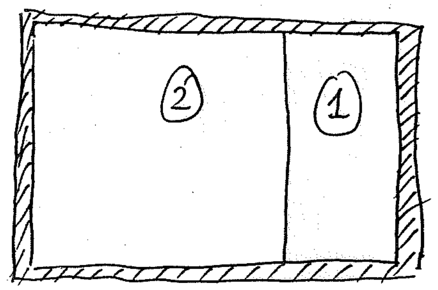
Part III: The Partition Function $Z(T,V,N)$ and the Canonical Ensemble Theory

- No new physics principle
- A twist opens up a "new" method
- Recall:



- energy in ① is not fixed
- but there is a value $\bar{E}_1$ that is almost always observed
- actually, energy in ① fluctuates about $\bar{E}_1$

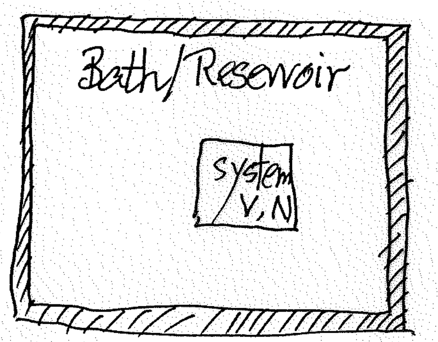
⊛ $$\frac{W_1(E_1,N_1,V_1)\cdot W_2(E-E_1,N_2,V_2)}{W_{total}}$$ = Prob. of finding ① to have energy E_1

where W_{total} = Just a number

$$= \sum_{E_1=0}^{E} W_1(E_1,N_1,V_1)\cdot W_2(E-E_1,N_2,V_2) = \text{Total \# microstates of composite system}$$

⊛ is based on "All microstates are equally probable"

Changing names:



Same Thing!

- Interested in the physics of the system $\boxed{\text{system}}$
- Bath is huge!

Copy results/arguments

$$\underset{\text{total}}{E_0} = E_{bath} + \overset{\text{system}}{E} = E_B + E$$

- energy in $\boxed{\text{system}}$ is not fixed
- but there is a sharp mean energy $\langle E\rangle$ that is always almost observed
- actually, energy in $\boxed{\text{System}}$ fluctuates about $\langle E\rangle$

Probability of finding $\boxed{\text{system}}$ to have energy E $$= \frac{W_S(E,V,N)\cdot W_B(E_0-E,V_b,N_b)}{W_{total}}$$

This is the discussion in Ch. IV.

If you follow everything, you may jump to p. V⑦.

V. A system in thermal equilibrium with a heat bath

- Boltzmann distribution and Canonical Ensemble

A. Motivations

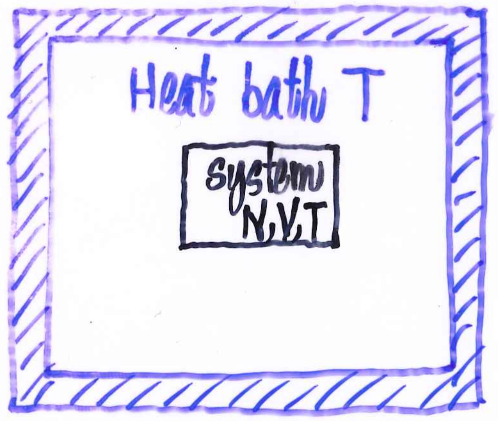
- $S = k \ln \underbrace{W}_{\uparrow}$ (isolated system in equilibrium)

  W(U,V,N) not easy to calculate

∴ Look for other equivalent methods of computation

- In many situations, it is the Temperature T that is controlled (instead of U)

B. System under investigation



- System is macroscopic (N,V)
- Heat bath is huge
- System and heat bath can exchange energy (diathermal walls)
- Wait and Wait

  ⇒ system in equilibrium with heat bath

  ∴ fixed (T,V,N)

Huge heat bath:

(i) Control temp.

(ii) Heat bath is so large that energy exchange does not affect the temperature of the bath.

$\boxed{\text{"System + heat bath"}}$ forms an $\underbrace{\text{isolated system}}$.

