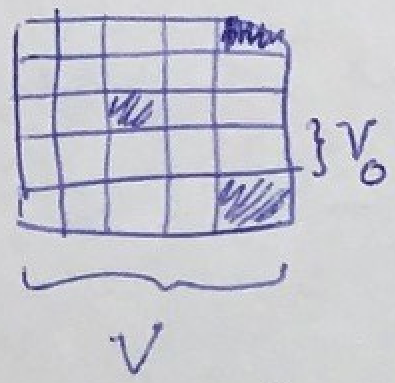
L24: review

* Heat capacity ($dE = C_v dT$, $dS = C_v dT/T$, similar for C_p)

* Calculating "laws" for systems:

① find W (or E, or F, or G...) for system

ex:



$W \approx \left(\frac{V}{NV_0}\right)^N \Rightarrow S = k_B \ln W$

$= S_0 + nR \ln\left(\frac{V}{n}\right) \Rightarrow \frac{\partial S}{\partial V} = \frac{nR}{V}$

also we know $\longrightarrow$ $PV = nRT$ $(nR = Nk_B)$

$\frac{\partial S}{\partial V} = \frac{P}{T}$ (see ② below)

② Use Postulates 1 & 2:

ex: $dE = TdS - PdV + \dots \Rightarrow S = \frac{1}{T} dE + \frac{P}{T} dV + \dots$

$\Rightarrow \frac{\partial S}{\partial V} = \frac{P}{T}$

Today: Working at constant T: the "canonical" ensemble

Derive the "Boltzmann factor", e.g.

rate $\sim e^{-E^{\ddagger}/RT}$

$K_{eq} \sim e^{-\Delta G/RT}$

etc

contribution of each state

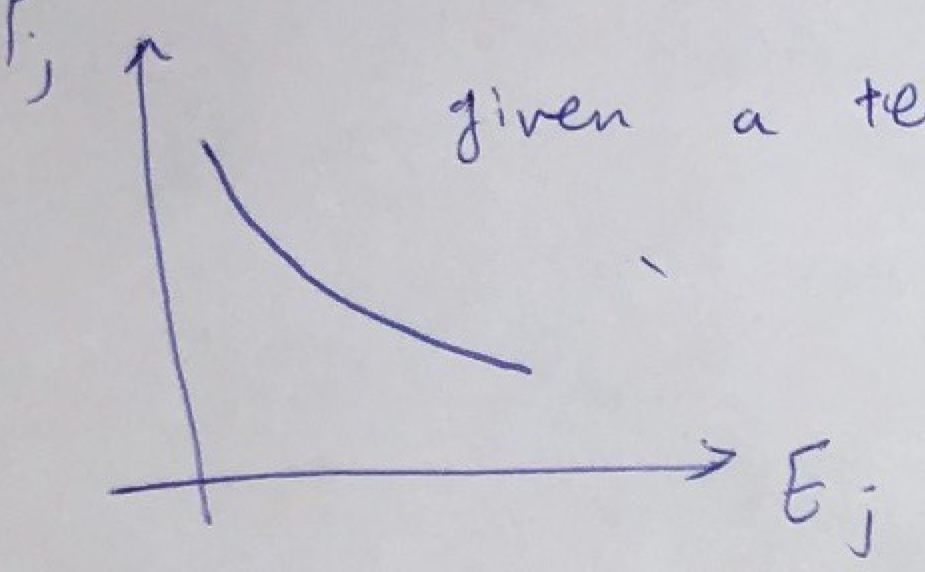
We know: if $E = const$, $P_j = \frac{1}{W}$

total number of states or "microcanonical partition function" → number of accessible states

What if $T = Const$? what is P_j?

