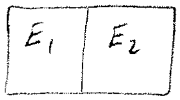
Equilibrium Conditions

① and ② independent subsystems



$$E_1 < \mathcal{H}_1 \leq E_1 + \delta E$$
$$E_2 < \mathcal{H}_2 \leq E_2 + \delta E$$
$$E < \mathcal{H}_1 + \mathcal{H}_2 \leq E + 2\delta E$$

$E = E_1 + E_2$ "fixed"

$$P(E_1) = \frac{\Omega(E, 2\delta E, E_1)}{\Omega(E, \delta E)} = \frac{\Omega_1(E_1, \delta E)\,\Omega_2(E_2, \delta E)}{\Omega(E, \delta E)}$$

$$\ln P(E_1) = \ln \Omega_1(E_1, \delta E) + \ln \Omega_2(E_2, \delta E) + \text{const.}$$

equilibrium corresponds to maximum probability : $d \ln P(E_1) = 0$

$$d \ln P(E_1) = \frac{\partial \ln \Omega_1(E_1, \delta E)}{\partial E_1} dE_1 + \frac{\partial \ln \Omega_2(E_2, \delta E)}{\partial E_2} dE_2$$

$dE_2 = -dE_1$

$\tilde{E}_1$ and $\tilde{E}_2$: most probable value

$$d \ln P(E_1) = \left[\left. \frac{\partial \ln \Omega_1(E_1, \delta E)}{\partial E_1} \right|_{E_1 = \tilde{E}_1} - \left. \frac{\partial \ln \Omega_2(E_2, \delta E)}{\partial E_2} \right|_{E_2 = \tilde{E}_2} \right] dE_1 = 0$$

$$\boxed{\beta = \frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E}}$$ in equilibrium $\Rightarrow$ $\boxed{T_1 = T_2}$

also consistent with $\frac{1}{T} = k \frac{\partial \ln \Omega}{\partial E} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \qquad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}$$

$$\boxed{dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN}$$ fundamental equation

Review (continued from last class)

Liouville Theorem: $\frac{d\rho}{dt} = 0 \Rightarrow \frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} = 0$

equilibrium: $\{\rho, \mathcal{H}\} = \sum_i \left[\frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right] = 0$

e.g. $\rho(p_i, q_i) = \text{const.}$ $\qquad$ $\rho[\mathcal{H}(p_i, q_i)] = \rho(p_i, q_i)$

constant of motion

E = fixed, isolated system
microcanonical ensemble
"equal a priori probabilities"

system in contact w/ heat-bath
"Boltzmann weights"

closed system: $\rho_{12} = \rho_1 \rho_2$

$\ln \rho_{12} = \ln \rho_1 + \ln \rho_2$

$\ln \rho$ for a subsystem can only depend on additive constant of motion (e.g. $\mathcal{H}(p_i, q_i)$)

$\boxed{\ln \rho \propto \mathcal{H}(p_i, q_i)} \to$ canonical ensem

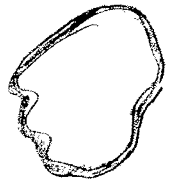
Microcanonical Ensemble

isolated system up to δE

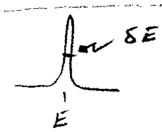
$E \leq \mathcal{H}(p_i, q_i) \leq E + \delta E$ $\qquad$ $\rho(p_i, q_i) = \begin{cases} 1/\Omega(E, \delta E) & \text{if } E < \mathcal{H} \leq E + \delta E \\ 0 & \text{otherwise} \end{cases}$

$\Omega(E, \delta E)$: number of states within infinitesimal shell in phase space

$$\boxed{\rho(p, q) = \frac{1}{\Omega(E, \delta E)} \delta(\mathcal{H}(p,q) - E)}$$

