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Last time:

Ideal Classical gas $\left(\begin{array}{l}\text{high } T \\ \text{low } n\end{array}\right)$

Quantum approach for energy levels:

$$S_q = Nk \ln V + \frac{3 Nk}{2} \ln \bar{E} + \frac{3}{2} Nk \left[1 + \ln \frac{4 \pi m}{3 V h^2} \right]$$

and with classical approach:

$$S_{class} = Nk \ln V + \frac{3Nk}{2} \ln \bar{E} + constant$$

In both approaches:

calculated classically assuming distinguishable particles

$$\Omega \propto (2 m \bar{E})^{\frac{3N}{2}} V^N = (2 m \bar{E} V^{2/3})^{3N/2}$$

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From S we can obtain :

$$\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{N,V} = \frac{3Nk}{2E} \implies E = \frac{3}{2}NkT$$

$$\therefore C_V = \frac{\partial E}{\partial T}\Big|_{V,N} = \frac{3}{2}Nk$$

$$\ln E = (S - kN\ln V - c)\frac{2}{3Nk}$$

$$E = c' \, e^{\frac{2S}{3Nk}} \, V^{-2/3}$$

$$P = -\frac{\partial E}{\partial V}\Big|_{N,S} = \frac{2}{3}\frac{E}{V} = \frac{2}{3}\cdot\frac{3}{2}\frac{kTN}{V} \implies PV = NkT$$

$$C_P = \frac{\partial H}{\partial T}\Big|_{P,N} = \frac{\partial}{\partial T}(E + PV)\Big|_{P,N} = \frac{\partial}{\partial T}\left(\frac{3}{2}NkT + NkT\right) = \frac{5}{2}Nk$$

$$\frac{C_p}{C_v} = \frac{5}{3} = \gamma$$

Isothermic process (reversible)

if $T = $ constant $\Rightarrow \mathcal{E} = $ constant

$N = $ constant

Then $P = \frac{nkT}{V} \propto \frac{1}{V}$ Boyle's law.

then

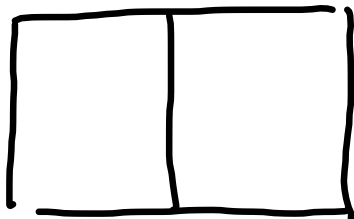$$\Delta S = S_f - S_i = Nk \ln \frac{V_f}{V_i}$$

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Gibbs paradox:

We found that

$$S(N,V,\bar{E}) = Nk \ln\left[\frac{V}{h^3}\left(\frac{4\pi m \bar{E}}{3N}\right)^{3/2}\right] + \frac{3Nk}{2} \quad \textcircled{1}$$

If $N \to \alpha N$, $V \to \alpha V$ and $\bar{E} \to \alpha N$

$S \not\to \alpha S!$ S is not extensive!

$$S_T \neq \sum_i S_i \qquad \text{Gibbs paradox.}$$

Mixing 2 gases:

N_1, V_1, T N_2, V_2, T

Consider mixing 2 ideal gases at the same T.

Before the mix:

$$S_i = N_i k \ln V_i + \frac{3}{2} N_i k \left\{ 1 + \ln \frac{2\pi m_i k T}{h^2} \right\}$$

After: $i = 1, 2$ $V = V_1 + V_2$

$$\text{(\textcircled{*})} \quad S_f = \sum_{i=1}^{2} \left[N_i k \ln V + \frac{3}{2} N_i k \left\{ 1 + \ln \frac{2\pi m_i k T}{h^2} \right\} \right]$$

$$\Delta S = S_T - \sum_{i=1}^{2} S_i = k \left[N_1 \ln \frac{V_1+V_2}{V_1} + N_2 \ln \frac{V_1+V_2}{V_2} \right]$$

$$\Delta S > 0 \qquad \text{irreversible process.}$$

If $\quad \dfrac{N_1}{V_1} = \dfrac{N_2}{V_2} \quad$ then

$$\frac{V_1+V_2}{V_1} = \frac{V_1 \frac{N_1}{V_1} + V_2 \frac{N_2}{V_2}}{V_1 \frac{N_1}{V_1}} = \frac{N_1+N_2}{N_1}$$

$$\frac{V_1+V_2}{V_2} = \frac{N_1+N_2}{N_2}$$

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Then we obtain ΔS^* (change of S for equal n gas)

$$\Delta S^* = k \left[N_1 \ln \left(\frac{N_1 + N_2}{N_1} \right) + N_2 \ln \left(\frac{V_1 + V_2}{N_2} \right) \right] > 0$$

If the 2 gases are the same $m_1 = m_2$

and

$$S_T = N k \ln V + \frac{3}{2} N k \left\{ 1 + \ln \left(\frac{2\pi m k T}{h^2} \right) \right\}$$

$N = N_1 + N_2$ and $V = V_1 + V_2$

If $\dfrac{N_1}{V_1} = \dfrac{N_2}{V_2}$

$\Delta S^* > 0$! This is wrong.'

