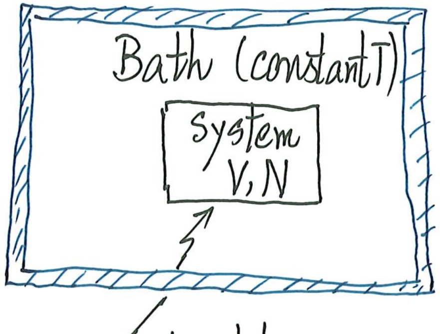
IX. System in Equilibrium with a Heat Bath and the Partition Function $Z(T,V,N)$

[Background: Ch. VIII Sec. J for two systems in Thermal Contact]

A. Physical Situation

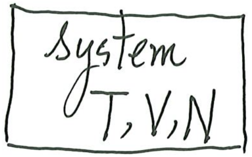


Bath is Huge!

even energy of bath goes in/out of system, bath's temperature doesn't change

wall allows energy exchange system and bath

At equilibrium†,



where T is T_b (temp. of bath)

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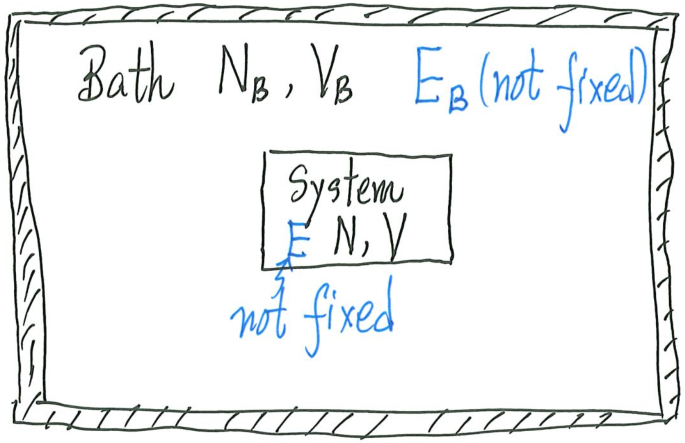
† With T, V, N, we aim to establish a theory of getting $F(T,V,N)$.

† As System and Bath exchange energy, system's energy is NOT fixed. Instead, energy fluctuates. But mean energy is well-defined and it plays the role of U in thermodynamics.

For an isolated[+] system at equilibrium, all microstates are equally probable.

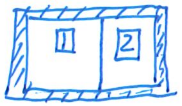
This is the "Only thing" we know!



$$\underset{\text{Fixed}^{+}}{E_0} = \overset{\text{not fixed}}{\underset{\text{energy of Bath}}{E_B}} + \overset{\text{not fixed}}{\underset{\text{energy of system}}{E}}$$

$\boxed{\text{exchange energy only}}$

N_B, V_B fixed ; N, V fixed (closed system)

(This is exactly the situation  in Ch. VIII Sec. J)

- E_0 can be distributed in any way between Bath and System.

E in system : $\underbrace{W_S(E, V, N)}_{\text{this is the } W(E,V,N) \text{ that goes into } S = k \ln W}$ microstates in System

$E_0 - E$ in bath : $W_B(E_0 - E, V_B, N_B)$ microstates in Bath

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[+] The Composite "System plus Bath" System forms an isolated system.

Immediately, we get an important result (see Eq. (23) in Ch. VIII)

$$\boxed{\text{Probability of finding } \boxed{\text{System}} \text{ to take on energy } E = \frac{W_S(E,V,N)\cdot W_B(E_0-E,V_B,N_B)}{W_{\text{total}}}} \tag{1}$$

Just a huge Constant

$$\propto W_S(E,V,N)\cdot \underbrace{W_B(E_0-E,V_B,N_B)}_{\text{explore this term and see how the bath control's the system's temperature}}$$

Meaning: Just having energy E, can be in any of $W_S(E,V,N)$ states of energy E

$\therefore \propto W_S(E,V,N)^{\dagger}$ makes sense!

