Stat Mech Final Exam Solution

Problem 1

$$E(j) = j(j+1)\varepsilon \quad , \quad \text{degeneracy} = 2j+1$$

(a) $$Z = \sum_{j=0}^{\infty} \underbrace{(2j+1)}_{\text{multiplicity factor due to degeneracy}} e^{-E(j)/kT} = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\varepsilon/kT}$$

(b) $$Z \xrightarrow{kT \gg 1} \int_0^{\infty} (2j+1)\, e^{-j(j+1)\varepsilon/kT}\, dj$$

$$x = j(j+1)\varepsilon/kT \quad \Rightarrow \quad dx = (2j+1)\,\varepsilon/kT\; dj$$

$$\therefore \; Z \simeq \int_0^{\infty} \frac{kT}{\varepsilon} e^{-x}\, dx = \frac{kT}{\varepsilon} = \frac{1}{\varepsilon\beta}$$

$$\bar{E} = -\frac{\partial}{\partial\beta} \log Z = \frac{1}{\beta} = kT$$

(c) Diatomic molecules have two rotational degrees of freedom. So equipartition theorem implies

$$\bar{E} = \underbrace{\left(\tfrac{1}{2}kT\right)}_{\text{average energy per degree of freedom}} \times 2 = kT$$

Problem 2.

$$Z = \frac{\zeta^N}{N!}$$

(a) For ideal gas there's no interactions between molecules. So the system can be considered as N non-interacting subsystems.
So the total partition is a product of all sub-systems.

(b) N! Stems from the indistinguishability of identical molecules.
If it weren't there, the entropy S wouldn't be extensive. ⇒ Gibbs paradox.

(c)

$$\zeta = \int d^3\vec{r}\, d^3\vec{p}\, e^{-\beta E}$$

$$E = \frac{|\vec{p}|^2}{2m} \quad \text{for a single molecule}$$

$$\Rightarrow \zeta = \left(\int d^3\vec{r}\right)\left(\int d^3\vec{p}\, e^{-\beta\frac{|\vec{p}|^2}{2m}}\right)$$

$$= V \cdot \bar{\zeta}(T)$$

$$\bar{\zeta}(T) = \int d^3\vec{p}\, e^{-\beta\frac{|\vec{p}|^2}{2m}}$$

(d)

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial}{\partial N}\left[-kT \log Z\right]$$

$$Z = \frac{V^N \bar{\xi}(T)^N}{N!}$$

$$\Rightarrow \quad \mu \cong \frac{\partial}{\partial N}\left[-kT\left(N \log(V\bar{\xi}) - N\log N + N\right)\right]$$

$$= -kT \log \frac{V\bar{\xi}(T)}{N}$$

(e). The energy of an individual molecule is now

$$E_i = \frac{|\vec{p}_i|^2}{2m} - \eta$$

The total energy can still be written as

$$E^{(0)} = \sum_i E_i = \sum_i \left(\frac{|\vec{p}_i|^2}{2m} - \eta\right)$$

sum of individual energy since the potential doesn't depend on interdistances between molecules

(f) $$\zeta' = \int d^3\vec{r}\, d^3\vec{p}\; e^{-\beta\left(\frac{|\vec{p}|^2}{2m} - \eta\right)}$$

$$= V \cdot e^{\beta\eta} \cdot \int d^3\vec{p}\; e^{-\beta\frac{|\vec{p}|^2}{2m}}$$

$$\Rightarrow \quad Z' = \frac{\zeta'^N}{N!} = \frac{V^N e^{N\beta\eta}\, \bar{\zeta}(T)^N}{N!}$$

(g) $$\mu' = \frac{\partial}{\partial N} F' = \frac{\partial}{\partial N}\left[-kT \log Z'\right]$$

$$= -kT\left[\log \frac{V\zeta}{N} + \beta\eta\right]$$

(h) at equilibrium $\mu = \mu'$

$$\Rightarrow \quad -kT\left[\log \frac{V\zeta}{N}\right] = -kT\left[\log \frac{V\zeta}{N'} + \beta\eta\right]$$

$$\Rightarrow \quad \log \frac{N'}{N} = e^{\beta\eta}$$

or $$\frac{N'}{N} = e^{+\beta\eta}$$