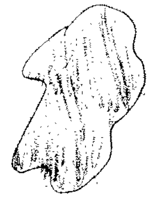


$$\int_{E < \mathcal{H}(p,q) \leq E + \delta E} \rho \frac{d^{3N}p \, d^{3N}q}{N! \, h^{3N}} = 1$$



N particles

$\Omega_<(E)$:



$$\frac{1}{N!}\frac{1}{h^{3N}}\int_{\mathcal{H}(p,q)\le E} d^{3N}p\, d^{3N}q$$

if particles are indistinguishable

$\Omega(E,\delta E)$

$$\frac{1}{N!}\frac{1}{h^{3N}}\int_{E<\mathcal{H}(p,q)\le E+\delta E} d^{3N}p\, d^{3N}q$$

$$\boxed{\Omega(E,\delta E) = \frac{d\Omega_<(E)}{dE}\,\delta E} \qquad = g_N(E)\,\delta E$$

N-particle density of states : $\boxed{g_N(E) = \dfrac{d\Omega_<(E)}{dE}}$

To be consistent with the general equilibrium conditions of thermodynamics:

$$\frac{1}{kT} = \frac{\partial \ln\Omega(E,\delta E)}{\partial E} \qquad \boxed{S(E,V,N) = k\ln\Omega(E,\delta E)}$$

$\frac{P}{kT} = \frac{\partial \ln\Omega}{\partial V}$

$\frac{\mu}{T} = \frac{\partial \ln\Omega}{\partial N}$

[show other cond.!!! + fundamental eq.]

for ideal gas: $$\Omega_<(E) = \frac{V^N}{N!\,h^{3N}}\frac{(2m\pi)^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)}E^{\frac{3N}{2}}$$

$$\Omega(E,\delta E) = \frac{V^N}{N!\,h^{3N}}\frac{(2m\pi)^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}E^{3N/2}\frac{\delta E}{E} \qquad \frac{\delta E}{E}\sim\frac{1}{\sqrt{N}}$$

$$g(E) = \frac{V^N}{N!\,h^{3N}}\frac{(2m\pi)^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}E^{3N/2-1}$$

Ideal Gas (using the microcanonical ensemble)

$$\Omega(E,\delta E,V,N) = \frac{V^N}{h^{3N} N!} \frac{(2m\pi)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} E^{\frac{3N}{2}} \left(\frac{\delta E}{E}\right)$$

$\frac{\delta E}{E} \sim \frac{1}{\sqrt{N}}$ (plausible it)

$\left|\ln\left(\frac{\delta E}{E}\right)\right| \sim \frac{1}{2}\ln(N)$

$\ll N$ needed

$$S(E,V,N) = k \ln \Omega(E,\delta E,V,N)$$

$$= N\ln V - 3N\ln h - \ln N! + \frac{3N}{2}\ln(2m\pi) - \ln\Gamma\left(\frac{3N}{2}\right) + \frac{3N}{2}\ln E + \cancel{\ln\left(\frac{\delta E}{E}\right)}$$

use $\ln(N!) \approx N\ln N - N$

$\ln\Gamma\left(\frac{3N}{2}\right) \approx \left(\frac{3N}{2}-1\right)\ln\left(\frac{3N}{2}-1\right) - \left(\frac{3N}{2}-1\right)$

$$S/k = N\ln V - N\ln N + N - \left(\frac{3N}{2}-1\right)\ln\left(\frac{3N}{2}-1\right) + \left(\frac{3N}{2}-1\right) + \frac{3N}{2}\ln E - 3N\ln h + \frac{3N}{2}\ln(2m\pi)$$

$$\approx N\ln\frac{V}{N} - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2}\ln E + \frac{5}{2}N - \frac{3N}{2}\ln h^2 + \frac{3N}{2}\ln(2m\pi)$$

$$= N\ln\frac{V}{N} - \frac{3N}{2}\ln N + \frac{3N}{2}\ln E + \frac{5}{2}N - \frac{3N}{2}\ln\frac{3}{2} - \frac{3N}{2}\ln h^2 + \frac{3N}{2}\ln(2m\pi)$$

