HW5 Solution

1. See textbook, sec. 7.9
2. See 7.5
3. See 8.2
4. Partition function: ~~see eq. 8.~~

$$Z = \frac{1}{N!} Z_{trans}^N Z_{rot}^N$$

$Z_{trans}$ is one-particle translation partition function given by eq (8.75) $\quad Z_{trans} = V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

$Z_{rot}$ is one-particle rotation partition function see eq. (8.78) - (8.81) for derivation

$$Z_{rot} = \frac{1}{\pi \hbar^3} \sqrt{\frac{2\pi I_1}{\beta}} \sqrt{\frac{2\pi I_1}{\beta}} \sqrt{\frac{2\pi I_3}{\beta}}$$

Free energy

$$F = -k_B T \ln Z$$

$$= -k_B T \left( N \ln Z_{trans} + N \ln Z_{rot} - N \ln N + N \right)$$

$$= -N k_B T \left( \ln \frac{Z_{trans} Z_{rot}}{N} + 1 \right)$$

entropy $\quad S = -\frac{\partial F}{\partial T}$

$$= N k_B \left( \ln \frac{Z_{trans} Z_{rot}}{N} + 1 \right) +$$

$$+ N k_B T \left( \frac{1}{Z_{trans}} \cdot \frac{\partial Z_{trans}}{\partial T} + \frac{1}{Z_{rot}} \frac{\partial Z_{\cancel{trans}}}{\partial T} \right)$$

$$= N k_B \left( \ln \frac{Z_{trans} Z_{rot}}{N} + 1 \right)$$

$$+ N k_B T \left( \frac{1}{Z_{trans}} \cdot \frac{3}{2} \frac{Z_{trans}}{T} + \frac{1}{Z_{rot}} \cdot \frac{3}{2} \frac{Z_{rot}}{T} \right)$$

$$= N k_B \left( \ln \frac{Z_{trans} Z_{rot}}{N} + 1 \right)$$

$$+ 3 N k_B T .$$

<u>heat capacity</u>

The internal energy is

$$E = \mathfrak{F} + TS = 3 N k_B T$$

the heat capacity is

$$C_V = \frac{\partial E}{\partial T} = 3 k_B N$$

It's constant doesn't depend on temperature.

5 The grand canonical partition function

$$\mathcal{Z}(T, V, \mu) = \sum_{n=0}^{N} e^{\beta \mu n} \cdot Z(T, V, n)$$

where $n$ is the number of absorbed molecules and

$$Z(T,V,n) = \sum_i e^{-\beta E_i}$$

is the canonical partition function. The sum is over all microstates. There are n ~~molecul~~ absorbed molecules distributed over N sites, so there are

$\frac{N!}{n!(N-n)!}$ microstates, all with energy ~~$n\varepsilon_0$~~

$$E_i = -n\varepsilon_0 .$$

So

$$\mathcal{Z} = \sum_{n=0}^{N} e^{\beta\mu n} \frac{N!}{n!(N-n)!} \cdot e^{\beta\varepsilon_0 n}$$

$$= \sum_{n=0}^{N} e^{\beta(\mu+\varepsilon_0)n} \frac{N!}{n!(N-n)!}$$

$$= \left[1 + e^{\beta(\mu+\varepsilon_0)}\right]^N$$

b) average covering $\theta = \frac{\langle n \rangle}{N}$ where

$$\langle n \rangle = + \frac{\partial}{\partial\mu}\left(k_B T \ln \mathcal{Z}\right)$$

$$= \frac{\partial}{\partial\mu} N k_B T \ln\left[1 + e^{\beta(\mu+\varepsilon_0)}\right]$$

$$= N k_B T \frac{e^{\beta(\mu+\varepsilon_0)} \cdot \beta}{1 + e^{\beta(\mu+\varepsilon_0)}}$$

$$= N \frac{e^{\beta(\mu+\varepsilon_0)}}{1 + e^{\beta(\mu+\varepsilon_0)}}$$

6 Partition function

$$Z(T,V,N) = \frac{1}{N!}\left[Z(T,V,1)\right]^N$$

$$Z(T,V,1) = \int \frac{d^3p\, d^3q}{h^3}\, e^{-\beta A p^\alpha}$$

$$= \frac{V}{h^3}\int_0^\infty 4\pi p^2 dp\; e^{-\beta A p^\alpha}$$

$$p^\alpha \equiv x, \qquad p^2 dp = x^{2/\alpha}\, d\left(x^{1/\alpha}\right)$$

$$= \frac{1}{\alpha}\, x^{3/\alpha - 1}\, dx$$

$$= \frac{V}{h^3}\,\frac{4\pi}{\alpha}\int_0^\infty x^{3/\alpha - 1}\, dx\; e^{-\beta A x}$$

$$= \frac{V}{h^3}\,\frac{4\pi}{\alpha}\cdot(\beta A)^{-3/\alpha}\cdot\Gamma\left(\frac{3}{\alpha}\right)$$

$$Z(T,V,N) = \frac{1}{N!}\left[\frac{V}{h^3}\,\frac{4\pi}{\alpha}\,\frac{\Gamma(3/\alpha)}{(\beta A)^{3/\alpha}}\right]^N$$

