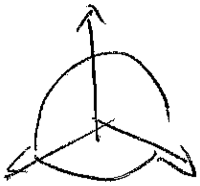
(4) Microcanonical Ensemble

Fixed int energy E and gen. coord. $\vec{x}$

Macrostate $M(E, \vec{x})$

mixed microstate(μ) → ensemble

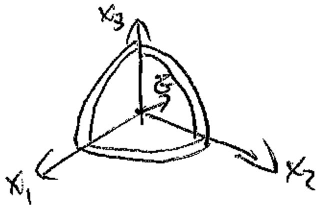
- μ # pt in phase space $\{q_i, p_i\} \to \{x_i\}$
- $H = H(\{q_i, p_i\})$
- H conserved i.e. $H(\mu) = E$
- total # states confined on surface area of constant energy (Ω) thus,



$$P(\mu) = \frac{1}{\Omega(E, \vec{x})}$$ (assume uniform distribution)

- usually constraint energy w/ uncertainty Δ s.t. $E - \Delta \leq H(\mu) \leq E + \Delta$
  more convention to describe # μ within energy shell

  $\Omega' \approx 2\Delta\Omega$



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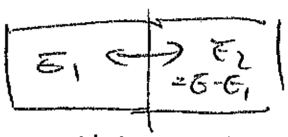
joint sys



only energy xchange allowed

$\mu = \mu_1 \otimes \mu_2$ $\quad H(\mu_1 \otimes \mu_2) = H_1(\mu_1) + H_2(\mu_2)$

$E_1 = E_1 + E_2$

then $$P_E(\mu_1 \otimes \mu_2) = \frac{1}{\Omega(E)} \cdot \begin{cases} 1 & H(\mu_1 \otimes \mu_2) = E \\ 0 & \text{else} \end{cases}$$

Note Entropy $S = k_B \ln \Omega$

Thus joint sys has

$$\Omega(E) = \int dE_1\, \Omega(E_1)\Omega(E - E_1) = \int dE_1 \exp\left[\frac{S_1(E_1) + S_2(E - E_1)}{k_B}\right]$$

At equilibrium, we have saddle point at (E_1^*, E_2^*)

By saddle point method,

i.e. $f, S : \mathbb{R}^n \to \mathbb{R}$ $\quad U \subset \mathbb{R}^n$ if $M = \sup_{x \in U} (S(x)) < \infty$ s.t. $\int_U |f(x) e^{\lambda_0 S(x)}| dx < \infty$

then $\left| \int_U f(x) e^{\lambda S(x)} dx \right| \leq \text{const} \cdot e^{\lambda M}$ $\quad \forall \lambda \in \mathbb{R} \quad \lambda \geq \lambda_0$

Thus, $S(E) = k_B \ln \Omega(E) \approx S_1(E_1^*) + S_2(E_2^*)$

extremum of $\Omega(E) \Rightarrow \left.\frac{\partial S_1}{\partial E_1}\right|_{\vec{x}_1} = \left.\frac{\partial S_2}{\partial E_2}\right|_{\vec{x}_2}$ here $\vec{x}_{1,2}$ seen as volume. V

Remark. Postulate of uniform distrb of state, but max # state at (E_1^*, E_2^*)
- this is because probabilistic avg. provides no info of dynamical evolution.

Since $\left.\frac{\partial S}{\partial E}\right|_{\vec{x}} = \frac{1}{T}$, at equilibrium $\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \Rightarrow$ temp. equilibrium!

Remark $\Omega_1(E_1^*, \vec{x}_1)\Omega_2(E_2^*, \vec{x}_2) \geq \Omega_1(E_1, \vec{x}_1)\Omega_2(E_2, \vec{x}_2)$ by Saddle Point Method.

thus $\delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geq 0$ 2nd Law ; $S = k_B \ln \Omega$

O.T.O.H $\delta S = \left(\left.\frac{\partial S}{\partial E_1}\right|_{\vec{x}_1} - \left.\frac{\partial S}{\partial E_2}\right|_{\vec{x}_2}\right)\delta E = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta E_1 \geq 0$

Heat flow from high temp to low temp.

Stab. Cond $\left.\frac{\partial^2 S_1}{\partial E_1^2}\right|_{\vec{x}_1} + \left.\frac{\partial^2 S_2}{\partial E_2^2}\right|_{\vec{x}_2} \leq 0$ at equilibrium where (E_1^*, E_2^*) maximum pt.

thus there must be $C_x \geq 0$

Two-level sys.