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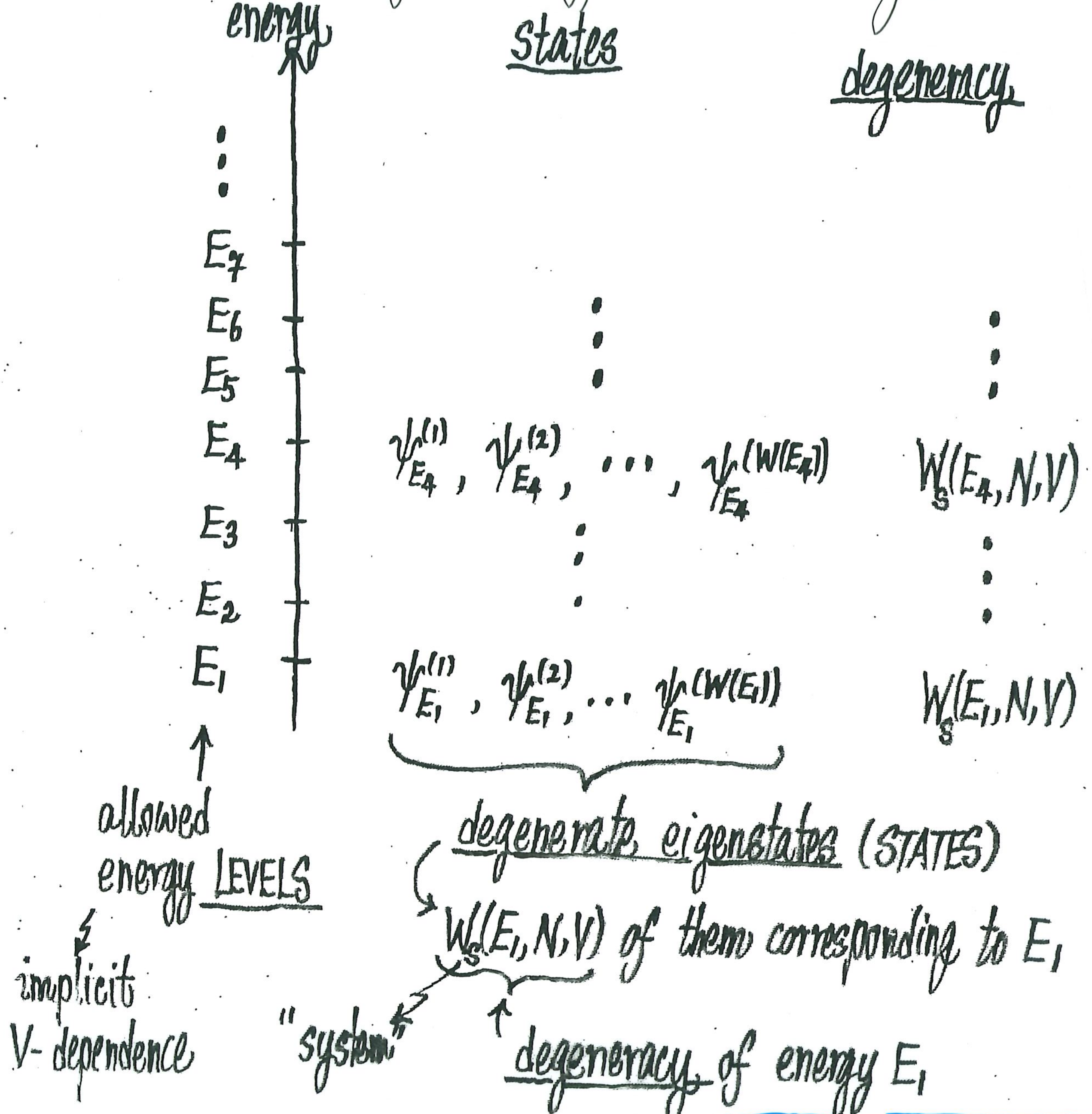
† Recall, Quantum Mechanically $W_S(E,V,N)$ is the degeneracy of energy E, after solving the Schrödinger Equation for the system's Hamiltonian (N-particle Hamiltonian).

