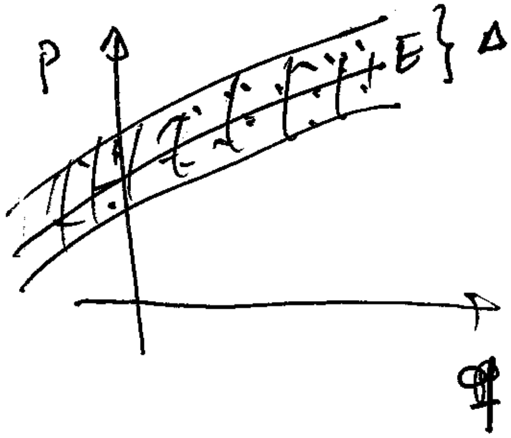
Classical statistical mechanics

Microcanonical ensemble



All states with energy in $\left(E-\frac{\Delta}{2}, E+\frac{\Delta}{2}\right)$

$\Gamma(E)$: number of states.

$(\Delta \ll E)$

We can think as a set of points in phase space

The density of points stays the same along a "stream line". (Liouville theorem).

$\rho(p,q,t)\, d^{3N}p\, d^{3N}q$: # of states in $d^{3N}p\, d^{3N}q$

$\rho(p, q, t)$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_j}\dot{p}_j$$

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho \dot{q}_i)}{\partial q_i} + \frac{\partial(\rho \dot{p}_i)}{\partial p_i} = 0$$

$$= \frac{d\rho}{dt} + \rho\frac{\partial \dot{q}_i}{\partial q_i} + \rho\frac{\partial \dot{p}_i}{\partial p_i} = \frac{d\rho}{dt} + \rho\cancel{\frac{\partial^2 H}{\partial q_i \partial p_i}} - \rho\cancel{\frac{\partial^2 H}{\partial p_i \partial q_i}}$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\frac{d\rho}{dt} = 0$$ "incompressible fluid"

if $\rho(q,p) = \rho(H(p,q))$

$$\Rightarrow \quad \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i = \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial p_i}\frac{\partial H}{\partial q_i} = 0.$$

$$\Rightarrow \frac{\partial \rho}{\partial t} = 0 \qquad \text{"equilibrium".}$$

If the distribution depends only on the energy $\Rightarrow$ is indep of time.

A given system will explore a surface of constant E as a function of time.

We replace the values of local quantities by their average over the ensemble.

$$\langle f \rangle = \frac{\int d^{3N}q\, d^{3N}p \;\; f(p,q)\, \rho(p,q)}{\int d^{3N}q \int d^{3N}p \;\; \rho(p,q)}$$

If fluctuations are small:

$$\frac{\langle f^2\rangle - \langle f\rangle^2}{\langle f\rangle^2} \ll 1$$

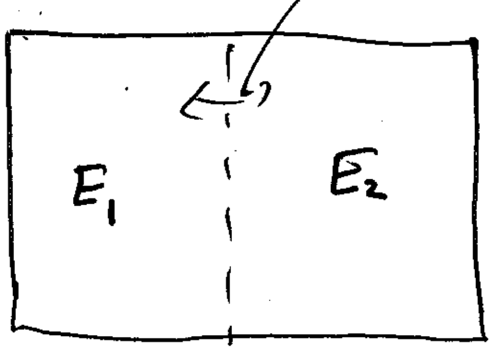
$\Rightarrow$ It does not matter how we take the average ($\rho(p,q)$)

Average over all states $\rho(p,q) = 1$.

or most likely (value of f that most states have)

etc.

energy can be interchanged (heat)



$$\Gamma_{12}(E_1+E_2) = \Gamma_1(E_1)\cdot\Gamma_2(E_2)$$

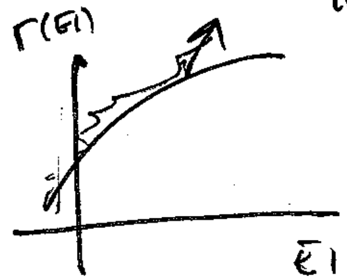
If we think $E_1+E_2 = E$ but E_1, E_2 can change then the most likely case is the one where

$\Gamma_{12}(E_1+E_2)$ is maximum. (like entropy!)