↗ useful in establishing the theory, as we only know how to deal with isolated systems

C. Features to note

- Consider $\boxed{\text{System}}$

  exchange energy with heat bath ⇒ U or E is not fixed! (Formally!)

  ⇒ Talk about mean or average of U, i.e., $\langle U \rangle$ or $\langle E \rangle$ (how to evaluate $\langle U \rangle$?)

- $\underbrace{\text{How sharp (representative)}}$ is $\langle U \rangle$?

  ↑ standard deviation of U-distribution (or E-distribution)

- For macroscopic systems, the physics obtained from calculations based on fixed (T, V, N) [canonical ensemble] is essentially identical to that obtained from calculations based on the microcanonical ensemble.

  [The key point is that we need a macroscopic system.]

D. The Key Question

What is the probability of finding the system (which is a macroscopic N-particle system) in a state of energy E_n, when the system is in thermal equilibrium with a heat bath at temp. T?

Remark: The "a" in "a state" is very important!

- You may imagine that we could solve the Quantum Mechanical problem†:

$$\underset{\text{N-particle Hamiltonian}}{\hat{H}_N}\,\psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N) = E\,\underbrace{\psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)}_{\text{N-body energy eigenstates}^{\ddagger}}$$

  - This is NOT an easy problem, but let's say you have solved it.

‡ For identical particles, need to worry about symmetry requirement.

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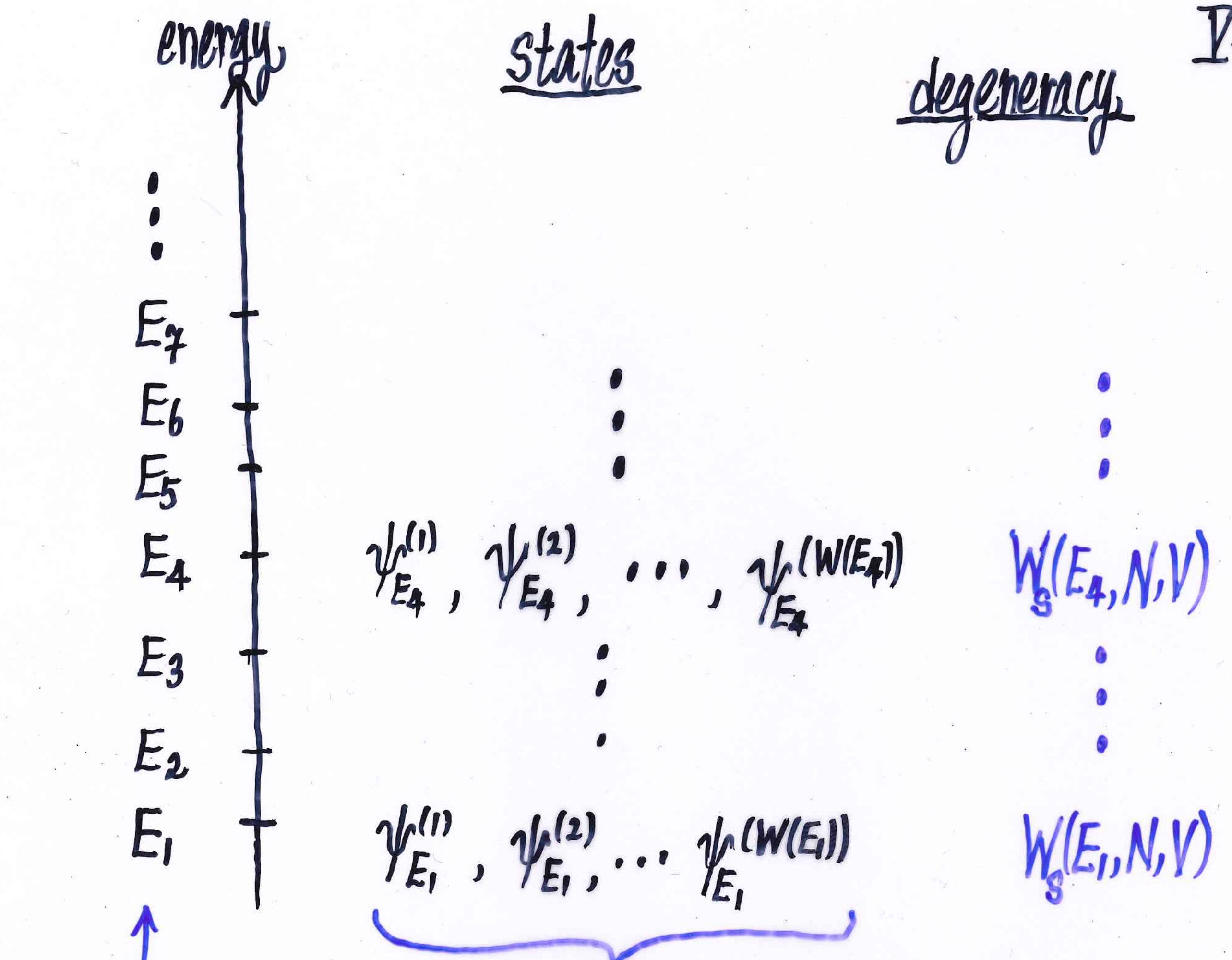
† In Stat. Mech., sometimes it is easier to think quantum mechanically than classically!