Aside: System having an energy E_i versus System in a state of energy E_i

N-particle Problem

$$\hat{H}_N \psi = E \psi$$



B. Answer to a Key Question

Question: For a[+] (N-particle) state of energy E_i, what is the Probability P_i of finding the system in such a state when it is in thermal equilibrium with a heat bath at temperature T?

Answer:

$$\boxed{P_i \doteq \frac{\text{Prob. of finding system to take on energy } E_i}{W_S(E_i, V, N)} \propto W_B(E_0 - E_i, V_B, N_B)} \qquad (2)$$

Two tasks: $\begin{cases} \text{Rewrite } W_B(E_0 - E_i, V_B, N_B) \text{ in terms of bath's temperature} \\ \text{Find the normalization factor} \end{cases}$

[+] In English, "a state" means one state. Though trivial, this is an important point.

$$W_B(E_0 - E_i, V_B, N_B) = ?$$

$\underbrace{\text{Bath is huge}}$, (system is big (big enough for studying thermodynamics))

$E_i \ll E_0$ (Energy in bath dominates and $\underbrace{(E_0 - E_i)}_{\text{energy in bath}}$ is close to E_0)

$\ln W_B$ is a better behaving function to work with.

Expand $\ln W_B(E_0 - E_i, V_B, N_B)$ about E_0:

$$\ln W_B(E_0 - E_i, V_B, N_B) \approx \ln W_B(E_0, V_B, N_B) - E_i \overset{\frac{1}{k}\frac{\partial S_B}{\partial E}}{\left(\frac{\partial \ln W_B(E, V_B, N_B)}{\partial E}\right)_{E=E_0}} + \frac{1}{2}E_i^2 \left(\frac{\partial^2 \ln W_B(E, V_B, N_B)}{\partial E^2}\right)_{E=E_0}$$

$$= (\text{a number}) - \frac{E_i}{kT_B} + (\text{ignored})^{+}$$

formally, it is bath of temp.
[system/bath in equilibrium, it is also system's temp.]

+ The ignored term is $\frac{1}{2}E_i^2 \frac{1}{k}\frac{\partial}{\partial E}\left(\frac{1}{T}\right) = -\frac{E_i^2}{2T^2 C_V^{(B)} k}$
and $C_V^{(B)}$ is huge (extensive) for the bath

$$\ln W_B(E_0-E_i, V_B, N_B) = (\text{a number}) - \frac{E_i}{kT}$$

$$\therefore\ W_B(E_0-E_i, V_B, N_B) = (\overbrace{\text{another constant}}^{W_B(E_0, V_B, N_B)})\, e^{-E_i/kT}$$

$$\boxed{P_i \propto W_B(E_0-E_i, V_B, N_B) \propto e^{-E_i/kT}} \qquad (3)\ \ (\text{Key Result}^{+})$$

Must understand meaning of question

must also understand meaning

More likely for a state of small E_i than a state high E_i

(**Warning**: Don't jump to conclusion! Still need to consider how many N-particle states of energy E_i are there, i.e. $W_S(E_i, V, N)$)

[+] This is the famous Boltzmann Distribution. Basically, we are getting something big from "nothing", just all microstates are equally probable for an isolated system in equilibrium.