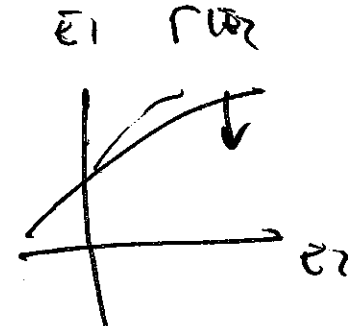
$$\Gamma_{12}(E_1) = \Gamma_1(E_1)\,\Gamma_2(E-E_1)$$

$$\frac{\partial \Gamma_{12}(E)}{\partial E_1} = \frac{\partial \Gamma_1}{\partial E_1}\Gamma_2 - \Gamma_1 \frac{\partial \Gamma_2}{\partial E_2} = 0$$

$$\frac{\partial \ln \Gamma_1}{\partial E_1} = \frac{\partial \ln \Gamma_2}{\partial E_2}$$



"wants to go up"



$$dS = \frac{1}{T}dE + \frac{P}{T}dV$$

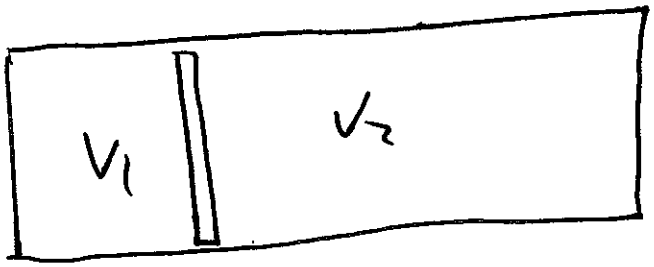
$$S = k_B \ln \Gamma(E) \quad ; \quad \frac{1}{T} = k_B \frac{\partial \ln \Gamma(E)}{\partial E}$$

$\Rightarrow T_1 = T_2$ equilibrium!

Also $\ln \Gamma_{12} = \ln \Gamma_1 + \ln \Gamma_2$

extensive!

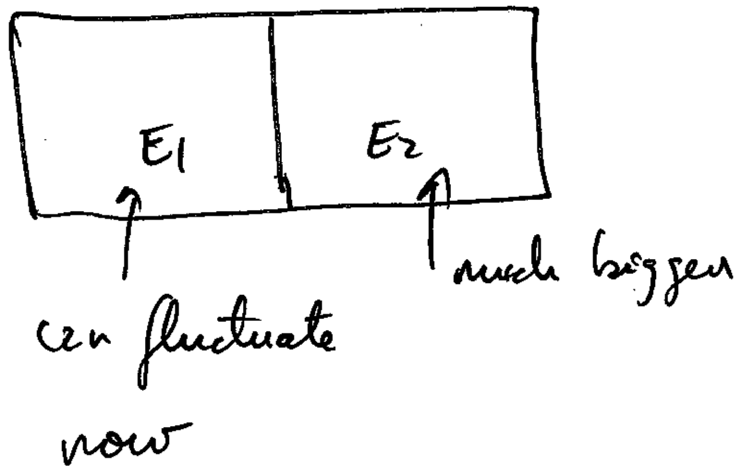
the same happens with volume

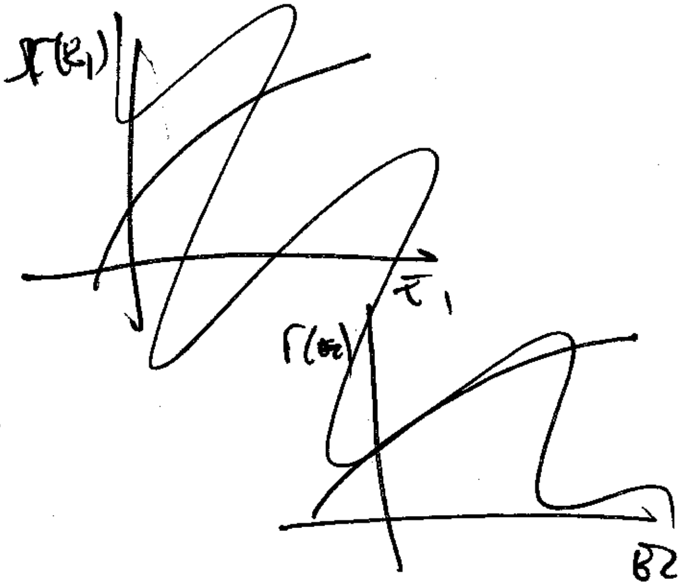


$V_1 + V_2 = V$

the piston moves until the # of states is maximum. (most likely scenario).