Energy

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left\{N \ln\left[\frac{V}{h^3}\,\frac{4\pi}{\alpha}\,\frac{\Gamma(3/\alpha)}{\beta^{3/\alpha}}\right] - N\ln N + N\right.$$

$$= +\frac{\partial}{\partial \beta}\left(N \ln \beta^{3/\alpha}\right)$$

$$= N\,\frac{1}{\beta^{3/\alpha}}\cdot\frac{3}{\alpha}\cdot\beta^{3/\alpha - 1} = \frac{3}{\alpha} N k_B T$$

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Pressure

$$P = -\frac{\partial F}{\partial V} = k_B T \frac{\partial}{\partial V} \ln Z$$

$$= k_B T \frac{\partial}{\partial V} \ln V = k_B T / V$$

heat capacity

$$C = \frac{\partial E}{\partial T} = \frac{3}{\alpha} k_B N$$

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$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{N!} Z(T,V,1)^N$$

$$= \sum_{N=0}^{\infty} \left[e^{\beta\mu} Z(T,V,1)\right]^N \frac{1}{N!}$$

$$= \exp\left(e^{\beta\mu} Z(T,V,1)\right)$$

$$= \exp\left[e^{\beta\mu} \frac{V}{h^3} \frac{4\pi}{\alpha} \frac{\Gamma(3/\alpha)}{(\beta A)^{3/\alpha}}\right]$$

(from problem 6)

## Internal energy



Because

$$\frac{\partial}{\partial\beta}\ln\mathcal{Z}\Big|_{\mu,V} = \frac{1}{\mathcal{Z}}\frac{\partial}{\partial\beta}\sum_{i,N} e^{-\beta(E_i-\mu N)}\Big|_{\mu,}$$

$$= \frac{1}{\mathcal{Z}}\sum_{i,N}(E_i-\mu N)\, e^{-\beta(E_i-\mu N)}$$

$$= -\langle E_i-\mu N\rangle = -\langle E\rangle + \mu\langle N\rangle$$

So

$$\langle E\rangle = -\frac{\partial}{\partial\beta}(\ln\mathcal{Z})\Big|_{\mu,V} + \mu\langle N\rangle$$

$$= -\frac{\partial}{\partial\beta}\left(e^{\beta\mu}\cdot\frac{V}{h^3}\,\frac{4\pi}{\alpha}\cdot\frac{\Gamma(3/\alpha)}{(\beta A)^{3/\alpha}}\right) + \mu\langle N\rangle$$

$$= \mu\langle N\rangle - \mu e^{\beta\mu}\,\frac{V}{h^3}\,\frac{4\pi}{\alpha}\,\frac{\Gamma(3/\alpha)}{(\beta A)^{3/\alpha}}$$

$$- e^{\beta\mu}\,\frac{V}{h^3}\,\frac{4\pi}{\alpha}\,\frac{\Gamma(3/\alpha)}{(\beta A)^{3/\alpha}}\cdot\left(-\frac{3}{\alpha}\right)\frac{1}{\beta}$$

$$= \mu\langle N\rangle + \left(\frac{3}{\alpha\beta}-\mu\right) e^{\beta\mu}\,\frac{V}{h^3}\,\frac{4\pi}{\alpha}\,\frac{\Gamma(3/\alpha)}{(\beta A)^{3/\alpha}}$$

Also

$$\langle N\rangle = k_B T\,\frac{\partial\ln\mathcal{Z}}{\partial\mu} = e^{\beta\mu}\,\frac{V}{h^3}\,\frac{4\pi}{\alpha}\,\frac{\Gamma(3/\alpha)}{(\beta A)^{3/\alpha}}$$

So

$$\langle E\rangle = \frac{3}{\alpha\beta}\cdot\langle N\rangle = \frac{3}{\alpha}\langle N\rangle k_B T$$

Pressure:

$$P = -\frac{\partial \Omega(T,V,\mu)}{\partial V} = k_B T \, \frac{\partial \ln \mathcal{Z}}{\partial V}$$

$$= e^{\beta\mu} \, \frac{1}{h^3} \, \frac{4\pi}{\alpha} \, \frac{\Gamma(3/\alpha)}{(\beta A)^{3/\alpha}} \cdot k_B T$$

$$= \frac{\langle N \rangle}{V} \cdot k_B T$$

Heat capacity

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = \frac{3}{\alpha} \langle N \rangle k_B$$