p(s,t) = \underset{\substack{\shortparallel \\ 1}}{A}\, e^{\lambda(s-1)t}$. 1 since $p(s,0) = 1$.

Finally,

$$p(s,t) = e^{\lambda(s-1)t} = e^{-\lambda t} \underbrace{\sum_{n=0}^{\infty} \frac{(\lambda t)^n}{n!} s^n}_{e^{\lambda s t}} .$$

Thus, $$p(n,t) = \frac{(\lambda t)^n}{n!} e^{-\lambda t} .$$

This is the Poisson distribution.