Canonical ensemble





f_1 some property of system 1. depends on E_1

$$\langle f_1 \rangle = \frac{\int_0^\infty dE_1\, f(E_1)\, \Gamma_{12}(E_1, E_2)}{\int \Gamma_{12}(E_1, E_2)}$$

$$= \frac{\int_0^\infty dE_1\, f(E_1)\, \Gamma_1(E_1)\, \Gamma_2(E - E_1)}{\int \Gamma_{12}(E_1, E_2)}$$

$$\Gamma_2(E - E_1) = e^{\frac{1}{k_B} S_2(E - E_1)} \simeq e^{\frac{S_2(E)}{k_B} - \frac{E_1}{k_B} \partial S_2/\partial E_1 + \ldots}$$

$$\simeq \underbrace{e^{\frac{S_2(E)}{k_B}}}_{\text{cancels.}}\; e^{-\frac{E_1}{k_B T_1}}$$

$$\langle f_1 \rangle = \frac{\int_0^\infty dE_1\, e^{-\frac{E_1}{k_B T_1}}\, \Gamma_1(E_1)\, f(E_1)}{\int_0^\infty dE_1\, e^{-E_1/k_B T_1}\, \Gamma_1(E_1)}$$

$$Z = \int \frac{d^{3N}p \, d^{3N}q}{N! \, h^{3N}} e^{-\beta H(p,q)}$$

$$\beta = \frac{1}{k_B T}$$

partition function.

what is Z?

$$Z = \int_0^\infty dE \; \Gamma(E) \, e^{-E/k_B T}$$

$$= \int_0^\infty dE \; e^{\frac{1}{k_B} S(E) - E/k_B T}$$

$$= \int_0^\infty dE \; e^{-\frac{1}{k_B T}(E - TS)}$$

$$= \int_0^\infty dE \; e^{-\beta A(E)}$$

Assuming fluctuations are small — smallest $A(E)$ contributes

$$Z \simeq c \, e^{-\beta A}.$$

$$\ln Z = \ln C - \beta A$$

$$A = -\frac{1}{\beta}\ln Z + \underbrace{\frac{1}{\beta}\ln C}_{\text{goes away in thermodynamic limit}}$$

$$\boxed{A = -k_B T \ln Z}$$

We check energy fluctuations.

$$\langle E \rangle = \frac{\int_0^\infty dE\, \Gamma(E)\, E\, e^{-\beta E}}{\int_0^\infty dE\, \Gamma(E)\, e^{-\beta E}} = -\frac{\partial}{\partial \beta}\ln \int_0^\infty dE\, \Gamma(E)\, e^{-\beta E}$$

$$= +\frac{\partial}{\partial \beta}(+\beta A) = A + \beta \frac{\partial A}{\partial \beta}$$

$$\frac{\partial A}{\partial \beta} = -\frac{1}{k_B \beta^2}\frac{\partial A}{\partial T} \qquad T = \frac{1}{\beta k_B}$$

$$\langle E \rangle = A + \beta\left(-\frac{1}{k_B \beta^2}\frac{\partial A}{\partial T}\right) = A - T\frac{\partial A}{\partial T}$$

$$dA = -SdT - pdV$$

$$E = A + TS \quad \checkmark$$

Fluctuations

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

$$\langle E^2\rangle = \frac{\int_0^\infty dE\, \Gamma(E)\, E^2 e^{-\beta E}}{\int_0^\infty dE\, \Gamma(E)\, e^{-\beta E}} = \frac{\frac{\partial^2}{\partial\beta^2}\int_0^\infty dE\,\Gamma(E) e^{-\beta E}}{\int_0^\infty dE\,\Gamma(E) e^{-\beta E}}$$

$$= \frac{\frac{\partial^2}{\partial\beta^2} e^{-\beta A}}{e^{-\beta A}} = \frac{1}{e^{-\beta A}} \frac{\partial}{\partial\beta}\left\{ e^{-\beta A} \underbrace{\left(-A - \beta\frac{\partial A}{\partial\beta}\right)}_{-E} \right\}$$