Normalization Gives the Partition Function

$$P_i = C\, e^{-E_i/kT}$$

a N-particle state

formally $\overbrace{E_i(V,N)}$

Hamiltonian: N particles in Volume V

system must be in one of the N-particle states

$$\underbrace{\sum_{\text{all N-particle states } i}}_{\text{meaning all states of all energies}} P_i = 1 = C \sum_{\substack{\text{all N-particle}\\ \text{states } i}} e^{-E_i/kT}$$

$$\therefore C = \frac{1}{\sum\limits_{\substack{\text{all N-particle}\\ \text{states } i}} e^{-E_i/kT}} = \frac{1}{Z(T,V,N)}$$

the partition function enters

Final Answers

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

$$= P_i = \frac{e^{-E_i/kT}}{Z(T,V,N)} = \frac{e^{-\beta E_i}}{Z(\beta,V,N)} \qquad (4) \qquad \beta \equiv \frac{1}{kT}$$

$$Z(T,V,N)^{+} = \text{Partition Function} = \sum_{\text{all N-particle states } i} e^{-\frac{E_i}{kT}} \qquad (5)$$

[It is just a number (no unit).]

Prob. of finding system to take on energy E_i

$$= \mathcal{P}_i = W_s(E_i,V,N)\cdot P_i = W_s(E_i,V,N)\cdot \frac{e^{-E_i/kT}}{Z(T,V,N)} \qquad (6)$$

also called Prob. of system showing up in an <u>Energy Level</u> of energy E_i

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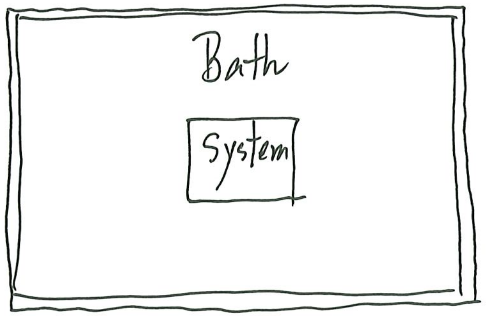
[+] Should understand where T, V, N are in $Z(T,V,N)$

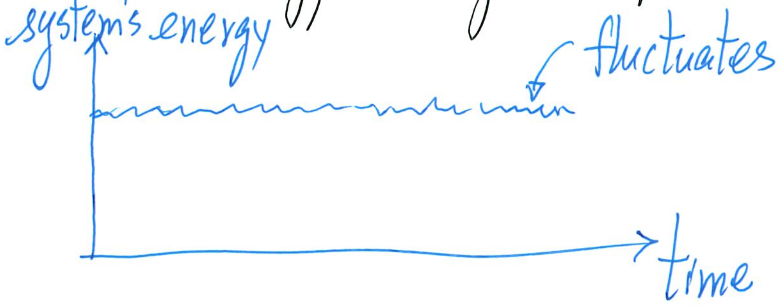
C. Key Physical Picture

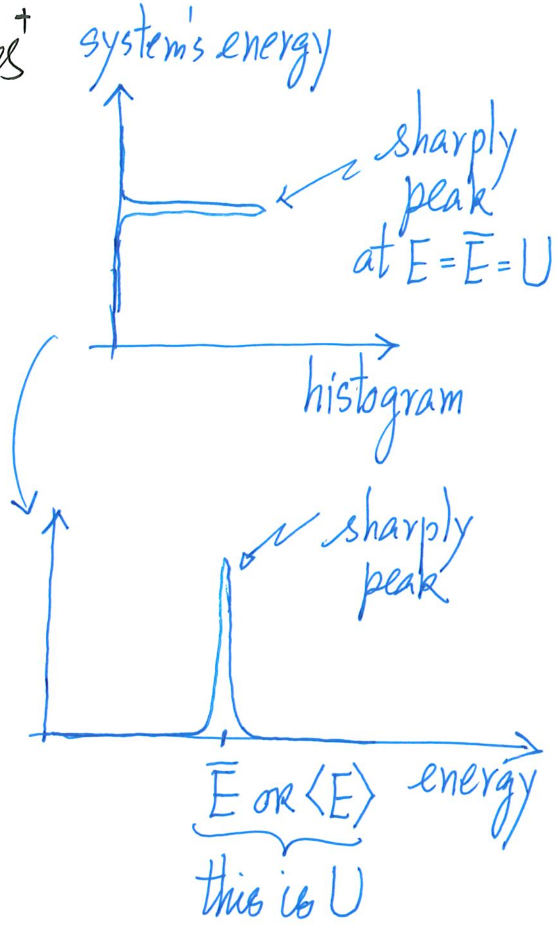
- Thermodynamics $\boxed{T, V, N}$ there is an internal energy $U(\underset{\Uparrow}{T})$

emphasizes T here (can also depend on V, N)