Excited state w/ energy ε
Ground state w/ " 0
total mixed states N
# of excited states N_1
total energy E

$$H(\{n_i\}) = \varepsilon \sum_{i=1}^{N} n_i = \varepsilon N_1 = E \Rightarrow N_1 = \frac{E}{\varepsilon}$$

$$P(\{n_i\}) = \frac{1}{\Omega(E,N)} \delta_{\varepsilon \sum n_i, E}$$

$$\Omega = \frac{N!}{N_1!(N-N_1)!} \quad S = k_B \ln \Omega$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = -\frac{k_B}{\varepsilon} \ln\left(\frac{E}{N\varepsilon - E}\right), \quad E(T) = \frac{N\varepsilon}{e^{\varepsilon/k_BT} + 1}$$

Probability distribution.

By Bayes-thm i.e. $P(x,v) = P(v|x)P(x)$

$$P(n_1) = \sum_{n_2 \cdots n_N} P(\{n_i\}) = \frac{\Omega(E - n_1\varepsilon, N-1)}{\Omega(E,N)}$$

$$P(n_1 = 0) = \frac{\Omega(E, N-1)}{\Omega(E,N)} = 1 - \frac{N_1}{N} ; \quad P(n_1 = 1) = 1 - P(n_1 = 0) = \frac{N_1}{N}$$

For $N_1 = \frac{E}{\varepsilon}$

$$P(0) = \frac{1}{1 + e^{-\varepsilon/k_BT}} \qquad P(1) = \frac{e^{-\varepsilon/k_BT}}{1 + e^{-\varepsilon/k_BT}}$$

(4) Micro-ensemble

ex Ideal Gas

N (free) particles. 6N dim for $\mu = \{\vec{p}_i, \vec{q}_i\}$ phase space.

PDF $$p(\mu) = \frac{1}{\Omega(E,V,N)}\delta(E-H)$$

$$\Omega = \int d\mu\, \delta(E-H) = \int \prod_{i=1}^{N} d^3q_i\, \underbrace{d^3p_i\, \delta(E-H)}_{3N \text{ spherical shell}} = V^N A^{3N} \Delta_{R(E)}$$

$R = \sqrt{2mE}$ b/c $\sum p_i^2 = 2mE$ $\qquad \Delta_{R(E)} = \Delta E \sqrt{2mE}$

For S^{d-1} surf. area $A^d = \underbrace{S_d}_{\text{solid angle}} R^{d-1}$

$$I = \int \prod_{i=1}^{d} dx_i\, e^{-x_i^2} = \pi^{d/2} = \int d^d x_i\, e^{-\sum x_i^2} = S_d \int dR\, R^{d-1} e^{-R^2}$$

For $y = R^2$, $\pi^{d/2} = S_d \left(\frac{d}{2}-1\right)!$ w/ $\left(\frac{d}{2}-1\right)! = \int y^{\frac{d}{2}-1} e^{-y} dy$

Thus $$\Omega = V^N (2mE)^{\frac{3N-1}{2}} \frac{2\pi^{d/2}}{\left(\frac{d}{2}-1\right)!}\Delta_{R(E)}$$

i.e. $(E,V,N) \to (\lambda E, \lambda V, \lambda N)$

$$S = k_B \ln \Omega = N k_B \ln\left[V\left(\frac{4\pi e m E}{3N}\right)^{3/2}\right]$$ ← Not extensive.

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{N,V} = \frac{3}{2}\frac{Nk_B}{E}, \quad \frac{P}{T} = \frac{\partial S}{\partial V}\bigg|_{N,E} = \frac{Nk_B}{V} \quad \text{so } PV = Nk_BT$$

Prob distrb

$$p(\vec{p}_1) = \int d^3q_1 \prod_{i=2}^{N} d^3q_i\, d^3p_i\, p(\{\vec{q}_i, \vec{p}_i\}) = \frac{V\Omega\left(E - \frac{p_1^2}{2m}, V, N-1\right)}{\Omega(E,V,N)}$$

using expression of Ω,

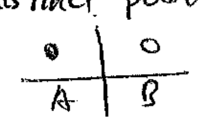
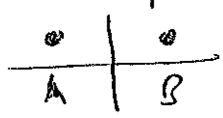
$$p(\vec{p}_1) = \left(\frac{3N}{4\pi mE}\right)^{3/2} \exp\left(-\frac{3N}{2}\frac{\vec{p}_1^{\,2}}{2mE}\right)$$

for $E = \frac{3Nk_BT}{2}$

$$p(\vec{p}_1) = \frac{1}{(2\pi m k_B T)^{3/2}} \exp\left(-\frac{\vec{p}^{\,2}}{2mk_BT}\right)$$