$$= \frac{-1}{e^{-\beta A}} \frac{\partial}{\partial\beta}\left(E e^{-\beta A}\right) = -\frac{1}{\cancel{e^{-\beta A}}} \frac{\partial E}{\partial\beta} \cancel{e^{-\beta A}} -$$

$$- E \underbrace{\frac{\partial/\partial\beta\,(e^{-\beta A})}{e^{-\beta A}}}_{-E} = E^2 + \frac{\partial E}{\partial\beta}$$

$$\langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial E}{\partial \beta} = \frac{1}{K_B\beta^2}\frac{\partial E}{\partial T} = K_B T^2 \frac{\partial E}{\partial T}$$ 11

$$\frac{\cancel{K_B}}{K_B^{\cancel{2}} T^2}$$

$$\boxed{\langle (E - \langle E\rangle)^2\rangle = K_B T^2 C_v}$$

$$\sqrt{\langle (E-\langle E\rangle)^2\rangle} = \delta E = \sqrt{K_B T^2 C_v}$$

$$\frac{\delta E}{E} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \sim 10^{-11}$$

$$N \sim 10^{23}$$

(12)

Going back to how we showed $Z = e^{-\beta A}$

$$Z = \int_0^\infty dE \; e^{-\beta A(E)}$$

$A(E)$ minimum for $\bar{E}$. (β fixed)

$A(\bar{E})$

$$A(E) = A(\bar{E}) + \underbrace{\frac{\partial A}{\partial E}}_{0} (E - \bar{E}) + \frac{1}{2} \frac{\partial^2 A}{\partial E^2} (E - \bar{E})^2 + \cdots$$

$$A = E - TS$$

$$\frac{\partial A}{\partial E} = 1 - T \underbrace{\frac{\partial S}{\partial E}}_{1/T} = 0 \quad \checkmark$$

$$\frac{\partial^2 A}{\partial E^2} = -T \frac{\partial^2 S}{\partial E^2} = -T \frac{\partial (1/T)}{\partial E} =$$

$$= T \frac{1}{T^2} \frac{\partial T}{\partial E} = \frac{1}{C_V T}$$

$$Z = \int_0^\infty dE \; e^{-\beta A(\bar{E}) - \frac{1}{2 C_v k_B T^2}(E-\bar{E})^2} \qquad (13)$$

$\uparrow$ gaussian.

$$= e^{-\beta A(E)} \sqrt{2\pi C_v k_B T^2}$$

$$\ln Z = \underset{\substack{\uparrow \\ N}}{-\beta A} + \underbrace{\frac{1}{2} \ln (\pi C_v k_B T^2)}_{\ln N}$$

ignore as $N \to \infty$

Each state has probability $P_n = \frac{e^{-\beta E_n}}{Z}$

$$\langle f \rangle = \sum_{\substack{n \\ \uparrow \\ \text{states}}} \frac{f_n e^{-\beta E_n}}{Z}$$

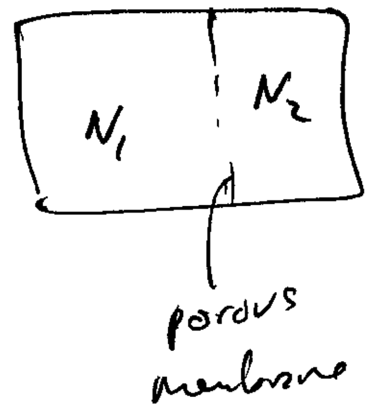
$$S \overset{?}{=} -k_B \sum_n P_n \ln P_n = -k_B \langle \ln P_n \rangle$$

$$= -k_B \sum_n \frac{e^{-\beta E_n}}{Z}(-\beta E_n - \ln Z) = \beta k_B \langle E \rangle + \overbrace{k_B \ln Z}^{-A/T} = \frac{E-A}{T} = S \checkmark$$

$$\boxed{S = -k_B \sum_n P_n \ln P_n}$$

Grand canonical ensemble.

Allows N to fluctuate



$$\Xi = \sum_{N=0}^{\infty} e^{+\beta\mu N} Z_N(V,T)$$

$Z_N(V,T)$: canonical partition function.

