Intensive Quantities

Basic object in microcanonical ensemble

$$S = S(N, E, V)$$ – entropy

is extensive $\Rightarrow$ $S \sim N$ $\Rightarrow$ we can make connection with thermo!

Define:
(from II law of thermo)

$$T = \left(\frac{\partial S}{\partial E}\right)^{-1}_{V,N}$$

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

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

For classical ideal gas:

$$\Rightarrow \left(\frac{\partial S}{\partial E}\right)_{V,N} = k_B \frac{Nd}{2}\frac{1}{E} \Leftrightarrow \boxed{T = \frac{2E}{k_B N d}}$$

$$\Rightarrow E/N \sim O(1)$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{k_B N}{V} \Leftrightarrow \boxed{P = \frac{k_B N T}{V}}$$

Calculation of μ little more involved

Note: d in V_d omitted!

$$\frac{\partial S}{\partial N} = k_B\Big[\Big(\frac{d}{2}+1\Big) + \frac{d}{2}\ln\frac{4\pi m E}{N d h^2} + \ln\frac{V}{N} +$$

$$+ \cancel{N}\Big\{-\frac{d}{2\cancel{N}} - \frac{1}{\cancel{N}}\Big\}\Big] =$$

$$= k_B \ln\Big[\frac{V}{N}\Big(\frac{4\pi m E}{N d h^2}\Big)^{d/2}\Big]$$

Use $E = \frac{1}{2}k_B N \underset{\uparrow \text{dim!}}{d} T$

$$\frac{\partial S}{\partial N} = k_B \ln\Big[\frac{V}{N}\Big(\frac{2\pi m k_B T}{h^2}\Big)^{d/2}\Big] = k_B \ln\Big[\frac{V}{N}\frac{1}{\lambda^d}\Big]$$

De Broglie "wavelength":

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$ – thermal wavelength of de Broglie

Reason: in Quantum Mech.: $\lambda = \frac{h}{p}$ ← momentum

Since $\frac{E}{Nd} = \frac{1}{2}k_B T = \frac{p^2}{2m}$ ← $p \sim \sqrt{m k_B T}$

$$\Rightarrow \boxed{\mu = k_B T \ln\Big(\frac{N}{V}\lambda^d\Big)}$$

$$\Big\{\mu = -T\Big(\frac{\partial S}{\partial N}\Big) = -k_B T \ln\Big(\frac{V}{N}$$

$$\frac{N}{V}\lambda^d = e^{\mu/k_B T} \Longleftarrow$$

$$\cancel{\frac{N}{V}\lambda^d} \neq \quad \boxed{N = \frac{V}{\lambda^d}e^{\mu/k_B T}}$$

38)

From II law of thermo:

$$dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN =$$

$$= \frac{1}{T} dE + \frac{1}{T} P dV - \frac{1}{T} \mu dN$$

$$\boxed{T dS = dE + P dV - \mu dN}$$

Heat & Thermal Interaction

Typically, a system described by some external parameter x_i:

e.g., volume V

B-field $\vec{H}$

e-field $\vec{E}$

Macrostate: specify external parameter + some other conditions

Microcanonical ensemble: "some other" → energy

Sometimes 2 systems A_1 and A_2 can exchange energies:

$$E = E_1 + E_2 \quad \left(\begin{array}{l}1 \,\&\, 2 \text{ interact} \\ \text{little} \rightarrow \text{ignore!}\end{array}\right)$$

Different members of microcanonical ensemble have same E, but different E_1 and E_2

Averaging over the various members of the ensemble, get

$$\langle E_1 \rangle ; \langle E_2 \rangle$$

Exchange of energies can come from various sources

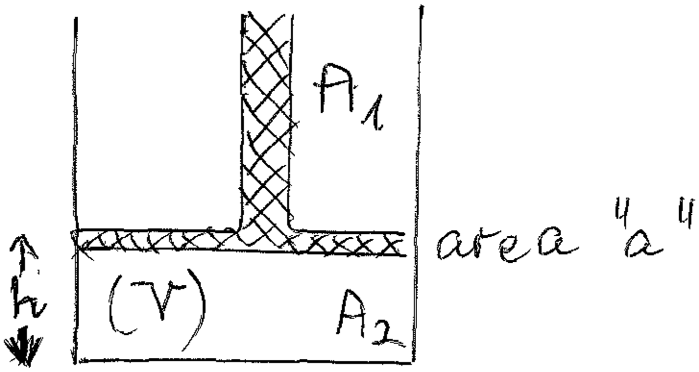
(a) Mechanical Interactions

System: gas + piston

A_2 $\quad$ A_1

A_1: specified by h, $\langle E_1 \rangle$

A_2: —"— V, $\langle E_2 \rangle$



h and V are not independent

$\Delta V = a\Delta h$

If $\Delta h > 0$, energy of a piston increases

$$\Delta E_1 = mg\Delta h \equiv W_1$$

where m – piston mass

$-W_1 \equiv$ work done by piston

$+W_1 =$ —"— on piston

P – gas pressure

Work done by gas $= Pa\Delta h = P\Delta V$

(b) Thermal Interaction

- * Two systems: A_1 & A_2 in thermal contact
- * None of external parameters change in the process (fixed!) i.e. systems cannot do work on one another