Notice that now

$$\Delta S^* = k \left[N_1 \ln (N_1 + N_2) - N_1 \ln N_1 + N_2 \ln (N_1 + N_2) - N_2 \ln N_2 \right] =$$

$$= k \left[(N_1 + N_2) \ln (N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2 \right]$$

$$= k \left[(N_1 + N_2) \ln (N_1 + N_2) - (N_1 + N_2) - (N_1 \ln N_1 - N_1) \right.$$

$$\left. - (N_2 \ln N_2 - N_2) \right] \approx k \left\{ \ln (N_1 + N_2)! - \ln N_1! - \ln N_2! \right\}$$

$$\neq 0$$

Stirling: $\ln n! \approx n \ln n - n$
(large n)

if N_i
very large

Gibbs decided to "fix" the problem by
subtracting $k \ln N! \approx k(N \ln N - N)$ from
the entropy.

This corresponds to fixing Ω by
dividing it by $N!$

$$\Omega \longrightarrow \frac{\Omega}{N!}$$

$N!$ takes into account the over counting
of available states because the particles are
not distinguishable (assuming that no state
has more than 1 particle in it; OK for ideal gas).

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Then

$$S = S - (NK \ln N - NK) = N k \ln \left[\frac{V}{h^3} \left(\frac{4\pi m \bar{\epsilon}}{3N} \right)^{3/2} \right.$$

$$\underset{\text{wrong } S}{S} \qquad + \frac{3}{2} NK - N k \ln N + NK =$$

$$S = NK \ln \left[\frac{V}{Nh^3} \left(\frac{4\pi m \bar{\epsilon}}{3N} \right)^{3/2} \right] + \frac{5}{2} Nk \quad \bigotimes$$

$$\oplus \quad S = N K \ln \left(\frac{V}{N} \right) + \frac{3}{2} N k \left\{ \frac{5}{3} + \ln \left(\frac{2\pi m kT}{h^2} \right) \right\}$$

$$\color{red}{\bar{\epsilon} = \frac{3}{2} kT}$$

Now S is extensive since

for $V \to \alpha V$ and $N \to \alpha N \Rightarrow S \to \alpha S$.

also $\Delta S^* = 0$ for equal gases

but $\Delta S^* > 0$ (same expression as before for different)

Now from Ⓧ

$$E(N, v, s) = \frac{3 h^2 N^{5/3}}{4 \pi m V^{2/3}} e^{\left(\frac{2s}{3Nk} - \frac{5}{3}\right)}$$

$$\mu = \frac{\partial E}{\partial N}\Big|_{V,s} = E\left[\cdot \frac{5}{3N} - \frac{2}{3N^2 k} \right]$$

Since $E = \frac{3}{2} kT$ and $P = \frac{2}{3} \frac{E}{V} = \frac{NkT}{V}$

$$\mu = \frac{1}{N}\left[\frac{5}{3} E - \frac{2 E s}{3Nk}\right] = \frac{1}{N}\left[\frac{5}{3} E - \frac{\cancel{2}}{\cancel{3Nk}} \cdot \frac{\cancel{3}}{\cancel{2}} \cancel{NkT} s \right]$$

$$= \frac{1}{N}\left[E + \underbrace{\frac{2}{3} E}_{NkT = PV} - TS\right] = \frac{1}{N}\left[E + PV - TS\right] = \frac{G}{N}$$

Replacing $\bar{E}$ and S in terms of N, V and T we get

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

and $\quad F = \bar{E} - TS = G - PV = \frac{M}{N} - NkT =$

$$= NkT \left\{ \ln \left[\frac{N}{V} \left(\frac{h^2}{2\pi m kT} \right)^{3/2} \right] \right\}.$$

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Correct enumeration of states:

Gibbs proposed $\Omega \longrightarrow \dfrac{\Omega}{N!}$

it works if we consider N indistinguishable particles in systems in which each level has one particle at most (correct for ideal gas).
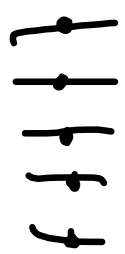
But if we consider a distribution $\{n_i\}$ where $n_i > 1$ for some i's there are fewer configurations so Gibbs recipe is too drastic.