μ: chemical potential

$$\Xi = \int_0^{\infty} dN \; e^{\beta\mu N - \beta A}$$

$$= \int_0^{\infty} dN \; e^{-\beta(A-\mu N)}$$

$$\ln \Xi = -\beta A + \beta\mu N$$

$$= -\beta(E-TS) + \beta\mu N$$

$$= \frac{1}{k_B} S - \frac{1}{k_B T} E + \frac{\mu}{k_B T} N$$

Gibbs – Duhem relation.

Suppose we have a function such that

$$f(\lambda x_1, \ldots \lambda x_n) = \lambda^n f(x_1, \ldots x_n)$$

$\partial/\partial\lambda$

$$\sum_j x_j \frac{\partial f}{\partial x_j}(\lambda x_1 \ldots \lambda x_n) = n\lambda^{n-1} f(x_1 \ldots x_n)$$

take $\lambda = 1 \Rightarrow$

$$\sum_j x_j \frac{\partial f}{\partial x_j}(x_1, \ldots x_n) = n f(x_1 \ldots x_n)$$

Consider $E(S, V, N)$ $\quad (dE = TdS - pdV + \mu dN)$

extensive $\Rightarrow$ $E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$

$$\Rightarrow \quad E(S,V,N) = S\frac{\partial E}{\partial S} + V\frac{\partial E}{\partial V} + N\frac{\partial E}{\partial N}$$

$$= TS - pV + \mu N$$

for extensive systems.

$\Rightarrow k_B T \ln \Xi = TS - E + \mu N = pV$

$$\boxed{\frac{pV}{T} = k_B \ln \Xi}$$

Now states can have any E, N

$$P_n = \frac{e^{-\beta E_n + \beta\mu N_n}}{\mathcal{Z}}$$

$$\langle f \rangle = \sum_n \frac{f_n\, e^{-\beta E_n + \beta\mu N_n}}{\mathcal{Z}}$$

$$-k_B \sum_n P_n \ln P_n = -k_B \sum_n \frac{e^{-\beta E_n + \beta\mu N_n}}{\mathcal{Z}} \left(-\beta E_n + \beta\mu N_n - \ln \mathcal{Z}\right)$$

$$= \beta k_B E - \beta\mu k_B N + k_B \ln \mathcal{Z}$$

$$= \frac{E}{T} - \frac{\mu}{T} N + \frac{pV}{T} = \frac{1}{T}(E + pV - \mu N) = \frac{TS}{T}$$

$$= S \checkmark$$

also works.

Given a probability distribution p_n and

defining $S = -k_B \sum_n p_n \ln p_n$

which prob. distribution maximizes S?

$$\mathcal{F} = -k_B \sum_n p_n \ln p_n + \lambda\Big(\sum_n p_n - 1\Big)$$

$\uparrow$ Lagrange multiplier $\sum_n p_n =$

$$\frac{\partial \mathcal{F}}{\partial p_n} = -k_B (\ln p_n + 1) + \lambda = 0$$

$$\ln p_n = \frac{\lambda}{k_B} - 1$$

all equal!

$$\sum p_n = 1 \Rightarrow \quad P_n = \frac{1}{\#\text{ of states}}$$

Work well for microcanonical. where S is maximized.

Ideal gas

$$Z = \int \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!} e^{-\beta \sum_j \frac{p_j^2}{2m}}$$

$$= \frac{V^N}{h^{3N} N!} \left(\sqrt{\frac{\pi 2m}{\beta}} \right)^{3N}$$

$$= \frac{1}{N!} \left(\frac{V}{h^3} \left(\frac{2m\pi}{\beta} \right)^{3/2} \right)^N$$

$$\ln Z = -N\ln N + N + N \ln\left(\frac{V}{h^3}\right) + \frac{3}{2} N \ln\left(\frac{2m\pi}{\beta}\right)$$

$$= N \ln\left(\frac{V}{Nh^3}\right) + N + \frac{3}{2} N \ln\left(\frac{2m\pi}{\beta}\right)$$

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \ln Z = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2} N k_B T \quad ; \quad \boxed{C_v = \frac{3}{2} N k_B}$$

$$\beta = \frac{3}{2}\frac{N}{E}$$

$$-\beta A = N\ln\left(\frac{V}{Nh^3}\right) + N + \frac{3}{2}N\ln\left(\frac{2m\pi}{\beta}\right)$$

$$-\beta E + \beta T S = N\ln\left(\frac{V}{Nh^3}\right) + N + \frac{3}{2}N\ln\left(\frac{2m\pi}{\beta}\right)$$

$$\frac{1}{k_B}S = \frac{3}{2}N + N\ln\left(\frac{V}{Nh^3}\right) + N + \frac{3}{2}N\ln\left(\frac{2m\pi}{\beta}\right)$$