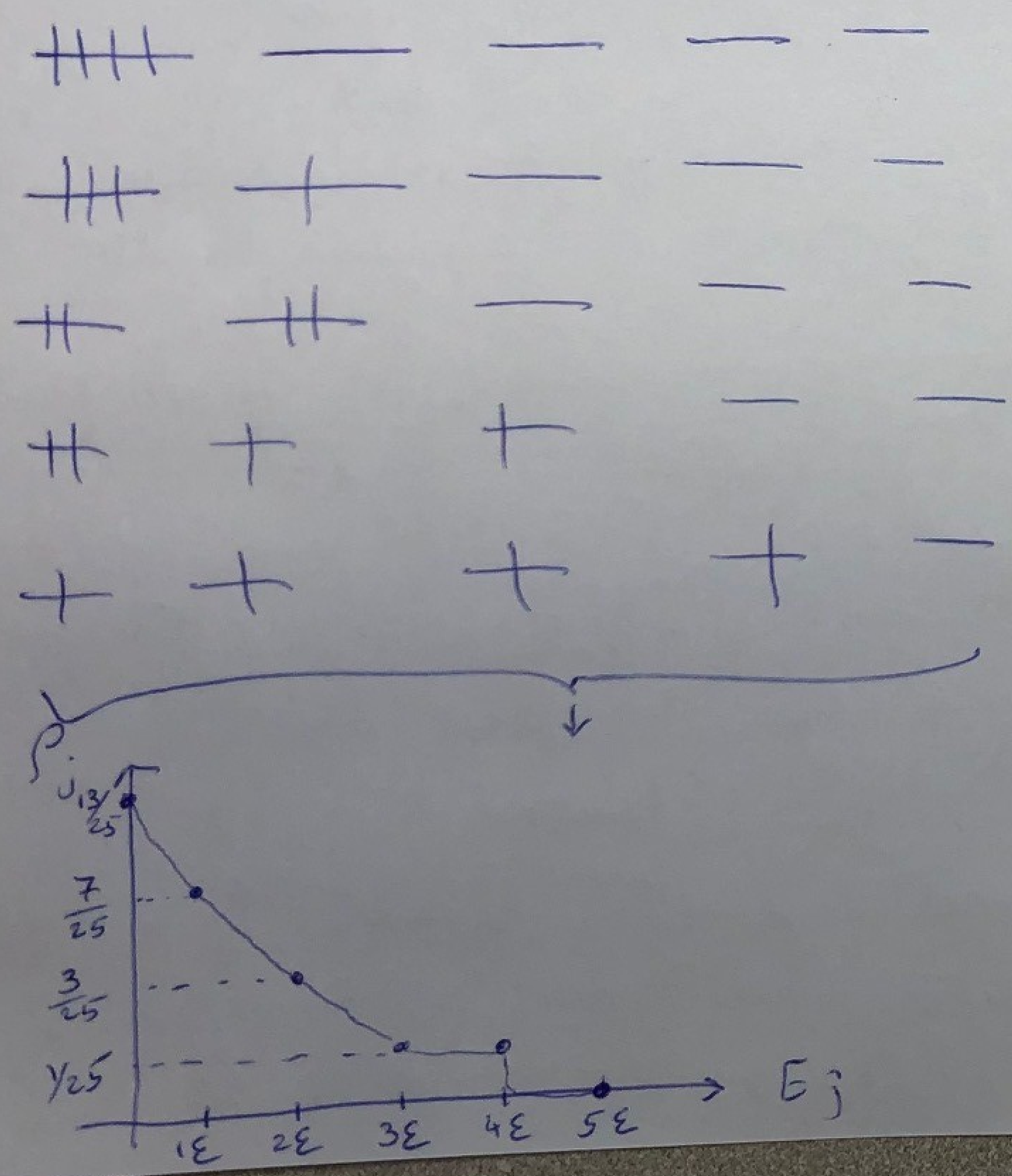
What is the "canonical partition function"?

We suspect that at a given T, P_j will be smaller when the energy of state "j" is higher.



ex: $N = 5$ molecules "—"

$k = 4$ energy packets, "ε" or "1"