allowed energy LEVELS → implicit V-dependence

degenerate eigenstates (STATES)

$W_s(E_1,N,V)$ of them corresponding to E_1

"system"

degeneracy of energy E_1

For macroscopic system, $W(E_1)$† varies with E_1 rapidly!

Our question:

- Prob. of finding the system in a state (there may be many of the same energy) of energy E?

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† This is indeed the same W(E,V,N) that goes into S = k ln W in microcanonical ensemble, i.e. the degeneracy.

E. The key result

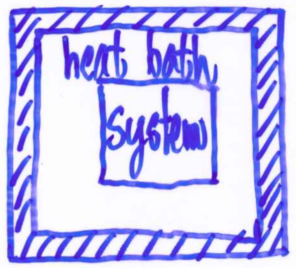
For a state with energy E_i, the prob. P_i of finding the system in such a state when the system is thermal equilibrium with a heat bath at temperature T is:

$$P_i \propto e^{-E_i/kT}$$

- Boltzmann distribution
- The most important and most useful result in statistical mechanics!

F. Derivation #1

- getting something from "nothing" (doing nothing new)!



- Whole system is isolated, (N_0, V_0, E_0) fixed

$$N_0 = \underset{\nwarrow}{N_B} + \underset{\nearrow}{N} \leftarrow \text{N-particle system}$$

fixed (no exchange of particles)

$$N_B \gg N \quad (N_0 \gg 1)$$

$$V_0 = \underset{\nwarrow}{V_B} + \underset{\nearrow}{V} \leftarrow \text{Volume of system}$$

fixed (no exchange of volume)

$$V_B \gg V$$

$$\underset{\text{fixed}\ \nearrow}{E_0} = \underset{\nwarrow}{E_B} + \underset{\nearrow}{E} \leftarrow \text{system}$$

not fixed (exchange of energy)

- E_0 could be partitioned (divided) between the bath and the system in many ways. For each way, many microstates.

System	Bath	# Microstates
E_1	$E_0 - E_1$	$W_B(E_0-E_1, N_B, V_B)\cdot W_S(E_1, N, V)$
$\vdots$	$\vdots$	$\vdots$
E_i	$E_0 - E_i$	$W_B(E_0-E_i, N_B, V_B)\cdot W_S(E_i, V, N)$
$\vdots$	$\vdots$	$\vdots$

- For the <u>whole composite system</u>, the number of accessible microstates (E_0, N_0, V_0) is:

$$\underset{\text{whole system}}{W} = \underbrace{\sum_i}_{\text{sum over all possible partitions of } E_0 \text{ between the system and the heat bath}} W_B(E_0 - E_i, N_B, V_B) \cdot W_S(E_i, N, V)$$

$$= \sum_i W_B(E_0 - E_i) \cdot W_S(E_i) \quad = \text{a number for given } (E_0, V_0, N_0)$$

- When the whole (isolated) system is in "internal" equilibrium, i.e., the system and the heat bath are in equilibrium, we have <u>equal a priori probabilities</u>

$\Downarrow$

every microstate is equally probable

- <u>It follows that</u>†:

Prob. of finding the system in an <u>energy level</u> E_i (NOT a state!) $= \dfrac{W_B(E_0 - E_i) \cdot W_S(E_i)}{W}$

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† This is the same discussion in Ch. IV. Only ① becomes "the system".