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$ for fixed E.

$$\cancel{\frac{\partial S}{\partial V}} \quad \frac{1}{k_B}S = \frac{5}{2}N + N\ln\left(\frac{V}{Nh^3}\right) + \frac{3}{2}N\ln\left(\frac{4m\pi E}{3N}\right)$$

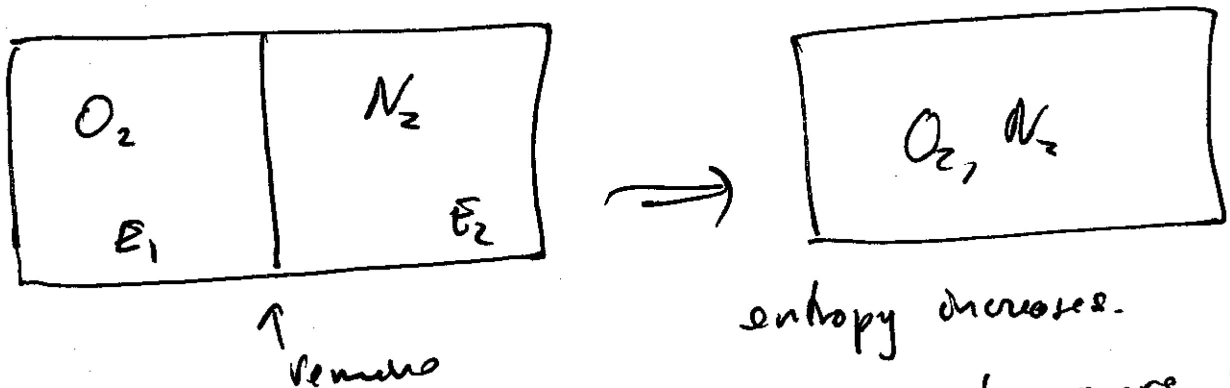
$$\left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{k_B N}{V} = \frac{P}{T} \Rightarrow \boxed{pV = Nk_BT} \checkmark$$

or $$dA = -SdT - pdV + \mu dN$$

$$A = -Nk_BT\ln\left(\frac{V}{Nh^3}\right) - Nk_BT - \frac{3}{2}Nk_BT\ln\left(\frac{2m\pi}{\beta}\right)$$

$$p = -\left.\frac{\partial A}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V} \checkmark$$

Gibbs paradox

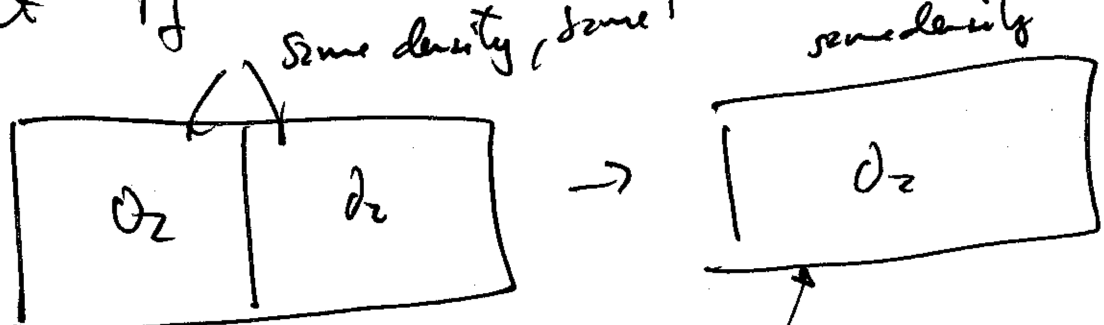


entropy increases.

