Problem 1: Ensemble with constant temperature and pressure (60 pts.)

Consider an ensemble of systems whose average energy and average volume and total number of particles are fixed. This can be achieved by coupling a system to a reservoir with which it can exchange energy and volume.

- Derive the density matrix D in terms of the Lagrange multipliers associated with the constraints for this ensemble.
- Determine the Lagrange multipliers in terms of physical quantities.
- Express the partition function of this ensemble Q in terms of the partition function of the canonical ensemble $Z(N,V,T)$.
- Determine the most probable volume $\tilde{V}$ (the volume whose contribution to Q is maximum).
- Determine the fluctuations in the volume, and argue that the ensemble Q is equivalent to $Z(N,V,T)$ in the thermodynamic limit.
- Evaluate Q explicitly for an ideal gas, and check your result by deriving the ideal gas law from Q.
- Using $\tilde{V}$ show that the pressure of associated with the ensemble Q is equal to the pressure of the canonical ensemble with volume $\tilde{V}$.
- Using $\tilde{V}$ calculate the quantity $-kT\ln Q$ in terms of the Gibbs free energy.

• $\frac{S}{k} = -\mathrm{Tr}\, D \ln D$ Constraints: $\mathrm{Tr}\,\hat{D}\hat{H} = \bar{E}$, $\mathrm{Tr}\,\hat{D}\hat{V} = \bar{V}$

$$\tilde{S} = S + \tilde{\beta}(\mathrm{Tr}\,\hat{D}\hat{H} - \bar{E}) + \gamma(\mathrm{Tr}\,\hat{D}\hat{V} - \bar{V})$$

~~$\delta\tilde{S} = -\mathrm{Tr}\,\delta D \ln D \ldots \delta D +$~~

$$-\delta D \ln D - \delta D + \tilde{\beta}\,\delta D \hat{H} + \gamma\,\delta\hat{D}\hat{V} = 0$$

$$\Rightarrow \boxed{\hat{D} = \frac{e^{+\tilde{\beta}\hat{H} + \gamma\hat{V}}}{Q}} \qquad Q = \mathrm{Tr}\, e^{-\beta\hat{H} + \gamma\hat{V}}$$

let $\tilde{\beta} = -\beta$

• $$\frac{S}{k} = -\mathrm{Tr}\, D[-\beta\hat{H} + \gamma\hat{V} - \ln Q] = \beta\bar{E} - \gamma\bar{V} + \ln Q$$

$$\frac{dS}{k} = d\beta\,\bar{E} + \beta\, d\bar{E} - \gamma\, d\bar{V} - \bar{V}\, d\gamma + d\ln Q$$

$$d\ln Q = \frac{\partial \ln Q}{\partial \beta} d\beta + \frac{\partial \ln Q}{\partial \gamma} d\gamma$$

$$= -\bar{E}\, d\beta + \bar{V}\, d\gamma$$

$$\frac{dS}{k} = \bar{E}d\beta + \beta d\bar{E} - \gamma d\bar{V} - \bar{V}d\gamma - \bar{E}d\beta + \bar{V}d\gamma$$
$$= \beta d\bar{E} - \gamma d\bar{V}$$

Worksheet:

but since: $\frac{dS}{k} = \frac{d\bar{E}}{kT} + \frac{P}{kT} d\bar{V} \Rightarrow \beta = 1/kT = \beta$

$\gamma = -P/kT = -\beta P$

• $Q = \cancel{\mathrm{Tr}\, Q} = \mathrm{Tr}\, e^{-\beta H - \beta P\hat{V}}$

$$= \int_0^\infty dV e^{-\beta PV} \mathrm{Tr}_V e^{-\beta H} = \int_0^\infty e^{-\beta PV} Z_V(\beta)$$

• $Q = \int dV \bar{P}(V)$. $\bar{P}(V) = e^{-\beta PV} Z_V(\beta)$

$$\frac{\partial \bar{P}(V)}{\partial V} = 0 = \underbrace{-\beta P + \frac{\partial \ln Z_V(\beta)}{\partial V} = 0}$$

$\tilde{V}$ solves this eq'n.

$$Q \sim e^{-\beta P\tilde{V}} Z_{\tilde{V}}(\beta)$$

• ~~for~~ $Q = \int_0^\infty e^{-\beta PV} Z_V(\beta)$

$$-\frac{1}{\beta}\frac{\partial \ln Q}{\partial P} = \bar{V} \rightarrow \frac{\partial \bar{V}}{\partial P} < 0 \quad \text{(stability)}$$

$$+\frac{1}{\beta^2}\frac{\partial^2 \ln Q}{\partial P^2} = \overline{V^2} - \bar{V}^2 = -\frac{1}{\beta}\frac{\partial \bar{V}}{\partial P}$$