Energy exchange: $\Delta\langle E_1 \rangle \equiv Q$ – heat absorbed by A_1

39a

Since $\Delta \langle E_1 \rangle + \Delta \langle E_2 \rangle = 0$

$$Q_1 + Q_2 = 0$$

Note: $A_1 + A_2$ – isolated

$(E_1 + E_2 = \underbrace{\text{const.}}_{E_0})$

$$\Omega_0 = \Omega_1(E_1)\,\Omega_2(\underbrace{E_0 - E_1}_{E_2})$$ – total nu. of accessible states

Canonical Ensemble

(Systems at fixed T)

Two systems A_1 and A_2 are in thermal contact → can exchange energy

$$E = E_1 + E_2 \quad \text{conserved}$$

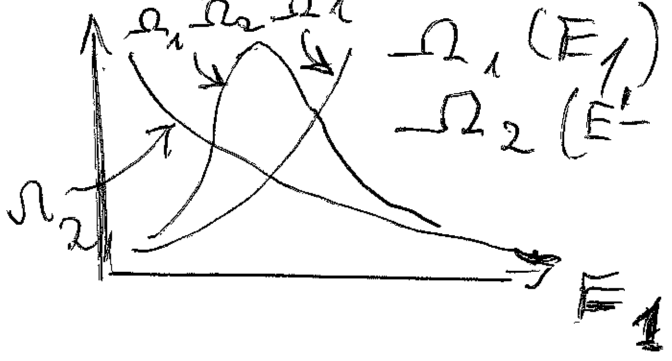
For the whole system:

$$\Omega(E) = \int_{E<E'<E+\delta E} \frac{dE'}{\delta E} \int_{-\infty}^{E'} \underbrace{\frac{dE_1}{\delta E}\,\Omega_1(E_1)}_{\left\{\text{density of states} = g(E)\delta E \sim E^N \delta E\right\}} \Omega_2(E'-E_1) \quad (*)$$

where $\Omega_1(E_1)$: nu. of accessible states with energy E_1 for system 1

For each such state of A_1, there are $\Omega_2(E'-E_1)$ accessible states of A_2, with energy $E_2' = E' - E_1$.

When A_1, A_2 have large nu. of degrees of freedom:



$$\Omega_1(E_1) \sim E_1^{n_1}$$

$$\Omega_2(E'-E_1) \sim (E'-E_1)^{n_2}$$

larger n_1, n_2 → sharper peak!

⇒ Even though we have to freely sum over E_1, in practice only a small region of E_1 contributes to integral!

Peak occurs at $\bar{E}_1$

$$\frac{\partial}{\partial E_1}\left[\Omega_1(E_1)\,\Omega_2(E'-E_1)\right]_{E_1=\bar{E}_1} = 0$$

Evaluate

$$\frac{\partial}{\partial E_1}\left[e^{S_1(E_1)/k_B}\,e^{S_2(E'-E_1)/k_B}\right] = 0$$

$$\frac{\partial S_1}{\partial E_1}\cancel{e^{S_1}e^{S_2}} - \frac{\partial S_2}{\partial E_1}\cancel{e^{S_1}e^{S_2}} = 0$$

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}\quad\left\{\begin{array}{l} E_2 = E' - E_1 \\ \partial E_2 = -\partial E_1 \\ e^{[S_2(E_2)-S_1(E_1)]/k_B} = 1 \\ \text{at max } S_1' = S_2' \end{array}\right.$$

Basis of 0-law of thermo:

$$\frac{1}{T} \equiv \Leftarrow \boxed{\frac{1}{T_1} = \frac{1}{T_2}}$$

Thus T must be the same for both systems!

Equilibrium ≡ state of max S.

For maximum:

$$\frac{\partial^2}{\partial E_1^2}\left[S_1(E_1) + S_2(E_2)\right]_{\bar{E}_1} < 0 \quad !$$

This condition satisfied when $E_2 >> E_1$ i.e., $E_1 << E'$ } To establ. canonical ensemble

Then, since $E_1 << E'$, expand S_2 in Taylor series!

$$\Rightarrow S_2(E_2) = S_2(\overbrace{E'-E_1}^{E_2})$$

$$= S_2(E') - E_1\left(\frac{\partial S_2}{\partial E_2}\right)_{E'} + \frac{1}{2}E_1^2\left(\frac{\partial^2 S_2}{\partial E_2}\right)_{E'}$$

$$= S_2(E') - \frac{E_1}{T} - \frac{1}{2}\underbrace{\frac{E_1^2}{T^2}\left(\frac{\partial T}{\partial E_2}\right)_{E'}}_{<<1}$$

$$\left(\frac{\partial T}{\partial E_2}\right) = \frac{1}{C_2}$$ where C_2 = specific heat of A_2

Since $A_2 >> A_1 \Rightarrow E_1 << C_2 T$

Thus, $S_2(E_2) \simeq S_2(E') - \frac{E_1}{T}$

By definition:

$$\Omega_2(E'-E_1) = e^{S_2(E')/k_B}\, e^{-E_1/k_B T}$$

The probability that A_1 is in energy range (E_1, E_1+dE_1) is then:

$$P(E_1)\,dE_1 = \frac{\Omega_1(E_1)\,\Omega_2(E'-E_1)\,dE_1}{\int dE_1\, \Omega_1(E_1)\,\Omega_2(E'-E_1)}$$ ← canonical distrib.

Thus, E_1 dependence

$$\boxed{P_1(E_1) = \Omega_1(E_1)\, e^{-E_1/k_B T}\,(\text{const.})}$$