

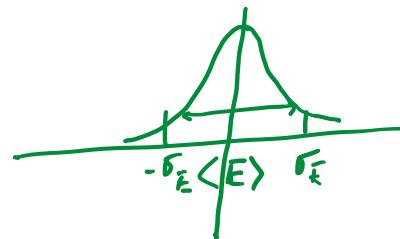
$\frac{\sigma_E}{\langle E \rangle} \sim$ How does it depend on
 the no. of particles ($\sim \frac{1}{\sqrt{N}}$)
 ↓
 Relative fluctuation

$$\frac{\sigma_E}{\langle E \rangle} \sim \frac{(k_B T^2 C_V)^{\frac{1}{2}}}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

$C_V \rightarrow$ Heat capacity at constant vol/m
 (Response function)
 (N, V, T)

$$\Delta = \sum_{j, V} e^{-\beta(E_j + \mu V)}$$

A partition f^n
 in (N, μ, T) ensemble



(signature of equilibrium fluctuation)

$C_p \rightarrow$ Heat capacity at constant pressure
 (N, p, T)

$$k_B T^2 C_V = \sigma_E^2$$

$$\Delta(N, \beta, T) = \sum_{j,v} e^{-\beta(E_j + \beta v)} \quad \langle H \rangle = \frac{\sum_{j,v} (E_j + \beta v) e^{-\beta(E_j + \beta v)}}{\sum_{j,v} e^{-\beta(E_j + \beta v)}} \leftarrow \text{Average enthalpy} \quad \langle H \rangle = \langle E_j + \beta v \rangle$$

$$\frac{\partial \langle H \rangle}{\partial \beta} = \frac{\sum_{j,v} -(E_j + \beta v) e^{-\beta(E_j + \beta v)} \left(\sum_{j,v} e^{-\beta(E_j + \beta v)} \right) - \sum_{j,v} (E_j + \beta v) e^{-\beta(E_j + \beta v)} \sum_{j,v} (E_j + \beta v) e^{-\beta(E_j + \beta v)} \frac{d}{dx} \left(\frac{f(x)}{g(x)} \right)}{\left(\sum_{j,v} e^{-\beta(E_j + \beta v)} \right)^2} = \frac{f'(x)g(x) - g'(x)f(x)}{g(x)^2}$$

$$= \frac{-\sum_{j,v} (E_j + \beta v)^2 e^{-\beta(E_j + \beta v)}}{\sum_{j,v} e^{-\beta(E_j + \beta v)}} \quad + \left(\frac{\left(\sum_{j,v} (E_j + \beta v) e^{-\beta(E_j + \beta v)} \right)^2}{\left(\sum_{j,v} e^{-\beta(E_j + \beta v)} \right)^2} \right)$$

\downarrow

$$= -\langle H^2 \rangle$$

$$\begin{aligned} \frac{\partial \langle H \rangle}{\partial \beta} &= \langle H \rangle^2 - \langle H^2 \rangle \\ \beta &= \frac{1}{k_B T} \\ \frac{\partial}{\partial \beta} &= -k_B T^2 \frac{\partial}{\partial T} \\ k_B T^2 \frac{\partial \langle H \rangle}{\partial T} &= \langle H^2 \rangle - \langle H \rangle^2 \\ C_p &= \sigma_H^2 \end{aligned}$$

$$k_B T^2 C_p = \sigma_H^2$$

Average Vol^m

$$\langle V \rangle = \frac{\sum_j V e^{-\beta(E_j + PV)}}{\sum_j e^{-\beta(E_j + PV)}}$$

$$\frac{\partial \langle V \rangle}{\partial P} = \frac{\sum_j V (-PV) e^{-\beta(E_j + PV)} \sum_j e^{-\beta(E_j + PV)} - \sum_j e^{-\beta(E_j + PV)} (-PV) \sum_j V e^{-\beta(E_j + PV)}}{\left(\sum_j e^{-\beta(E_j + PV)} \right)^2}$$

$$= (-\beta) \left[\frac{\sum_j V^2 e^{-\beta(E_j + PV)}}{\sum_j e^{-\beta(E_j + PV)}} - \frac{\left(\sum_j e^{-\beta(E_j + PV)} V \right)^2}{\left(\sum_j e^{-\beta(E_j + PV)} \right)^2} \right] = -\beta [\langle V^2 \rangle - \langle V \rangle^2]$$

