

Last time

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$$V_1 + V_2 = V$$

N_1	T	T	N_2
V_1			V_2

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

$$S_0 = \sum_{i=1}^2 S_i$$

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

$$\Delta S = S_F - S_0 = k \left[N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right] > 0$$

$$\text{If } \frac{N_1}{V_1} = \frac{N_2}{V_2} \quad \text{equal densities}$$

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

even if the 2 gases are the same!!

Gibbs paradox!

Notice that if both gases are the same we have that:

$$\begin{aligned}
 (\Delta S)^{\ddagger} &= k [N_1 \ln(N_1 + N_2) - N_1 \ln N_1 + \\
 &\quad + N_2 \ln(N_1 + N_2) - N_2 \ln N_2] = \\
 &= k [(N_1 + N_2) \ln(N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2] \\
 &= k \left[\overbrace{(N_1 + N_2)}^N \ln(N_1 + N_2) - (N_1 + N_2) - \right. \\
 &\quad \left. - (N_1 \ln N_1 - N_1) - (N_2 \ln N_2 - N_2) \right] \overset{\text{large } N_i}{\approx} \\
 &\approx k [\ln N! - \ln N_1! - \ln N_2!] \neq 0
 \end{aligned}$$

Stirling approximation: $\ln N! \approx N \ln N - N$

The paradox is fixed by reducing S_i by $k \ln N_i!$ and S_F by $k \ln N!$.

Gibbs proposed this solution. It is equivalent to replace Ω by $\frac{\Omega}{N!}$.

With this correction $\Delta S^* = 0$ for equal gases but still $\Delta S^* > 0$ for different gases.

Now with Gibbs correction:

$$\begin{aligned}
 S &= \underset{\substack{\uparrow \\ \text{old } S}}{S^*} - (Nk \ln N - Nk) = Nk \ln \left[\frac{V}{h^3} \left(\frac{4\pi m \bar{E}}{3N} \right)^{3/2} \right] + \\
 &\quad + \frac{3Nk}{2} - Nk \ln N + Nk = \\
 &= Nk \ln \left[\frac{V}{\cancel{N} h^3} \left(\frac{4\pi m \bar{E}}{3N} \right)^{3/2} \right] + \frac{5}{2} Nk \\
 &\quad \text{make } S \text{ extensive}
 \end{aligned}$$

Now $S(\alpha \bar{E}, \alpha V, \alpha N) = \alpha S$.

Now

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

Now $\bar{E}(\alpha N, \alpha V, \alpha S) = \alpha \bar{E}$ (also extensive).

All the expressions we obtained before as derivatives of E are unchanged. The only quantity that depends on the "correct" form of S is:

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

For ideal gas $E = \frac{3}{2} NkT$ and $P = \frac{2}{3} \frac{E}{V} = \frac{NkT}{V}$

then

$$\begin{aligned} \mu &= \frac{1}{N} \left[\frac{5}{3} E - \frac{2ES}{3Nk} \right] = \frac{1}{N} \left[\frac{5}{3} E - 2 \frac{\frac{2}{3} NkT S}{3Nk} \right] = \\ &= \frac{1}{N} \left[E + \frac{2}{3} E - TS \right] = \frac{1}{N} [E + PV - TS] = \frac{1}{N} G = \frac{G}{N} \end{aligned}$$

If we replace E and S in terms of N, V, T
 in $\mu = \frac{1}{N} \left[\frac{\partial}{\partial N} (E - TS) \right]$ we obtain:

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

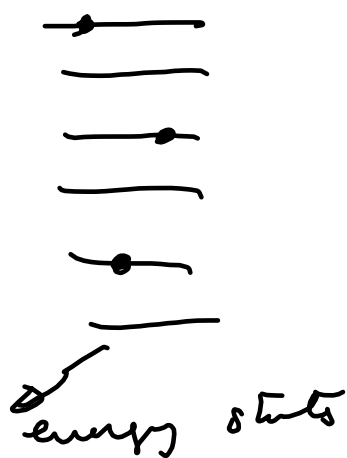
and

$$\begin{aligned} F &= E - TS = G - PV = \mu N - NkT = \overset{\text{replacing } \mu}{=} \\ &= kT N \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m kT} \right)^{3/2} \right\} - NkT = \\ &= NkT \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m kT} \right)^{3/2} \right\} - 1 \right]. \end{aligned}$$

Correct enumeration of states in the classical ideal gas:

Gibbs proposed $\Omega \rightarrow \frac{\Omega}{N!}$

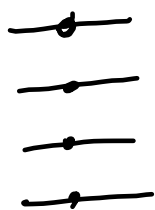
Ideal gas:



each state is either empty or contains one particle at most.