Prob. of finding the system in <u>a state</u> of energy E_i

$$= P_i = \frac{W_B(E_0 - E_i)}{\underset{\text{a number}}{W}}$$

$$\therefore \boxed{P_i \propto W_B(E_0 - E_i)}$$

Check point!
- check if you follow the argument up to here, the rest is just arithmetics.

- Next, we want to get $W_B(E_0 - E_i)$

Since $E_i \ll E_0$‡, we <u>expand</u> $\ln W_B(E_0 - E_i)$ about E_0†:

$$\ln W_B(E_0 - E_i) \approx \underset{\text{some number}}{\ln W_B(E_0)} - E_i \underbrace{\left(\frac{\partial \ln W_B(E)}{\partial E}\right)_{E=E_0}}_{\frac{1}{kT}} + \underbrace{\cancel{\frac{1}{2} E_i^2 \left(\frac{\partial^2 \ln W_B(E)}{\partial E^2}\right)_{E=E_0}}}_{\approx 0} + \cdots$$

T = temp. of <u>heat bath</u>

≈ 0 by definition of heat bath

$$\approx \ln W_B(E_0) - \frac{E_i}{kT}$$

‡ Bath is huge!

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† $\ln W_B$ is a slowly varying function ⇒ easier to handle

$$\therefore \; W_B(E_0-E_i) = \underbrace{W_B(E_0)}_{\substack{\text{a number} \\ \text{independent of the} \\ \text{state of the system} \\ \text{(a constant)}}} \; \underbrace{e^{-E_i/kT}}_{\text{key result}}$$

$$\therefore \; \underset{\substack{\uparrow \\ \text{recall: talking about a state}}}{P_i} \propto W_B(E_0-E_i) \propto e^{-E_i/kT}$$

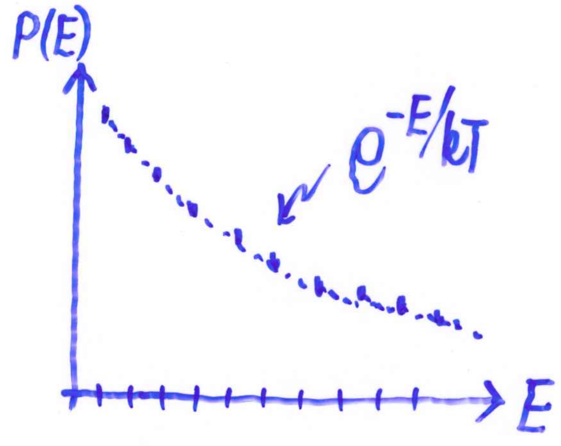
as claimed!

recall: talking about <u>a state</u>

OR $\boxed{P_i = \frac{1}{Z} e^{-E_i/kT}}$ → $P(E_i)$

where <u>Z is a normalization factor</u> called the <u>Partition function</u>

- Boltzmann distribution
- Canonical distribution



$P(E)$ = Prob. that the system shows up to be in <u>a state</u> of energy E

<u>Normalization:</u>

$$\underbrace{P_i}_{\text{talking about a state}} \propto e^{-E_i/kT} = C e^{-E_i/kT}$$

$$\sum_{\text{all states}} P_i = C \sum_{\text{all states}} e^{-E_i/kT} = 1$$

↳ all states of the N-particle system (all microstates of the N-particle system)

↖ The system must be in one of the states

$$\therefore \; C = \frac{1}{\sum_{\text{all states } i} e^{-E_i/kT}}$$

↖ now "i" labels the states, which may be degenerate

$$\therefore \; \boxed{P_i = \frac{e^{-E_i/kT}}{\sum_{\text{all states } i} e^{-E_i/kT}} = \frac{e^{-\beta E_i}}{\sum_{\text{all states } i} e^{-\beta E_i}}} \equiv \frac{1}{\underset{\substack{\uparrow \\ Z \text{ comes in} \\ \text{at this point}}}{Z}} e^{-\beta E_i}$$