- 

Energy goes in/out of system
⇒ energy in system fluctuates[†]



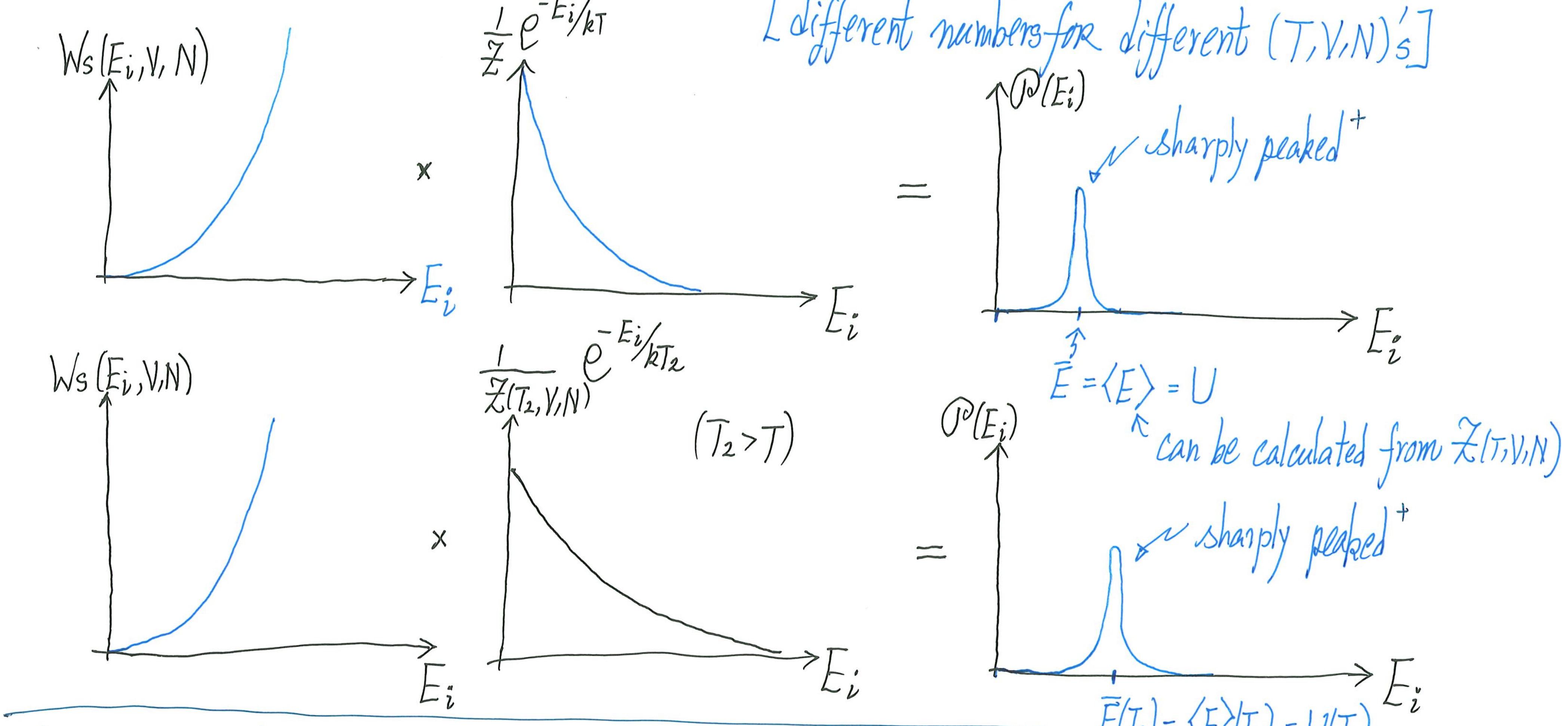


[†] When we talk about P_i or $\mathcal{P}_i$, we implicitly mean that the system can take on many values of energy. For system big enough for thermodynamic consideration, the mean energy $\langle E \rangle$ dominates and it is U in thermodynamics.