Consider 5 indistinguishable particles.

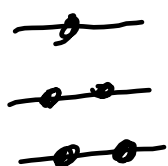
$$5 \times 4 \times 3 \times 2 \times 1 = 5! = 120$$



In this case it is OK to correct using the factor $N!$.

However, if more than 1 particle could be in one single state this is not true:

$$5 \binom{4}{2} = 5 \frac{4!}{2! (4-2)!} = \frac{5!}{2 \times 2} = \frac{120}{4} = 30.$$



Instead of $N!$ we will have

$$\frac{N!}{n_1! n_2! \dots}$$

So Gibbs correction misses $\omega\{n_i\} = \frac{1}{n_1! n_2! \dots}$

This becomes important for fermion gases when n is no longer small or $T \rightarrow 0$.

Ensemble theory.

Macrostate \longrightarrow very large # of equally likely microstates
 N, V, E compatible with N, E and V .

Thermodynamic properties result from a time average over all the microstates.

Ensemble picture: consider a number N of systems prepared in the N accessible microstates of a given macrostate.

Thermodynamic properties result from an instant time

average over all the ~~members~~ members of the ensemble.

Classical system: Phase space.

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

There are $3N + 3N = 6N$ coordinates that define the microstate.

$$\{q_i\} = q_1, \dots, q_{3N}$$

$$\{p_i\} = p_1, \dots, p_{3N}$$

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

Also $q_i = q_i(t)$ and $p_i = p_i(t)$

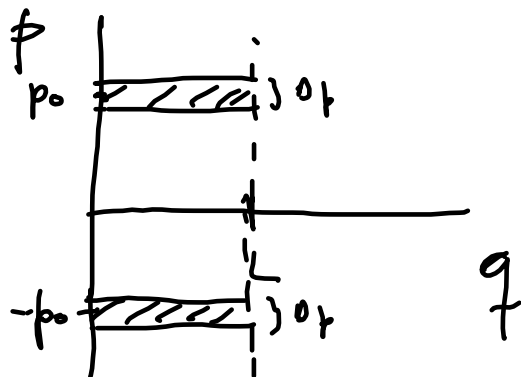
$$\dot{q}_i = \frac{\partial H(q_i, p_i)}{\partial p_i} \quad \dot{p}_i = - \frac{\partial H(q_i, p_i)}{\partial q_i} .$$

$H(q_i, p_i)$ hamiltonian.

Each q_i and p_i will describe a trajectory in phase space through the accessible regions defined by $H(q_i, p_i) = E$ for all t . (System with fixed energy).

We will assume that our system have a fixed energy such that $E - \frac{1}{2}\Delta \leq E \leq E + \frac{1}{2}\Delta$.

Example in 1D: a particle with energy E in a "box" of length L .



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

$$p_0 = \pm \sqrt{2mE}$$

Density function:

We want to find how many microstates are in a differential of volume in phase space.

Define $\rho(q, p, t) \equiv \rho(\{q_i\}, \{p_i\}, t)$

$$\rho(q, p, t) dw = \lim_{N \rightarrow \infty} \frac{dN(\bar{p}, \bar{q}, t)}{N}$$

differential of
volume in
phase space

of microstates
inside dw

of microstates
inside the
accessible space.

ρ provides a weight that allows to calculate
statistical averages in the ensemble:

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

The integral is over $6N$ phase space but restricted to the regions where $\rho \neq 0$.

In general from $\rho \doteq \rho(\zeta, p, t) \Rightarrow \langle f \rangle = \langle f \rangle(t)$.

Stationary systems: equilibrium.

$\langle f \rangle$ is time independent in a stationary system.

It happens when $\frac{\partial \rho}{\partial t} = 0 \Rightarrow \rho$ is constant in time

$$\rho = \rho(\zeta, p) \text{ but not } t.$$

A thermodynamic system is in equilibrium if
 $\langle f \rangle \neq \langle f \rangle(t)$ for all f this means that

$$\frac{\partial \rho}{\partial t} = 0.$$