- this is the normalized Boltzmann distribution
- $\beta \equiv \frac{1}{kT}$
- $e^{-E_i/kT}$ or $e^{-\beta E_i}$ is sometimes called the Boltzmann factor

Probability of a system showing up in an <u>energy level</u> of energy E_i

<u>note</u>: not a state

$$= \underbrace{W_s(E_i)}_{\#\text{ states with energy } E_i \text{ (i.e. degeneracy)}} \cdot P_i$$

$$= \underbrace{\frac{1}{Z}\underbrace{W_s(E_i)}_{\text{increases rapidly}^{+}\text{ with } E_i}\;\underbrace{e^{-E_i/kT}}_{\text{drops rapidly with } E_i}}_{\text{product: sharply peaked at some energy } \bar{E}}$$

+ E.g., recall ideal gas result

thus, at temp. T, highly probable that the system will be found with energy $\bar{E}$, although formally, there is no fixed E for the system! This energy is close to the mean energy $\langle E\rangle$ OR $\langle U\rangle$.

∴ We see how fixing T leads to <u>sharply defined $\langle U\rangle$</u>.

[c.f.: Mircocanonical ⇒ fixing U leads to a derived temp. T]

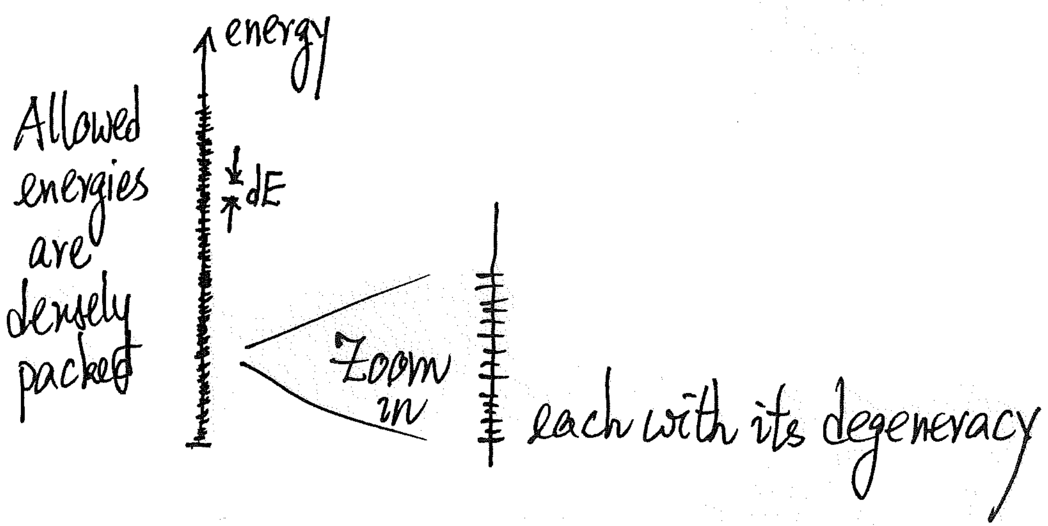
In <u>discrete</u> forms, i.e. allowed states and allowed energy levels are treated as discrete values

$$Z = Z(T,V,N) = \sum_{\text{all } \underline{\text{states}}\ i} e^{-E_i/kT} = \sum_{\text{all } \underline{\text{states}}\ i} e^{-\beta E_i}$$

$$= \sum_{\text{all } \underline{\text{levels}}\ i} W_s(E_i,V,N)\, e^{-E_i/kT} = \sum_{\text{all } \underline{\text{levels}}\ i} W_s(E_i,V,N)\, e^{-\beta E_i}$$

(discrete forms)

- For macroscopic systems, allowed E_i's are very close to each other ⇒ treat allowed E_i as continuous



$\underbrace{\mathcal{W}_s(E)}\,dE$ = # states (N-particle states) in the energy interval E to E+dE

Density of states [units: $\frac{1}{\text{energy}}$]