Gibbs Paradox. mixing of same gas w/ same density.

distinct particle. identical particle

 $\Delta S > 0$  $\Delta S = 0$ (should expect).

due to overcount $N!$ thus.

$$\Omega(N,E,V) = \frac{V^N}{N!}\frac{2\pi^{3N/2}}{(3N/2-1)!}(2mE)^{\frac{3N-1}{2}}\Delta_R \Rightarrow S = Nk_B\left(\ln\frac{eV}{N} + \delta\right)$$ not extensive!

Canonical Ensemble

$$p(\mu_s \otimes \mu_R) = \frac{1}{\Omega_{S\otimes R}(E_{tot})} \begin{cases} 1 & H_R(\mu_R) + H_s(\mu_s) = E_{tot} \\ 0 & \text{else} \end{cases}$$

$$p(\mu_s) = \frac{\Omega_R(E_{tot} - H_s(\mu_s))}{\Omega_{S\otimes R}(E_{tot})} \propto \exp\left(\frac{1}{k_B} S_R(E_{tot} - H_s(\mu_s))\right)$$

Since $E_{tot} \gg H_s(\mu_s)$ then $S_R(E - H_s(\mu_s)) \approx S_R(E) - H_s \frac{\partial S_R}{\partial E_R} = S_R(E) - \frac{H_s}{T}$

Thus
$$p(\mu) = \frac{e^{-\beta H(\mu)}}{Z} \qquad \text{here } \mu = \mu_s$$

$$Z = \sum_{\{\mu\}} e^{-\beta H(\mu)}$$

Note. $p(\varepsilon) = \int dH\, p(H)\, \delta(H - \varepsilon) = \int d\mu\, p(\mu)\, \delta(H(\mu) - \varepsilon)$

$$\rightarrow p(\varepsilon) = \sum_\mu p(\mu)\,\delta(H(\mu) - \varepsilon) = \frac{e^{-\beta\varepsilon}}{Z} \underbrace{\sum_\mu \delta(H(\mu) - \varepsilon)}_{\Omega}$$

thus $p(\varepsilon) = \frac{\Omega(\varepsilon) e^{-\beta\varepsilon}}{Z} = \frac{1}{Z} \exp\left(\frac{-F(\varepsilon)}{k_B T}\right)$

now we have also
$$Z = \sum_\mu e^{-\beta H(\mu)} = \sum_\varepsilon e^{-\beta F(\varepsilon)} \approx e^{-\beta F(E^*)} \quad \text{most probable}$$

$$\langle H \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

Since $E = F + TS = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right) = \frac{\partial(\beta F)}{\partial \beta}$

$$\Rightarrow \quad F(T, \vec{x}) = -k_B T \ln Z$$

Cumulant of H

$Z = \sum_\mu e^{-\beta H(\mu)}$ if $\beta \to ik$ $\sum \to \int$ we have F.T. $Z \to \tilde{Z}(k)$

so $\langle H \rangle_c = -\frac{\partial \ln Z}{\partial \beta}$ $\langle H^2 \rangle_c = \frac{\partial^2 \ln Z}{\partial \beta^2}$ Generally $\langle H^n \rangle_c = (-1)^n \frac{\partial^n \ln Z}{\partial \beta^n}$

Central limit thm

$\langle H^2 \rangle = k_B T^2 C_x$ where $C_x \sim N$ width of $p(\varepsilon) \propto \sqrt{\langle H^2 \rangle_c} \propto N^{1/2}$

relative error $\sqrt{\langle H^2 \rangle_c} / \langle H \rangle_c \to 0$ clearly all $\langle H^n \rangle_c \sim N$ thus.

$$p(\varepsilon) = \frac{1}{Z} e^{-\beta F(\varepsilon)} \approx \frac{1}{\sqrt{2\pi k_B T^2 C_x}} \exp\left(-\frac{(\varepsilon - \langle H \rangle)^2}{2 k_B T^2 C_x}\right)$$

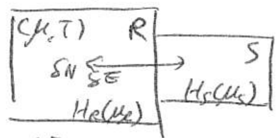
④ Can. ensem.