$$= N\ln\frac{V}{N} + \frac{3}{2}N\ln\frac{E}{N} + \frac{5}{2}N + \frac{3N}{2}\ln\frac{4m\pi}{3h^2}$$

$$\boxed{S(E,V,N) = Nk\ln\left(\frac{V}{N}\right) + \frac{3}{2}Nk\ln\left(\frac{E}{N}\right) + \frac{5}{2}Nk + \frac{3}{2}Nk\ln\frac{4m\pi}{3h^2}}$$

$Nk\ln V - Nk\ln N \quad \xrightarrow{\frac{\partial}{\partial N}} : \quad k\ln V - k\ln N - k = k\ln\frac{V}{eN}$

$\frac{3}{2}\left[k\ln E - k\ln N - k\right] = \frac{3}{2}k\ln\left(\frac{E}{eN}\right)$

fundamental equation:

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \qquad \text{for } S(E,V,N)$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \qquad \frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2}Nk\frac{1}{E} \quad \Rightarrow \quad \boxed{E = \frac{3}{2}NkT}$$ internal energy

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = Nk\frac{1}{V} \quad \Rightarrow \quad \boxed{PV = NkT}$$ equation of state

thermodyn. limit: $N/V = \text{const.}$ and E, S extensive, P, T, μ intensive

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V} = k\ln\frac{V}{eN} + \frac{3}{2}k\ln\frac{E}{eN} + \frac{5}{2}k + \frac{3}{2}k\ln\frac{4m\pi}{3h^2}$$

$$= k\ln\left[\frac{V}{eN}\cdot\left(\frac{E}{eN}\right)^{3/2}\cdot e^{5/2}\cdot\left(\frac{4m\pi}{3h^2}\right)^{3/2}\right] = k\ln\left[\frac{V}{N}\left(\frac{3}{2}kT\right)^{3/2}\left(\frac{4m\pi}{3h^2}\right)^{3/2}\right]$$

$$= k\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

$$\boxed{\lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}}$$ ← thermal wavelength

$$\boxed{\mu = kT\ln\left(\frac{\lambda^3}{V/N}\right)}$$

physical meaning of λ:

$r_0^3 \equiv V/N$ typical (average) volume occupied by one particle

$$\mu = kT\ln\left[\left(\frac{\lambda}{r_0}\right)^3\right]$$

classical justification: $\boxed{r_0 \gg \lambda}$

Example: $\boxed{N \text{ quantum oscillator}}$ (with the same frequency ω)

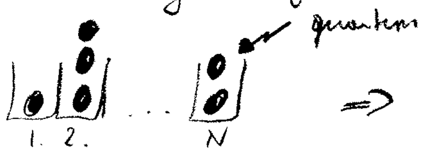
$$\varepsilon_i = \hbar\omega\left(n_i + \tfrac{1}{2}\right) \qquad n_i = 0, 1, 2, \ldots \qquad (\text{"quanta" or occupation numbers})$$

$$E = \sum_{i=1}^{N} \varepsilon_i = \sum_{i=1}^{N} \hbar\omega\left(n_i + \tfrac{1}{2}\right) = \frac{N\hbar\omega}{2} + \sum_{i=1}^{N} \hbar\omega\, n_i = E_0 + \hbar\omega \sum_{i=1}^{N} n_i$$

$$\frac{E - E_0}{\hbar\omega} = Q = \sum_{i=1}^{N} n_i \qquad \text{total number of quanta}$$

microcanonical ensemble: E = fixed (N fixed)

How many ways can we distribute Q quanta among N particles ("bins")



$\Rightarrow$ Q quanta, $N-1$ "wall" between oscillators

equivalently: $\bullet \,|\, \bullet\bullet\bullet \,|\, \ldots \,|\, \bullet\bullet$