Isothermal Compressibility

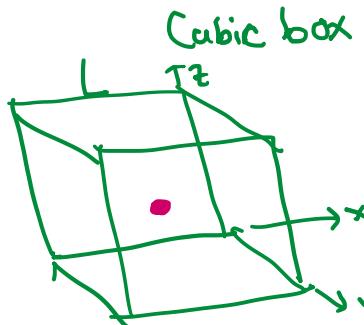
$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \Rightarrow \boxed{\kappa = \frac{\langle V^2 \rangle - \langle V \rangle^2}{V k_B T}}$$

Canonical Ensemble

1 single particle \rightarrow structureless (point particle)
 N such particles (Non-interacting) \rightarrow vol^m V, temperature T
single particle
 $q_{\text{trans}} = ?$

Only translational motion

How to calculate
 q_{trans} ?



$$q_{\text{trans}} = \sum_{n_x, n_y, n_z} e^{-\beta \frac{(n_x^2 + n_y^2 + n_z^2) h^2}{8 m L^2}}$$

$$= \sum_{n_x} e^{-\beta \frac{n_x^2 h^2}{8 m L^2}} \cdot \dots \quad \dots \quad \dots$$

(particle in 3D box)

(N, V, T)

$$Q(N, V, T) = \sum_j e^{-\beta E_j^a} \times \sum_j e^{-\beta E_j^b} \dots$$

← particle index

If the particles are
 distinguishable

$$Q(N, V, T) = q_{\text{trans}}^a q_{\text{trans}}^b \dots$$

$$Q(N, V, T) = (q_{\text{trans}})^N$$

$m \Rightarrow$ mass of the particle

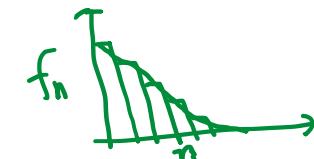
$$e^{abc} = e^a e^b e^c$$

$$q_{\text{trans}} = \sum_{n_x} e^{-\frac{\beta n_x^2 h^2}{8mL^2}} \sum_{n_y} e^{-\frac{\beta n_y^2 h^2}{8mL^2}} \sum_{n_z} e^{-\frac{\beta n_z^2 h^2}{8mL^2}}$$

$$= \left(\sum_n e^{-\frac{n^2 h^2 \beta}{8mL^2}} \right)^3$$

$$\approx \left\{ \int_0^\infty dn e^{-\frac{n^2 h^2 \beta}{8mL^2}} \right\}^3$$

$$= \left\{ \int_0^\infty dn e^{-\frac{n^2 h^2}{8mL^2 k_B T}} \right\}^3$$

$$q_{\text{trans}} = \left\{ \frac{1}{2} \left(\frac{\pi 8mL^2 k_B T}{h^2} \right)^{1/2} \right\}^3$$


Recall

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = (\pi/\alpha)^{1/2}$$

$$8^{1/2} = (2 \cdot 2 \cdot 2)^{1/2} = 2^{3/2}$$

$$q_{\text{trans}} = \frac{1}{8} 8^{3/2} \left(\frac{3}{2}\right) \left(\frac{\pi m k_B T}{h^2}\right)^{3/2}$$

$$q_{\text{trans}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

Then C_V (per particle)

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

Equipartition theorem

$$\langle E \rangle = k_B T^2 \frac{\partial \ln q_{\text{trans}}}{\partial T} \quad \text{independent of } T$$

$$= k_B T^2 \frac{\partial}{\partial T} \left[\ln \left(\frac{1}{2} \left(\frac{\pi 8mL^2 k_B T}{h^2} \right)^{1/2} \right)^3 + \dots \right]$$

$$\boxed{\langle E \rangle = k_B T^2 \frac{3}{2} \frac{1}{T} = \frac{3}{2} k_B T}$$

$$Q(N, V, T) = q_{\text{trans}}^N$$

$$Q = V^N \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}}$$

$$\langle E \rangle = \frac{3}{2} N k_B T$$

$$C_V = \frac{\partial}{\partial T} \langle E \rangle = \frac{3}{2} N k_B$$

$$\text{if } N = N_A \quad C_V = \frac{3}{2} R$$

Entropy:

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

$$= k_B \ln(q_{\text{trans}}^N) + k_B T \frac{\partial}{\partial T} \ln(q_{\text{trans}}^N)$$

$$= N k_B \ln q_{\text{trans}} + N k_B T \frac{\partial}{\partial T} (\ln q_{\text{trans}})$$

$$= N k_B \ln q_{\text{trans}} + N k_B T \frac{3}{2} \frac{1}{T} = N k_B \ln q_{\text{trans}} + \frac{3}{2} N k_B$$

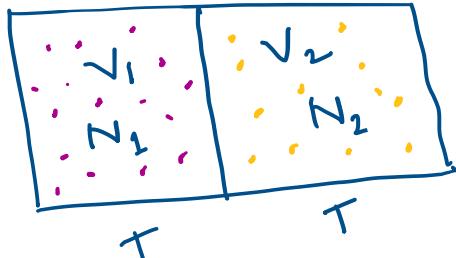
$$S = N k_B \ln \left[\left(\frac{2\pi m k_B T e}{h^2} \right)^{3/2} V \right] = N k_B \ln V$$

$$+ N k_B \ln \left[\left(\frac{2\pi m k_B T e}{h^2} \right)^{3/2} \right]$$

$\overbrace{\qquad\qquad\qquad}^{N k_B \ln(e^{3/2})}$

$\sigma \text{ (say)}$

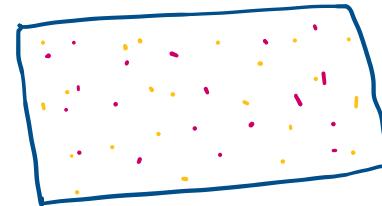
$$S = N k_B \ln V + N k_B \sigma$$



Distinct gas molecules
(atoms)

→ "Remove the partition"

$$\Delta S_{\text{mix}} > 0 \quad (\text{Should be positive})$$



"Mixing"

When the partition is on:

$$S_i = S_1 + S_2 = N_1 k_B \ln V_1 + \sigma_1 N_1 k_B + N_2 k_B \ln V_2 + \sigma_2 N_2 k_B$$

↓
Entropy of
the initial
state

$$S_f = N_1 k_B \ln(V_1 + V_2) + N_2 k_B \ln(V_1 + V_2) + (N_1 \sigma_1 + N_2 \sigma_2) k_B$$

(after
removing
the partition)

$$\begin{aligned}\Delta S_{\text{mix}} &= S_f - S_i \\ &= N_1 k_B \ln(v_1 + v_2) + N_2 k_B \ln(v_1 + v_2) - N_1 k_B \ln v_1 - N_2 k_B \ln v_2 \\ &= N_1 k_B \ln\left(\frac{v}{v_1}\right) + N_2 k_B \ln\left(\frac{v}{v_2}\right) > 0\end{aligned}$$

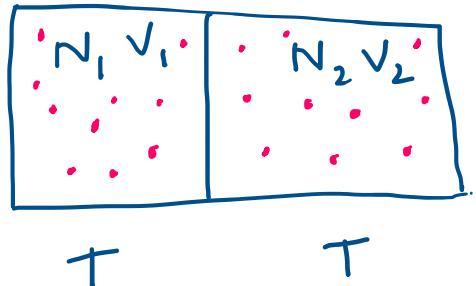
$v_1 + v_2 = V$
 $N_1 + N_2 = N$

$$\Delta S_{\text{mix}} = -Nk_B \left[\frac{N_1}{N} \ln\left(\frac{v_1}{V}\right) + \frac{N_2}{N} \ln\left(\frac{v_2}{V}\right) \right]$$