2-level. $Z = \sum_{\mu} e^{-\beta H(\mu)} = \sum_{\{n_i\}} e^{-\beta \varepsilon \sum_{i=1}^{N} n_i} = \prod_{i=1}^{N} \left(\sum_{\{n\}} e^{-\beta \varepsilon n_i} \right)$

$Z = (1 + e^{-\beta \varepsilon})^N$

Ideal gas. $Z = \int \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3 q_i \, d^3 p_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} \right] = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$ w/ $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

Grand canonical ensemble



Prob distrib $p(\mu_s) = \frac{e^{\beta \mu N(\mu_s) - \beta H(\mu_s)}}{Q}$

$Q(T, \mu, \vec{x}) = \sum_{\mu_s} e^{\beta \mu N(\mu_s) - \beta H(\mu_s)}$

reorganized. $Q = \sum_{N=0}^{\infty} e^{\beta \mu N} \underbrace{\sum_{(\mu_s | N)} e^{-\beta H(\mu_s)}}_{Z(T, N, \vec{x})}$

we have $\langle N \rangle = \frac{\partial}{\partial(\beta\mu)} \ln Q$ $\quad \langle N^2 \rangle_c = \frac{\partial^2}{\partial(\beta\mu)^2} \ln Q$

Approx. Max$\{N\} = N^* \approx \langle N \rangle$ sharpness of distribution

$Q(T, \mu, \vec{x}) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T, N, \vec{x}) = e^{\beta \mu N^*} Z(T, N^*, \vec{x}) = e^{\beta \mu N^* - \beta F}$

since grand potential $\boxed{\mathcal{G} = E - TS - \mu N}$

$Q = e^{-\beta \mathcal{G}}$

thus. $\mathcal{G} = -k_B T \ln Q$ w/ therm. $-S = \left.\frac{\partial \mathcal{G}}{\partial T}\right|_{\mu, \vec{x}}$ $\quad N = -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{T, \vec{x}}$ $\quad J = \left.\frac{\partial \mathcal{G}}{\partial x}\right|_{T, \mu}$

ex ideal gas

$Q = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{N!} \int \left(\prod_{i=1}^{N} \frac{d^3 q_i \, d^3 p_i}{h^3} \right) \exp\left(-\beta \sum_i \frac{p_i^2}{2m} \right) = \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{N!} \left(\frac{V}{\lambda^3} \right)^N = \exp\left(e^{\beta \mu} \frac{V}{\lambda^3} \right)$

Remark - can recover ideal gas law $PV = N k_B T$ from calculating therm prop.

Gibbs canonical ensemble

$M \equiv (T, \vec{J})$
constant force acts on sys.

Thus $\quad p(\mu_s, \vec{x}) = \dfrac{e^{-\beta H(\mu_s) + \beta \vec{J}\cdot\vec{x}}}{Z}$

$$Z(N, T, \vec{J}) = \sum_{\mu_s, \vec{x}} e^{\beta \vec{J}\cdot\vec{x} - \beta H(\mu_s)}$$

Gibbs $\quad G = E - TS - \vec{x}\cdot\vec{J} \quad \Rightarrow \quad \vec{x} = -\dfrac{\partial G}{\partial \vec{J}}$

Since $\quad \langle x \rangle = k_B T \dfrac{\partial \ln Z}{\partial \vec{J}} \quad \Rightarrow \quad \boxed{G(N, T, \vec{J}) = -k_B T \ln Z}$

Enthalpy $\quad H = E - \vec{x}\cdot\vec{J}$

$$-\frac{\partial \ln Z}{\partial \beta} = \langle \mathcal{H} - \vec{x}\cdot\vec{J} \rangle = H \quad \Rightarrow \quad C_{\vec{J}} = \frac{\partial H}{\partial T}$$

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ex Ideal gas in isobaric ensemble

$M = (N, T, P) \quad \mu = \{\vec{p}_i, \vec{q}_i\}$ and V

thus

$$P(\{\vec{p}_i, \vec{q}_i\}, V) = \frac{1}{Z} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta P V\right] \quad \text{if within box vol } V \text{ else } 0.$$

$$Z = \int_0^\infty dV\, e^{-\beta P V} \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3 p_i\, d^3 q_i}{h^3} \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)$$

$$= \int_0^\infty dV\, V^N e^{-\beta P V} \frac{1}{N!\,\lambda^{3N}} = \frac{1}{(\beta P)^{N+1} \lambda^{3N}}$$