$\sigma_V^2 \sim \bar{V}$ (extensive)

relative fluctuations $\Rightarrow \frac{\sigma_V}{\bar{V}} \sim \frac{1}{\sqrt{\bar{V}}}$

as $\bar{V} \to \infty$ $\frac{\sigma_V}{\sqrt{V}} \to 0$

• $Q = \int_0^\infty e^{-\beta P V} Z_V(\beta)$ ideal gas: $Z_V(\beta) = \frac{V^N}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}}$

$$= \underbrace{\left[\int_0^\infty e^{-\beta P V} V^N\right]}_{\text{evaluate integral:}}\left[\frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}}\right]$$

Worksheet:

$$-\frac{d}{da} \rightarrow \int_0^\infty e^{-av}\, dv = \frac{1}{a}$$

$$\int_0^\infty e^{-av}\, v\, dv = \frac{1}{a^2}$$

$$\int_0^\infty e^{-av}\, v^2\, dv = \frac{2}{a^3} \Rightarrow \int_0^\infty e^{-\beta P V} V^N dV = \frac{N!}{(\beta P)^N}$$

$$Q = \frac{1}{(\beta P)^N}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}}$$

$$\bar{V} = -\frac{1}{\beta}\frac{\partial \ln Q}{\partial P} = -\frac{1}{\beta}\left(-\frac{N}{P^{N+1}}\right)P^N = \frac{NkT}{P}$$

$$\Rightarrow \boxed{P\bar{V} = NkT}$$

• $Q = \int_0^\infty e^{-\beta P V} Z_V(\beta)\, dV$

$$\Rightarrow \bar{V} \Rightarrow -\beta P + \frac{\partial \ln Z(\beta)}{\partial V} \Rightarrow P = \underbrace{\frac{1}{\beta}\frac{\partial \ln Z_V}{\partial V}}_{\text{canonical pressure}}$$

• $-kT\ln Q = PV + \frac{1}{\beta}\ln Z_V$

$$= F + PV = \underline{\underline{G}}$$

Problem 2: Lattice gas model (40 pts.)

Consider a one-dimensional lattice system. Each lattice site can have one particle or none. When two particles are on neighboring lattice sites they interact with an energy -*J*. Solve for the thermodynamic behaviour of this system using the grand canonical ensemble. Calculate the average energy and the average particle number for a given temperature and chemical potential.

$H = -J\sum_i R_i R_{i+1}$ $\qquad R_i = 0, 1$

grand canonical: $Q = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\{\sigma\}} \prod_i e^{\beta J R_i R_{i+1}}$

$N = \sum_i R_i$

$$\Rightarrow \quad Q = \sum_{\sigma_1}\cdots\sum_{\sigma_N} e^{\underbrace{\beta J\sum_i R_i R_{i+1} + \beta\mu\sum_i R_i}_{\tilde{H}}}$$

just like canonical Ising under magnetic field

$$\tilde{H} = -J\sum_i R_i R_{i+1} - \mu\sum_i R_i$$

define $\sigma_i = 2(R_i - 1/2)$ $\qquad \sigma_i = \pm 1$

$$\Rightarrow \quad \boxed{\frac{\sigma_i + 1}{2} = R_i}$$

$$\tilde{H} = -\frac{J}{4}\sum_i (\sigma_i + 1)(\sigma_{i+1} + 1) - \mu\sum_i \frac{\sigma_i + 1}{2}$$

$$= -\frac{J}{4}\sum_i \sigma_i\sigma_{i+1} - \frac{J+\mu}{2}\sum_i \sigma_i - \frac{JN}{4} - \frac{\mu N}{2}$$

Ising model with coupling $J/4$

magnetic field $\frac{J+\mu}{2}$

Worksheet:

solution is basically in book (Eq. 3.34)

$$\lambda_+ = e^{K}\left[\cosh K' + \sqrt{\sinh^2 K' + e^{-4K}}\,\right] \qquad K = \frac{\beta J}{4}$$

$$Q = \lim_{M\to\infty} \lambda_+^{M} \qquad M \text{ sites} \qquad K' = \frac{\beta}{2}(\mu + J)$$

$$\bar{E} = -\frac{\partial \ln \lambda_+}{\partial \beta} + \frac{J}{4} - \frac{\mu}{2} \qquad \bar{N} = \frac{1}{\beta}\frac{\partial \ln \lambda_+}{\partial \mu}$$

$$\frac{\partial \lambda_+}{\partial \beta} = \frac{J}{4}\lambda_+ + e^{K}\left[\sinh K'\left(\frac{\mu+J}{2}\right) + \frac{2\sinh K'\cosh K'\left(\frac{\mu+J}{2}\right) + e^{-4K}(-J)}{2\sqrt{\sinh^2 K' + e^{-4K}}}\right]$$

$$\frac{\partial \lambda_+}{\partial \mu} = \frac{\beta \sinh K'}{2} + \frac{2\sinh K'\cosh K'}{2\sqrt{\sinh^2 K' + e^{-4K}}}\,\frac{\beta}{2}$$