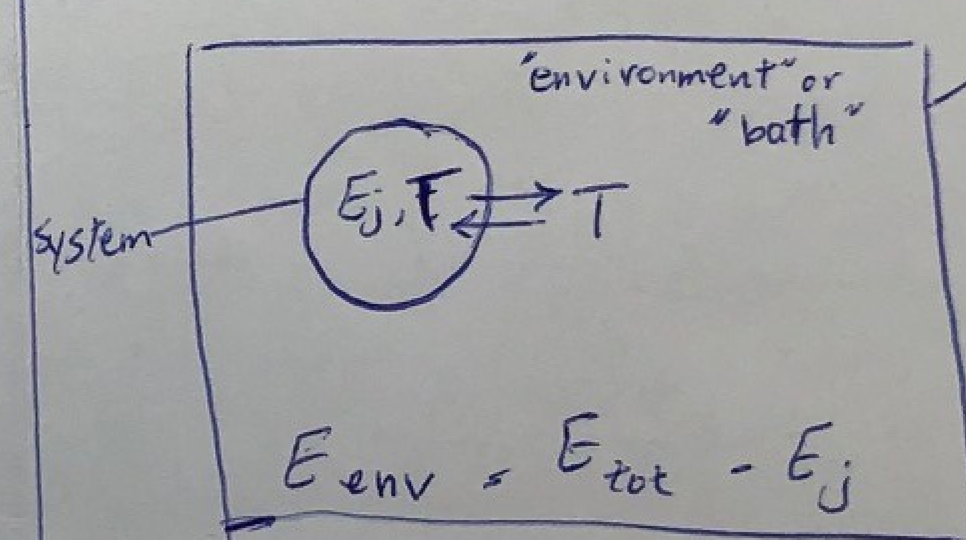
Property of the exponential function,

$$y = e^{\underbrace{-x-a}_{E_j}} = e^{-a} e^{-x} = ce^{-x},$$

where $c \equiv e^{-a}$

↳ for the simple example in the previous page, P_j drops almost exponentially with increasing E_j (drops almost two-fold for every ε).

Picture to have in mind:



⇒ thermal equilibrium system and environment.

At constant T what is P_j at energy E_j?

Step 1) Get formula fo P_j from W.

The number of ways the sys. can be at energy E_j

$$W(E_j) \cdot W_{env}(E_{tot} - E_j)$$

system ↩

The number of ways the sys can be at any energy $= W_{tot}(E_{tot})$

$$P_j = \frac{W(E_j) \cdot W_{env}(E_{tot} - E_j)}{W_{tot}(E_{tot})}$$

using $S = k_B \ln W \Rightarrow W = e^{S/k_B}$

Rewrite P_j in terms of S instead of W:

$$P_j = W(E) \cdot e^{\underbrace{\{S_{env}(E_{tot} - E_j) - S_{tot}(E_{tot})\}/k_B}}$$

↓

goal: replace this by simple quantities we know, e.g. E_j and T

Step 2) Get rid of these S's in favor of known quantities of the system like E_j, S, G, T, ...

(a) $S_{tot}(E_{tot}) = S(E) + S_{env}(E_{tot} - E)$

this is true for any energy of the system. Here I pick the average energy $\langle E_j \rangle$

(b) Now we do a Taylor series expansion of $S_{env}(E_{tot} - E)$ about the actual energy of the system, E_j:

$$\left.\begin{aligned} y(x) &= y(x)_0 + \left.\frac{\partial y}{\partial x}\right|_{x_0}(x - x_0) + \dots \\ y &= S_{env} \;;\; x_0 = E \;;\; x = E_j \end{aligned}\right\} \Rightarrow$$

$$S_{env}(E_{tot} - E_j) = S_{env}(E_{tot} - E_j) + \frac{\partial S_{env}}{\partial E_j}(E_j - E)$$

$$+ \dots = S_{env}(E_{tot} - E_j) + \underbrace{\frac{\partial S_{env}}{\partial E_{env}} \cdot \frac{\partial E_{env}}{\partial E_j}}(E_j - E) + \dots$$

applied the chain rule here

→ continued in the next page

$$S_{env}(E_{tot} - E_j) = S_{env}(E_{tot} - E) + \frac{1}{T} \cdot (-1) \cdot (E_j - E)$$

$+ \dots$, where we used energy conservation to derive $\frac{\partial E_{env}}{\partial E_j}$. $dE_j = -dE_{env}$

We can isert this into our formula for p_j:

$$p_j = W(E_j)\, e^{\{S_{env}(E_{tot} - E_j) - S_{tot}(E_{tot})\}/k_B}$$

$$= W(E_j)\, e^{\{S_{env}(E_{tot} - E_j) - S(E) - S_{env}(E_{tot} - E)\}/k_B}$$

$$= W(E_j)\, e^{\{\cancel{S_{env}(E_{tot} - E)} - \frac{1}{T}(E_j - E) - S(E) - \cancel{S_{env}(E_{tot} - E)}\}/k_B}$$

$$= W(E_j)\, e^{\{-\frac{1}{T} E_j + \frac{1}{T} E - S(E)\}/k_B}$$

$$= W(E_j)\, e^{-\frac{E_j}{k_B T}}\, e^{\frac{E - T S(E)}{k_B T}}$$

$$= W(E_j)\, e^{-\frac{E_j}{k_B T}}\, \underbrace{e^{\frac{F}{k_B T}}}_{\frac{1}{Z}}, \text{ where } F = E - TS$$