$$\mathcal{P}_i \equiv \mathcal{P}(E_i) = \underbrace{W_s(E_i,V,N)}_{\text{rapidly increasing with } E_i} \cdot \frac{e^{-E_i/kT}}{\underbrace{Z(T,V,N)}_{\text{a number for given } (T,V,N)}}$$

← dropping rapidly with E_i (for fixed T)

[different numbers for different (T,V,N)'s]



+ Macroscopic systems have sharp peaks that the widths are too narrow to draw.

D. Formulas of $Z(T,V,N)$

$$Z(T,V,N) = \sum_{\text{all N-particle states } i} e^{-E_i/kT} \qquad (5)$$

the sum is over states (including each of degenerate states)

If we group the degenerate states together, i.e.

$$\underbrace{W_s(E_i,V,N)\text{ different states corresponding to same energy } E_i}_{W_s(E_i,V,N)\text{ terms of } e^{-E_i/kT}\text{ in Eq.(5)}}$$

$$\boxed{Z(T,V,N) = \sum_{\text{all energy levels } i} W_s(E_i,V,N)\, e^{-E_i/kT} \qquad (7)}$$

the sum is over all different N-particle energies

Aside: Let's say a system has 11 states

states i : 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11

energy : $\underbrace{E_0}_{1}, \underbrace{E_1, E_1}_{2}, \underbrace{E_2, E_2, E_2}_{3}, \underbrace{E_3, E_3, E_3, E_3, E_3}_{5}$

degeneracy

$\left(\beta = \frac{1}{kT}\right)$

Using Eq.(5), $Z = e^{-\beta E_0} + e^{-\beta E_1} + e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_2} + e^{-\beta E_2} + e^{-\beta E_3} + e^{-\beta E_3} + e^{-\beta E_3} + e^{-\beta E_3} + e^{-\beta E_3}$

$= \sum_{\text{all 11 states } i} e^{-E_i/kT}$ (thus 11 terms)

Using Eq.(7), the sum is over the 4 different energies E_0, E_1, E_2, E_3

$$Z = \sum_{\text{4 different energies}} W_s(E_i)\, e^{-E_i/kT} = e^{-\beta E_0} + 2e^{-\beta E_1} + 3e^{-\beta E_2} + 5e^{-\beta E_3}$$

the result is, of course, the same

When the N-particle energies are densely packed, we can invoke

$$\underbrace{\mathcal{W}(E,V,N)}_{\text{Density of (N-particle) states}} dE = \text{Number of N-particle states with energies in the interval } E \text{ to } E+dE$$

$$\boxed{Z(T,V,N) = \int \mathcal{W}(E,V,N)\, e^{-E/kT}\, dE} \qquad (8)$$

Eqs. (5), (7), (8) [and (9)] are equivalent.

Ex: In Ch. VIII, we found $\mathcal{W}(E,V,N)$ for classical ideal gas, using that result to find $Z(T,V,N)$ for a classical ideal gas.