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If $n_i > 1$ we have $\dfrac{N!}{n_1! \, n_2! \cdots}$

$\{M_i\}$ $\displaystyle\sum_i M_i = N$

$\displaystyle\sum_i \varepsilon_i \cdot M_i \cdot \bar{E}$

Example : $N = 5$

$N! = 120$

configurations
that are not
different so
we need to
correct

$5 \binom{4}{2}$

$= \dfrac{5 \times 4 \times 3 \times 2}{2 \times 2}$

$= 30$

n_3 ———•——— 1

n_2 ——•—•—— 2

n_1 ——•—•—— 2

$\dfrac{N!}{n_1! \, n_2!} = \dfrac{5!}{2! \; 2!} = 30$

$$\omega\{m_i\} = \frac{1}{m_1! \, m_2! \cdots}$$ needs to be considered if n is large or T is very low. (for non ideal gas)

@Quantum mechanics will take care of this.

Ensemble Theory

Macrostate $\longrightarrow$ very large # of equally likely microstates compatible with $N, V, \bar{E}$
N, V, E

Thermodynamic properties are obtained from a time average of the macrostate.

Ensemble picture: consider $\mathcal{N}$ systems representing each of the $\mathcal{N}$ possible microstates. This group of systems forms an ensemble.

The average at a fixed time t over
the members of the ensemble provides
the thermodynamical properties.

Classical System: Phase space.

The position $\bar{q}_i$ and momenta $\bar{p}_i$ at
a given time t of each of the N particles
that form a classical system provide the
microstate of the system.

Then phase space has $3N + 3N = 6N$
dimensions $(N \sim 10^{23})$

We will label:

$$\{q_i\} = q_1 \cdots q_{3N}$$

$$\{p_i\} = p_1 \cdots p_{3N}$$

then (q_i, p_i) $i = 1, \cdots 3N$ defines a point (microstate) in phase space.

p_i and q_i are $p_i(t)$ and $q_i(t)$.

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The time dependence is given by:

$$\dot{q}_i = \frac{\partial H(q_i, p_i)}{\partial p_i} \quad \text{①}$$

$$\dot{p}_i = -\frac{\partial H(q_i, p_i)}{\partial q_i} \quad \text{②}$$

$H(q_i, p_i)$ is the system's Hamiltonian.

Each (q_i, p_i) evolves as a function of t describing a trajectory in phase space.

If E in the system is fixed we know
that $H(q_i, p_i) = \bar{E}$ for all t.

The trajectory of (q_i, p_i) will define
a hypersurface in phase space (not all
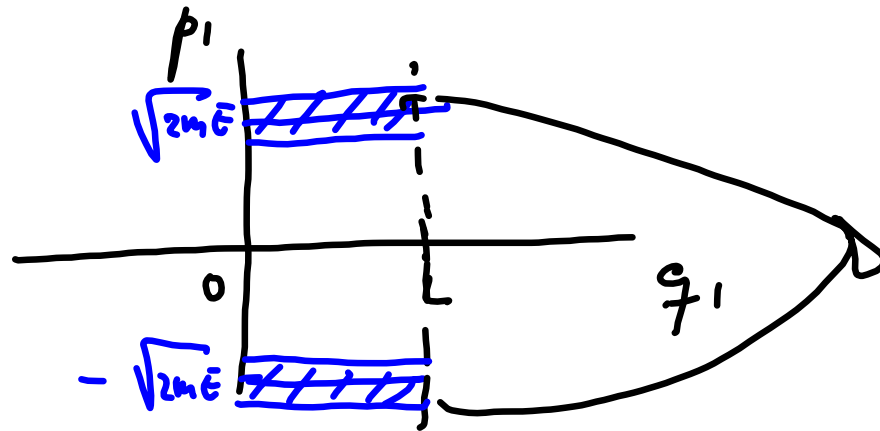microstates will be possible).

If $\bar{E}$ is given within a range

$$\bar{E} - \tfrac{1}{2}\Delta \leq \bar{E} \leq \bar{E} + \tfrac{1}{2}\Delta$$ the accessible
points define a shell of width Δ.

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Example: $N = 1$, 1D free particle.

$$E = \frac{p_1^2}{2m}$$

box of length L.

$$p_1 = \pm\sqrt{2mE}$$

hypershell of accessible states.