8. *Statistical Mechanics and Thermodynamics* (Fall 2006)

(a) Consider a grand canonical ensemble of particles, at fixed temperature T and in a container of volume V. Show that the mean square fluctuation in the number of particles $\overline{(\Delta N)^2}$ is:

$$\overline{(\Delta N)^2} = k_B T \frac{\partial \bar{N}}{\partial \mu}.$$

(b) Using the relation:

$$S dT - V dp + N d\mu = 0 \qquad (1)$$

express the solution in terms of $\left(\frac{\partial \rho}{\partial p}\right)_{T,V}$ where $p =$ pressure and $\rho = \frac{N}{V}$ is the density of the system.

(c) Since intensive quantities are independent of extensive quantities by definitino, we can change external constraints to obtain:

$$\left(\frac{\partial \rho}{\partial p}\right)_{T,V} = \left(\frac{\partial \rho}{\partial p}\right)_{T,N}.$$

Using this relation, find an expression for $\overline{(\Delta N)^2}$ in terms of the isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$.

a) $\overline{(\Delta N)^2} = \overline{N^2} - \bar{N}^2$

Grand partition function: $\mathcal{Z} = \sum_N Z(N)\, e^{\beta\mu N}$ where $Z(N) = \sum_{R(N)} e^{-\beta E_{R(N)}}$

$\Rightarrow \mathcal{Z} = \sum_N \sum_{R(N)} e^{-\beta(E_{R(N)} - \mu N)} = \sum_i e^{-\beta(E_i - \mu N_i)}$

$$\bar{N} = \frac{\sum_i N_i e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}} = \frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu}; \quad \overline{N^2} = \frac{\sum_i N_i^2 e^{-\beta(E_i-\mu N_i)}}{\mathcal{Z}} = \frac{1}{\beta^2}\frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$

$$kT\frac{\partial \bar{N}}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\left(\frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial\mu}\right) = \frac{1}{\beta^2}\left(-\frac{1}{\mathcal{Z}^2}\frac{\partial \mathcal{Z}}{\partial\mu}\right)\frac{\partial \mathcal{Z}}{\partial\mu} + \frac{1}{\beta^2}\frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\mu^2}$$

$$= -\bar{N}^2 + \overline{N^2} = \overline{(\Delta N)^2}$$ ✓

b) $\left(\frac{\partial \rho}{\partial P}\right)_{T,V} \Rightarrow \rho = \rho(P,T,V) = \frac{N'(P,T,V)}{V}$ $\qquad N'(P,T,V) = N(\mu(P,T),T,V)$

$N = N(\mu, T, V)$

$$\left(\frac{\partial \bar{\rho}}{\partial P}\right)_{T,V} = \frac{1}{V}\left(\frac{\partial \bar{N}'}{\partial P}\right)_{T,V} \overset{\star}{=} \frac{1}{V}\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}\left(\frac{\partial \mu}{\partial P}\right)_T \Rightarrow \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = V\left(\frac{\partial \bar{\rho}}{\partial P}\right)_{T,V} \Big/ \left(\frac{\partial \mu}{\partial P}\right)_T$$

$(1) \Rightarrow d\mu = \frac{VdP - SdT}{N} = \frac{V}{N}dP - \frac{S}{N}dT \Rightarrow \mu = \mu(P,T)$ and $\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{V}{N}$

$$\Rightarrow kT\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} = kTN\left(\frac{\partial \bar{\rho}}{\partial P}\right)_{T,V}$$

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c) $\left(\frac{\partial \rho}{\partial P}\right)_{T,N} \Rightarrow \rho = \rho(P,T,N) = \frac{N}{V(P,T,N)}$

$$\Rightarrow \left(\frac{\partial \rho}{\partial P}\right)_{T,N} = \frac{\partial}{\partial P}\left(\frac{N}{V}\right)_{T,N} = -\frac{N}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,N} = \frac{N}{V}\kappa_T$$

$$\Rightarrow \overline{(\Delta N)^2} = kTN\left(\frac{\partial \rho}{\partial P}\right)_{T,V} = kTN\left(\frac{\partial \rho}{\partial P}\right)_{T,N} = \boxed{kT\frac{N^2}{V}\kappa_T}$$

★ Proof:

$\bar{N}' = \bar{N}'(P,T,V)$ $\quad d\bar{N}' = \left(\frac{\partial \bar{N}'}{\partial P}\right)_{T,V} dP + \left(\frac{\partial \bar{N}'}{\partial T}\right)_{P,V} dT + \left(\frac{\partial \bar{N}'}{\partial V}\right)_{P,T} dV$

$\bar{N} = \bar{N}(\mu,T,V)$ $\quad d\bar{N} = \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V} d\mu + \left(\frac{\partial \bar{N}}{\partial T}\right)_{\mu,V} dT + \left(\frac{\partial \bar{N}}{\partial V}\right)_{\mu,T} dV$

$\mu = \mu(P,T)$ $\quad = \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}\left[\left(\frac{\partial \mu}{\partial P}\right)_T dP + \left(\frac{\partial \mu}{\partial T}\right)_P dT\right] + \left(\frac{\partial \bar{N}}{\partial T}\right)_{\mu,V} dT + \left(\frac{\partial \bar{N}}{\partial V}\right)_{\mu,T} dV$

$= d\bar{N}'$

equating the coefficients of dP $\Rightarrow \left(\frac{\partial \bar{N}'}{\partial P}\right)_{T,V} = \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}\left(\frac{\partial \mu}{\partial P}\right)_T$ ✓