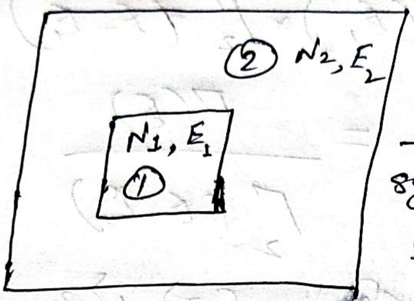
Canonical ensemble: —

Q. → What ensemble is appropriate for the description of a non-isolated system, but in thermal equilibrium with a larger system (reservoir)?



→ Isolated composite system made up of two subsystems ~~with~~ 1 & ②

↑ we call it reservoir

where $N_2 >> N_1$ and $E_2 >> E_1$.

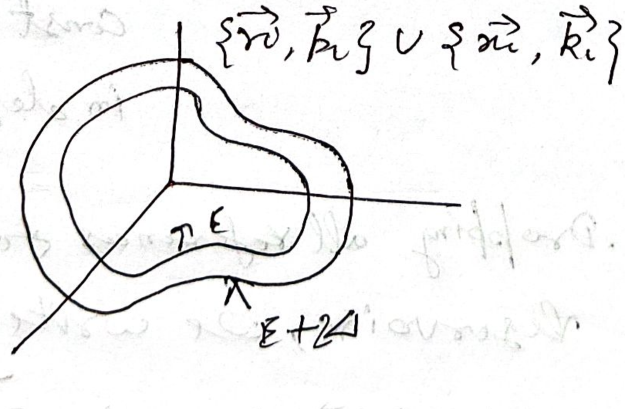
· Subsystem Hamiltonian $H_1(\underbrace{\vec{r_i}, \vec{k_i}})$ → coordinates of N_1 particles in subsystem

Reservoir Hamiltonian $H_2(\underbrace{\vec{x_0}, \vec{k_0}})$ → coordinates of N_2 particles in reservoir

Total Hamiltonian $\boxed{H = H_1 + H_2}$

↑ for short range interactions

The whole system (Subsystem ① + Reservoir ②) lies in a microcanonical ensemble with H lying between → $E \leq H \leq E + 2\Delta$



$$\Gamma(E) = \int d\vec{x}_i \int d\vec{k}_i \int d\vec{x}_0 \int d\vec{k}_0$$
$$E \leq H_1 + H_2 \leq E + 2\Delta$$

$$= \int d\vec{x}_i \int d\vec{k}_i \times \int d\vec{x}_i \int d\vec{k}_i$$
$$E_1 \leq H_1 \leq E_1 + \Delta \quad E - E_1 \leq H_2 \leq E - E_1 + \Delta$$

$$= \Gamma_1(E_1) \times \Gamma_2(E - E_1)$$

or $$\Gamma_1(E_1) = \frac{\Gamma(E)}{\Gamma_2(E - E_1)}$$

Prob. of finding ① in $\{\vec{x}_i, \vec{k}_i\} \to \{\vec{x}_i + d\vec{x}_i, \vec{k}_i + d\vec{k}_i\}$

$$\rho(\vec{x}_i, \vec{p}_v) \propto \frac{1}{\Gamma_1(E_1)} \propto \Gamma_2(E - E_1)$$

$$\ln \Gamma_2(E - E_1) = S_2(E - E_1) = -S_2(E) - E_1 \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{E_2 - E} + \cdots$$

$$= S_2(E) - \frac{E_1}{T} + \cdots$$

$\{$ take $k = 1\}$

or $$\Gamma_2(E - E_1) \approx \underbrace{\exp(S_2(E))}\exp(-\beta E_1)$$

const. prefactor
independent of E_1

~~at~~ . Dropping all references to subsystem and reservoir, we write

$$\rho(\{\vec{x}_v, \vec{p}_v\}) = N_0\, e^{-\beta H(\vec{x}_v, \vec{p}_v)}$$

$N_0 \rightarrow$ normalization factor ; determined by requiring that $\frac{1}{N!}\int d\vec{r}_i \int d\vec{p}_i \, e^{-\beta(\vec{r}_i, \vec{p}_i)} \, N_0 = 1$

Partition function $Z(T, V, N) = \frac{1}{N_0}$

or $\boxed{Z(T, V, N) = \frac{1}{N_0} = \frac{1}{N!}\int d\vec{r}_i \int d\vec{p}_i \, e^{-\beta H}}$

To obtain the thermodynamic parameters of the system we write $e^{-\beta F(T, V, N)} = Z(T, V, N)$

or $\boxed{F(T, V, N) = -T \ln Z(T, V, N)}$

($k = 1$ is assumed here)

<u>H.W.</u> obtain the relative mean square fluctuation in energy of canonical ensemble and discuss its implications.