each gas has more volume
and it is irreversible. } ✓

Entropy of mixing

But if



entropy cannot increase, otherwise depends on how we got

Indeed

$$\frac{1}{k_B} S_1 = \frac{5}{2} N_1 + N_1 \ln\left(\frac{V_1}{N_1 h^3}\right) + \frac{3}{2} N_1 \ln\left(\frac{2\pi m}{\beta}\right)$$

$$\frac{1}{k_B} S_2 = \frac{5}{2} N_2 + N_2 \ln\left(\frac{V_2}{N_2 h^3}\right) + \frac{3}{2} N_2 \ln\left(\frac{2\pi m}{\beta}\right)$$

$$\frac{1}{k_B} S = \frac{1}{k_B}(S_1 + S_2) = \frac{5}{2} N + \underbrace{N \ln\left(\frac{V}{N h^3}\right)}_{\text{same density}} + \frac{3}{2} N \ln\left(\frac{2\pi m}{\beta}\right)$$

But without $N!$

$$\frac{1}{K_B} S_1 = \frac{3}{2} N_1 + N_1 \ln\left(\frac{V_1}{h^3}\right) + \frac{3}{2} N_1 \ln\left(\frac{2m\pi}{\beta}\right)$$

$$\frac{1}{K_B} S_2 = \frac{3}{2} N_2 + N_2 \ln\left(\frac{V_2}{h^3}\right) + \frac{3}{2} N_2 \ln\left(\frac{2m\pi}{\beta}\right)$$

$$\frac{S}{K_B} = \frac{3}{2} N + N_1 \ln\left(\frac{V_1}{N_1 h^3}\right) + N_1 \ln N_1 + \frac{3}{2} N \ln\left(\frac{2m\pi}{\beta}\right)$$

$$+ N_2 \ln\left(\frac{V_2}{N_2 h^3}\right) + N_2 \ln N_2 +$$

$$= \frac{3}{2} N + N \ln\left(\frac{V}{N h^3}\right) + \frac{3}{2} N \ln\left(\frac{2m\pi}{\beta}\right) +$$

$$+ N_1 \ln N_1 + N_2 \ln N_2$$

~~instead~~ not extensive

Identical particles.

$$\cancel{\boxed{N_1 \mid N_2} \quad \binom{N_1+N_2}{N_1} = \frac{(N_1+N_2)!}{N_1!\, N_2!}}$$

Equipartition theorem.

$$x_j = p_j, q_j \qquad \mathcal{H}(x_j)$$

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{Z} \int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}} \; x_i \frac{\partial H}{\partial x_j} \; e^{-\beta H(x_k)}$$

$$= \frac{1}{Z} \frac{1}{N!\, h^{3N}} \int d^{6N}x_j \; \frac{x_i}{(-\beta)} \; \frac{\partial e^{-\beta H}}{\partial x_j}$$

by parts

$$= \frac{1}{Z} \frac{1}{N!\, h^{3N}} \int \frac{d^{6N}x_j}{\beta} \; \underbrace{\frac{\partial x_i}{\partial x_j}}_{\delta_{ij}} \; e^{-\beta H}$$

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} \; k_B T$$

$$\sum_i \left\langle q_i \underbrace{\frac{\partial H}{\partial q_i}}_{-\dot{p}_i} \right\rangle = 3N k_B T$$

$$\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = -3N k_B T \qquad \text{virial theorem}$$

$$H = \sum_i \left(A_i p_i^2 + B_i q_i^2\right)$$ quadratic.

A_i, B_i can vanish.

homogeneous. 2

$$\sum_i P_i \frac{\partial H}{\partial P_i} + Q_i \frac{\partial H}{\partial Q_i} = 2H$$

$$\left\langle P_i \frac{\partial H}{\partial P_i} \right\rangle = K_B T$$

no sum

$$\left\langle Q_i \frac{\partial H}{\partial q_i} \right\rangle = K_B T.$$

f constants non-vanishing

$$2\langle H\rangle = f K_B T$$

$$\boxed{\langle H\rangle = \frac{1}{2} f K_B T}$$ ← equipartition

$\frac{1}{2} K_B T$ for each quadratic term in H.

$$\boxed{C_V = \frac{1}{2} K_B f.}$$

But also, for each non-vanishing A, or B

$$\frac{1}{Z}\int dq \; Bq^2 \; e^{-\beta B q^2} = -\frac{\partial}{\partial\beta} \ln \int dq \; e^{-\beta B q^2}$$

$$= -\frac{\partial}{\partial\beta} \ln \sqrt{\frac{\pi}{\beta B}} = \frac{1}{2}\frac{\partial}{\partial\beta}\ln\beta = \frac{K_B T}{2}$$ ← ✓ agrees