One can generalize the above expression

$$\Delta S_{\text{mix}} = -Nk_B \sum_d \left(\frac{N_d}{N} \right) \ln\left(\frac{v_d}{V}\right)$$

monatomic identical (indistinguishable)
ideal gas



$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}$$

$$\left. \begin{array}{l} N = N_1 + N_2 \\ V = V_1 + V_2 \end{array} \right\}$$

Now we remove the partition
What do you expect in terms of
entropy (change)?

$$\Delta S = 0 \text{ } ^{\circ} \text{(should be)}$$

mix
But if we use the formula (we used few
minutes back)

$$\Delta S > 0$$

"Gibbs Paradox"

$$Q(N, V, T) = \frac{q_{\text{trans}}^N}{N!} \xleftarrow{\text{Divide by } N!}$$

Non-interacting
indistinguishable
(identical)
particles

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

$$\begin{aligned} S &= k_B \ln \left(\frac{q_{\text{trans}}^N}{N!} \right) + k_B T \frac{\partial}{\partial T} \ln \left(\frac{q_{\text{trans}}^N}{N!} \right) \\ &= N k_B \ln q_{\text{trans}} - k_B \ln N! + \frac{3}{2} N k_B \end{aligned}$$

$$S = N k_B \ln q_{\text{trans}} - N k_B \ln N + N k_B + \frac{3}{2} N k_B$$

$$S = N k_B \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{V}{N} \right) \right] + \frac{5}{2} N k_B$$

$$S = N k_B \ln\left(\frac{V_e}{N}\right) + N k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]$$

σ

$$S = N k_B \ln\left(\frac{V_e}{N}\right) + N k_B \sigma$$

$$V = V_1 + V_2$$

$$N = N_1 + N_2$$

$$S_i = N_1 k_B \ln\left(\frac{V_1 e}{N_1}\right) + N_1 k_B \sigma + N_2 k_B \ln\left(\frac{V_2 e}{N_2}\right) + N_2 k_B \sigma$$

$$S_f = N_1 k_B \ln\left(\frac{V_e}{N_1}\right) + N_1 k_B \sigma + N_2 k_B \ln\left(\frac{V_e}{N_2}\right) + N_2 k_B \sigma$$

(if distinct
gas particles) (particle type 1 has available volume V_1 , $V_1 + V_2 = V$)

$$\begin{aligned} \Delta S_{mix} &= S_f - S_i = N_1 k_B \ln\left(\frac{V_e}{N_1} \cdot \frac{N_1}{V_1}\right) + N_2 k_B \ln\left(\frac{V_e}{N_2} \cdot \frac{N_2}{V_2}\right) \\ &= -N k_B \left[\frac{N_1}{N} \ln\left(\frac{V_1}{V}\right) + \frac{N_2}{N} \ln\left(\frac{V_2}{V}\right) \right] > 0 \end{aligned}$$

But particles are identical !!

$$S_f = (N_1 + N_2) k_B \ln \left(\underbrace{\frac{e(N_1 + N_2)}{(N_1 + N_2)}}_N \right) + N_1 k_B \sigma_1 + N_2 k_B \sigma_2$$

$$\sigma_1 = \sigma_2$$



$$S_i = N_1 k_B \ln \left(\frac{V_1 e}{N_1} \right) + N_1 k_B \sigma_1 + N_2 k_B \ln \left(\frac{V_2 e}{N_2} \right) + N_2 k_B \sigma_2$$

$$\Delta S_{mix}$$

$$\hookrightarrow = N_1 k_B \ln \left(\frac{eV}{N} \cdot \frac{N_1}{eV_1} \right) + N_2 k_B \ln \left(\frac{eV}{N} \cdot \frac{N_2}{eV_2} \right)$$

Now

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V} \quad (\text{density is uniform})$$

$$\Delta S_{mix} = N_1 k_B \ln \left(\underbrace{\left(\frac{V}{N} \cdot \frac{N_1}{V_1} \right)}_1 \right) + N_2 k_B \ln \left(\underbrace{\left(\frac{V}{N} \cdot \frac{N_2}{V_2} \right)}_1 \right) = 0$$

(What we expect)