

Problem III. 2

We have treated the energy fluctuation in the canonical ensemble and the number of particles fluctuations in the grand canonical ensemble in class.

Following the usual procedure, we obtain

$$\langle (\Delta E)^2 \rangle_{\text{grand CA}} = - \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{\mu, V} = T^2 \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{\mu, V}$$

For the number fluctuations the result was:

$$\langle (\Delta N)^2 \rangle = T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V, T} = \left(\frac{\partial \langle N \rangle}{\partial (\frac{\mu}{T})} \right)_{V, T} = \left(\frac{\partial \langle N \rangle}{\partial \alpha} \right)_{V, T}, \alpha = \frac{\mu}{T}$$

Regarding E as a function of T and N , from

$$dE = \left(\frac{\partial E}{\partial T} \right)_N dT + \left(\frac{\partial E}{\partial N} \right)_T dN \quad \text{we can easily}$$

obtain:

$$\left(\frac{\partial E}{\partial T} \right)_\alpha = \left(\frac{\partial E}{\partial T} \right)_N + \left(\frac{\partial E}{\partial N} \right)_T \left(\frac{\partial N}{\partial T} \right)_\alpha$$

Since $\langle (\Delta E)^2 \rangle_{\text{CANONICAL}} = T^2 \left(\frac{\partial E}{\partial T} \right)_N$, we have

$$\langle (\Delta E)^2 \rangle - \langle (\Delta E)^2 \rangle_{\text{CANONICAL}} = T^2 \left(\frac{\partial E}{\partial N} \right)_T \left(\frac{\partial N}{\partial T} \right)_\alpha$$

$$\boxed{E \leftrightarrow \langle E \rangle}$$

To relate this to $\langle (\Delta N)^2 \rangle$, consider

$d\Omega = p dV + S dT + N d\mu$. For a system with fixed volume ($dV=0$) in terms of α : $d\mu = dT + T d\alpha \Rightarrow$

$$d\Omega = (S + \alpha N) dT + NT d\alpha$$

From this expression, for second derivatives:

$$\left(\frac{\partial (S + \alpha N)}{\partial \alpha} \right)_T = \left(\frac{\partial (NT)}{\partial T} \right)_\alpha = N + T \left(\frac{\partial N}{\partial T} \right)_\alpha$$

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for the left hand side

The expression ~~above~~ is obtained writing

$$dE = TdS - pdV + \mu dN \quad \text{as}$$

$$d(S + \alpha N) = \frac{1}{T} dE + N d\alpha$$

\Downarrow

$$\left(\frac{\partial (S + \alpha N)}{\partial \alpha} \right)_T = N + \frac{1}{T} \left(\frac{\partial E}{\partial \alpha} \right)_T$$

Thus ;

$$T^2 \left(\frac{\partial N}{\partial T} \right)_\alpha = \left(\frac{\partial E}{\partial \alpha} \right)_T = \left(\frac{\partial E}{\partial N} \right)_T \left(\frac{\partial N}{\partial \alpha} \right)_T = \left(\frac{\partial E}{\partial N} \right)_T \langle (\Delta N)^2 \rangle$$

\therefore

$$\underline{\langle (\Delta E)^2 \rangle = \langle (\Delta E)^2 \rangle_{\text{CANONICAL}} + \left[\left(\frac{\partial E}{\partial N} \right)_T \right]^2 \langle (\Delta N)^2 \rangle}$$

□