1 2 N

$$\Omega = \binom{Q+N-1}{N-1} = \frac{(Q+N-1)!}{(N-1)!\,Q!}$$

$$S = +k\ln\Omega = +k\left\{(Q+N-1)\ln(Q+N-1) - (Q+N-1) - (N-1)\ln(N-1) + (N-1) - Q\ln Q + Q\right\}$$

$$\approx +k\left\{(Q+N)\ln(Q+N) - (Q+N) - N\ln N + N - Q\ln Q + Q\right\}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \left(\frac{\partial S}{\partial Q}\right)_N \frac{dQ}{dE} = \frac{1}{\hbar\omega}\left(\frac{\partial S}{\partial Q}\right)_N =$$

$$= +\frac{k}{\hbar\omega}\left\{\ln(Q+N) + 1 - 1 - \ln Q - 1 + 1\right\}$$

$$= \frac{k}{\hbar\omega} \ln\frac{Q+N}{Q} \qquad \Rightarrow \qquad \frac{Q+N}{Q} = e^{\frac{\hbar\omega}{kT}}$$

$$Q + N = Q e^{\frac{\hbar\omega}{kT}}$$

$$E_0 = \frac{N\hbar\omega}{2}$$

$$N = Q\left(e^{\frac{\hbar\omega}{kT}} - 1\right) \qquad Q = \frac{E - E_0}{\hbar\omega}$$

$$E - E_0 = \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1} \qquad \boxed{E = E_0 + \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}}$$

$kT \gg \hbar\omega$: $\quad E \simeq E_0 + \dfrac{N\hbar\omega}{1 + \frac{\hbar\omega}{kT} - 1} = E_0 + NkT = N\left(\frac{\hbar\omega}{2} + kT\right) \approx NkT$

classical limit: $\quad Q \gg N \gg 1 \quad$ "lots of quanta" per oscillator

for HW

$$S = k\left\{(Q+N)[\ln(Q+N) - 1] - N[\ln N - 1] - Q[\ln Q - 1]\right\}$$

$$= kQ\left\{\left(1 + \frac{N}{Q}\right)\left[\ln\left[Q\left(1 + \frac{N}{Q}\right)\right] - 1\right] - \frac{N}{Q}[\ln N - 1] - [\ln Q - 1]\right\}$$

$$= kQ\left\{\left(1 + \frac{N}{Q}\right)\left[\ln Q + \ln\left(1 + \frac{N}{Q}\right) - 1\right] - \frac{N}{Q}[\ln N - 1] - [\ln Q - 1]\right\}$$

$$= kQ\left\{\left(1 + \frac{N}{Q}\right)\left[\ln Q + \frac{N}{Q} - 1\right] - \frac{N}{Q}[\ln N - 1] - [\ln Q - 1]\right\}$$

$$= kQ\left\{\cancel{\ln Q} + \cancel{\frac{N}{Q}} \cancel{- 1} + \frac{N}{Q}\ln Q + \cancel{\left(\frac{N}{Q}\right)^2} \cancel{- \frac{N}{Q}} - \frac{N}{Q}\ln N + \frac{N}{Q} \cancel{- \ln Q} \cancel{+ 1}\right\}$$

$$= kQ\left\{\frac{N}{Q}\ln Q - \frac{N}{Q}\ln N + \frac{N}{Q}\right\} =$$

$$= Nk\left\{\ln Q - \ln N + 1\right\} = Nk\ln\frac{Q}{N} + Nk$$

$$\boxed{S(E,N) = Nk\ln\left(\frac{E - E_0}{N\hbar\omega}\right) + Nk}$$

since $Q \gg N \Rightarrow E \gg E_0$

$$S(E,N) \simeq Nk\ln\left(\frac{E}{N\hbar\omega}\right) + Nk = Nk\left[\ln\left(\frac{E}{N\hbar\omega}\right) + 1\right]$$