42) However, by definition,

$\Omega_1(E_1)$ = nu. of states $E_1 < E < E_1 + \delta E$

Define partition function (the normalized term $P_1(E_1)$)

$$Z_c = \int \frac{dE_1}{\delta E} \Omega_1(E_1) e^{-\beta E_1}$$ where $\beta \equiv 1/k_B T$

Thus, $$\boxed{Z_c = \sum_{\text{states}} e^{-\beta E}}$$ canonical partition function

Average energy:

$$\langle E \rangle = -\frac{1}{Z_c}\frac{\partial Z_c}{\partial \beta} = \frac{\sum E e^{-\beta E}}{\sum e^{-\beta E}}$$

Fluctuations:

$$\langle (\Delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

(mean square fluctuation variance)

Consider

$$\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\frac{1}{Z_c}\frac{\partial Z_c}{\partial \beta}\right] = \frac{1}{Z_c^2}\left(\frac{\partial Z_c}{\partial \beta}\right)^2 - \frac{1}{Z_c}\frac{\partial^2 Z_c}{\partial \beta^2}$$

Re-arrange:

$$\underbrace{\frac{1}{Z_c}\frac{\partial^2 Z_c}{\partial \beta^2}}_{\langle E^2 \rangle} = \underbrace{\frac{\partial}{\partial \beta}\left(\frac{1}{Z_c}\frac{\partial Z_c}{\partial \beta}\right)}_{\frac{\partial^2}{\partial \beta^2}\ln Z_c} + \underbrace{\frac{1}{Z_c^2}\left(\frac{\partial Z_c}{\partial \beta}\right)^2}_{\langle E \rangle^2}$$

$$\langle E^2 \rangle = \underbrace{\frac{\partial^2}{\partial \beta^2}\ln Z_c}_{\langle (\Delta E)^2 \rangle} + \langle E \rangle^2$$

$$\Rightarrow \boxed{\langle (\Delta E)^2 \rangle = \frac{\partial^2}{\partial \beta^2}\ln Z_c}$$

However,

$$\frac{\partial^2}{\partial \beta^2} \ln Z_c = -\frac{\partial \langle E \rangle}{\partial \beta} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}$$

$$\Rightarrow \boxed{\langle (\Delta E)^2 \rangle = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}} = k_B T^2 c_V$$

c_V: specific heat at V, N

For large systems

$$c_V = \frac{\partial \langle E \rangle}{\partial T} \propto N$$

Also $\langle E \rangle \propto N$

Thus $$\frac{(\Delta E)^2}{\langle E \rangle^2} \propto \frac{N}{N^2} \propto \frac{1}{N}$$

Hence, as $N \to \infty$

(i) system overwhelmingly likely to have energy $\langle E \rangle$

(ii) system is identical to all isolated systems with $E = \langle E \rangle$

If this holds,

$$\begin{bmatrix} \text{canonical ensemble} \\ \text{with temp. } T \text{, such} \\ \text{that } \langle E \rangle = E_0 \end{bmatrix} \equiv \begin{bmatrix} \text{Microcanonical} \\ \text{with } E_0 \\ \end{bmatrix}$$

In microcanonical ensemble:

states with specified $E(S, V, N)$
and T, P, μ – derived quantities

In canonical ensemble:

The system is kept at fixed T

$\Downarrow$

change of independent variable
$S \rightarrow T$
is achieved by replacing $E \rightarrow \underbrace{A}_{\text{Helmholtz free energy}}$

A is defined: $A = E - TS$ using II law
$dA = dE - TdS - SdT = \mu dN - PdV - SdT$

Stat. mech: $A = -k_B T \ln Z_c$

Both agree for large systems:

$$A = \underbrace{\langle E \rangle}\; - T \underbrace{\langle S \rangle}$$

most probable values
for canonical distribution

Free Energy (Helmholtz): $A = E - TS$

In stat. mech: $\boxed{A \equiv -k_B T \ln Z_c}$ $\Big\{$ both thermo. & stat. mech. definitions agree for $N \to \infty$

Note, we are now focusing on the subsystem A_1 ($<< A_2$ system!)
Energy E_1 fluctuates, so do quantities like entropy $S(E, \dots)$

$$Z_c = \int \frac{\partial E}{\delta E} \Omega(E)\, e^{-\beta E} = \int \frac{dE}{\delta E} e^{\frac{1}{k_B} S(E) - E/k_B T}$$

For a large system: overwhelmingly probable: $E \to \langle E \rangle$

Exp. maximum is obtained for $E = E_m$

$$\frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)_{E_m} = \frac{1}{k_B T} \equiv \beta$$

$\Big\{$ given by $\frac{1}{k_B}\langle S \rangle - \frac{\langle E \rangle}{T} = max$

Expand around E_m

where $E_m = \langle E \rangle$

$$\frac{1}{k_B} S(E) - \beta E = \frac{1}{k_B}\Big[S(E_m) + \overbrace{(E - E_m)\left(\frac{\partial S}{\partial E}\right)_{E_m}}^{\text{at max } = 0} + \frac{1}{2}(E - E_m)^2 \left(\frac{\partial^2 S}{\partial E^2}\right)_{E_m} + \dots\Big] - \underbrace{-\beta E_m}_{0 \text{ order}} - \underbrace{\beta(E - E_m)}_{1\text{st order (at max} = 0)}$$

Use β:

$$\frac{1}{k_B} S(E) - \beta E \approx \frac{1}{k_B} S(E_m) - \beta E_m + \frac{1}{2}(E - E_m)^2 \left(\frac{\partial^2 S}{\partial E^2}\right)_{E_m}$$

$$\Rightarrow \frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2 c_v} \quad \Leftarrow \quad c_v \text{ because we use } v = \text{const}; \; N = \text{const}.$$

$S'' < 0$ for maximum

Thus, $c_v > 0 \Rightarrow$ maximum

Approximating integral by $E = E_m + E'$, treat E' small ($E' \ll E$):

$$Z_e = e^{-[\beta E_m - S(E_m)/k_B]} \int \frac{dE'}{\delta E} e^{-\frac{(E')^2}{2T^2 c_v k_B}} =$$

$$= e^{-[\beta E_m - S(E_m)/k_B]} \frac{1}{\delta E} (2\pi k_B c_v T^2)^{1/2}$$

So,

$$\boxed{A = E_m - T S(E_m) - k_B T \ln \frac{\sqrt{2\pi k_B c_v T^2}}{\delta E}}$$

δE appears in the non-extensive piece

In the same approximation ($N \to \infty$)

$$E_m = \langle E \rangle$$

$$S(E_m) = \langle S \rangle$$

$\Downarrow$

$\delta E \propto \sqrt{\langle E \rangle}$

choice!

$\Downarrow$

$$\Rightarrow A = \langle E \rangle - T \langle S \rangle$$

$\ln \propto 1$ while $\langle E \rangle$ and $\langle S \rangle$ extensive