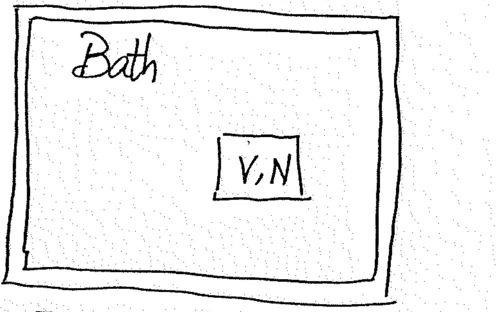
[a quantity we calculated in ideal gas]

Prob. of a system showing up with energy in E to E+dE

$$= \underbrace{\frac{1}{Z}e^{-E/kT}}_{\text{Prob. per state}}\ \underbrace{\mathcal{W}_s(E)\,dE}_{\#\ \text{states}} \qquad \left[\text{c.f. } W_s(E_i)\,\frac{e^{-E_i/kT}}{Z}\right]$$

$$Z(T,V,N) = \int_{\text{over all energies}} \mathcal{W}_s(E)\, e^{-E/kT}\, dE \qquad (\text{continuum form})$$

What have we done?

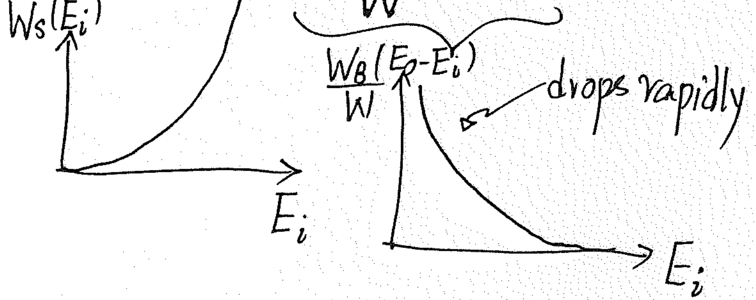


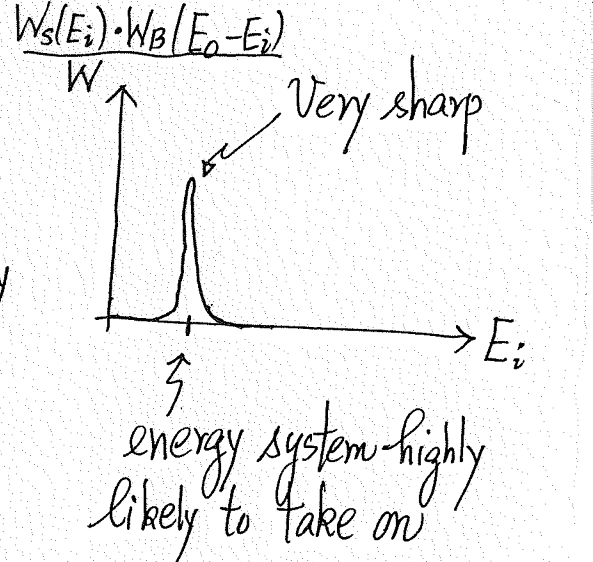
p. V⑦/Ch. IV

Prob. of finding system in an energy level E_i

$$= \frac{W_s(E_i)\cdot W_B(E_0-E_i)}{W}$$

$$= \underbrace{W_s(E_i)}\cdot\underbrace{\frac{W_B(E_0-E_i)}{W}}$$





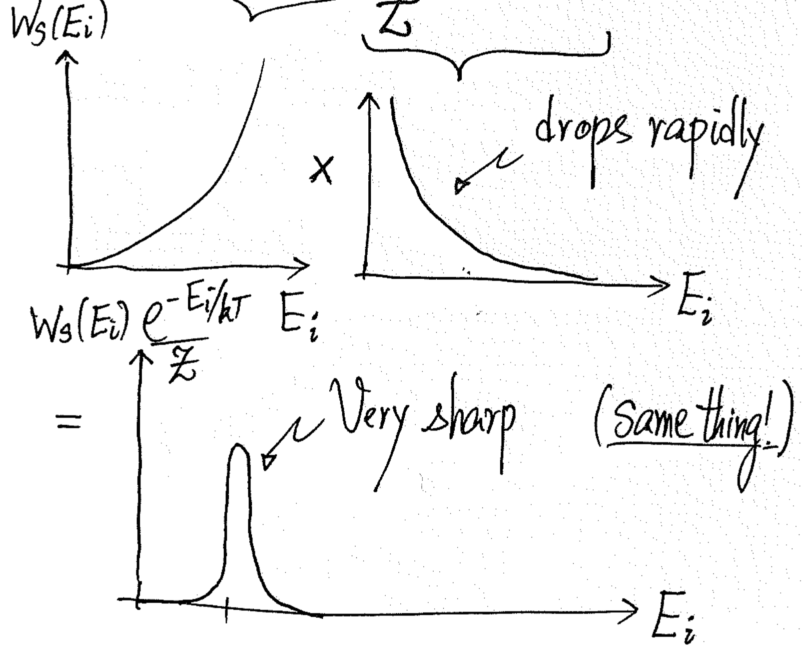
In terms of Boltzmann Distribution,

Prob. of finding system in an energy level E_i (when it is in equilibrium at a temp. T)

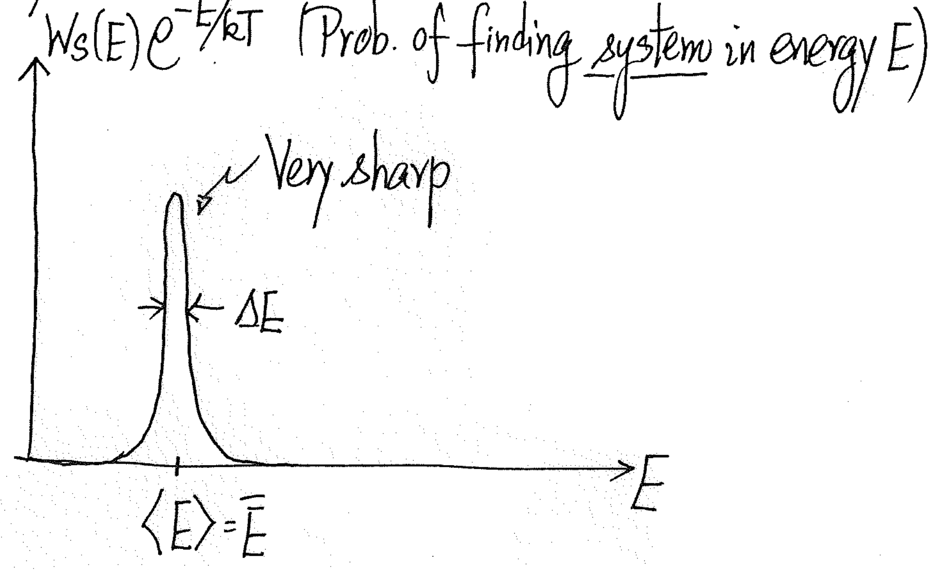
$$= \underbrace{W_s(E_i)}\cdot\underbrace{\frac{1}{Z}e^{-E_i/kT}}$$

∴ $\boxed{\text{Replaced } \frac{W_B(E-E_i)}{W} \text{ by } \frac{1}{Z}e^{-E_i/kT}}$

"T" is formally T_B, but at equilibrium T becomes system's temperature



One way or another:



Typically, $\frac{\Delta E}{\langle E\rangle} \sim \frac{1}{\sqrt{N}} \ll 1$ (tiny for macroscopic systems)

$\therefore$ Although formally the system does not have a fixed energy, it has a very sharp and thus representative mean (usually called $\langle E\rangle$ or $\bar{E}$). This is the U of the system in thermodynamics. Thermodynamics does not care about fluctuations of U. In Stat. Mech., only T is fixed by the bath and <u>E in system fluctuates</u>. But it is highly unlikely that E fluctuates away from $\langle E\rangle$.

Comparing $\frac{W_B(E_0-E_i)}{W}$ and $\underbrace{\frac{1}{Z}e^{-E_i/kT}}$

- shows explicitly how fast is the drop with E_i (a functional form)
- shows explicitly how fast is the drop as temperature T is lowed
- Bath's property is reflected by the temperature T
- Involves properties of the system $Z(T,V,N)$ as $\underbrace{E_i(N,V)}_{\text{N-particle Schrödinger problem}}$