<u>A fully quantum form:</u> $\hat{H}_N$ = N-particle Hamiltonian

Schrödinger Equation $$\hat{H}_N |i\rangle = \underbrace{E_i}_{\text{energy eigenvalue}} \; \underbrace{|i\rangle}_{\text{symbol for energy eigenstate}}$$

$e^{-\beta \hat{H}_N}$ is a function of the Hamiltonian $\hat{H}_N$

$$e^{-\beta \hat{H}_N} |i\rangle = e^{-\beta E_i} |i\rangle, \quad \text{thus} \quad \langle i| e^{-\beta \hat{H}_N} |i\rangle = e^{-\beta E_i} \overbrace{\langle i|i\rangle}^{\overset{\text{(normalized } |i\rangle)}{1} \,\|} = e^{-\beta E_i}$$

$$Z = \sum_{\text{all N-particle states } i} e^{-\beta E_i} = \sum_{\{|i\rangle\}} \langle i| e^{-\beta \hat{H}_N} |i\rangle = \sum_{\text{"basis } \{|i\rangle\}\text{"}} \text{diagonal matrix elements} \left(e^{-\beta \hat{H}_N}\right)_{ii}$$

$$\boxed{Z(T,V,N) = \underbrace{Tr}_{\text{trace}} \, e^{-\beta \hat{H}_N}} \qquad (9)$$

"free of representation"

∴ can evaluate "Trace" using any other basis set of functions, not only energy eigenstates $\{|i\rangle\}$

E. $Z(T,V,N)$ gives all other thermodynamic quantities

(a) Mean Energy $\langle E\rangle$

$$\langle E\rangle = \sum_{\text{all N-particle states } i} E_i\, P_i \quad \text{(by definition)} \quad = \sum_{i} E_i\, \frac{e^{-E_i/kT}}{Z}$$

→ i : short-hand when there is no confusion

$$= \frac{\sum_i E_i\, e^{-E_i/kT}}{\underbrace{\sum_i e^{-E_i/kT}}_{\text{this is } Z}} = \frac{\sum_i E_i\, e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \overset{\text{key step}}{=} -\frac{\partial}{\partial\beta}\left[\ln\left(\sum_i e^{-\beta E_i}\right)\right] \qquad \left(\beta \equiv \frac{1}{kT}\right)$$

$$\therefore \boxed{\langle E\rangle = -\left(\frac{\partial}{\partial\beta}\left(\ln Z(T,V,N)\right)\right)_{V,N} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial\beta}\right)_{V,N}}$$

this is $U(T,V,N)$ in thermodynamics

[this is also where $\mathcal{P}(E_i)$ peaks]

(b) $F(T,V,N) = -kT \ln Z(T,V,N)$

- Many ways to obtain this relation
- Take advantage of our background in thermodynamics

Know $\langle E \rangle = U = -\left(\frac{\partial}{\partial \beta} \ln Z\right)_{V,N} = kT^2 \left(\frac{\partial}{\partial T} \ln Z\right)_{V,N}$

Question: What is the quantity in thermodynamics that gives

$$U = kT^2 \left(\frac{\partial}{\partial T}[??]\right)_{V,N} \quad ?$$

Hint: We have been working with (T, V, N), they are the natural variables of the Helmholtz free energy $F(T,V,N)$. May be [??] has F in it.

$\beta = \frac{1}{kT}$, $\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial}{\partial T} = -kT^2 \frac{\partial}{\partial T}$

$$(F = U - TS)$$

Try $$d\left(\frac{F}{T}\right) = \frac{1}{T}dF - \frac{F}{T^2}dT = \frac{1}{T}(dU - TdS - SdT) - \frac{F}{T^2}dT$$

$$= \frac{1}{T}\left(\cancel{TdS} - pdV + \mu dN - \cancel{TdS} - SdT\right) - \frac{(U - TS)}{T^2}dT$$

$$= -\frac{p}{T}dV + \frac{\mu}{T}dN - \cancel{\frac{S}{T}dT} - \frac{U}{T^2}dT + \cancel{\frac{S}{T}dT}$$

$$\therefore \quad \frac{U}{T^2} = -\left(\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right)_{V,N}$$

$$\Rightarrow U = -kT^2\left(\frac{\partial}{\partial T}\left(\frac{F}{kT}\right)\right)_{V,N} = kT^2\left(\frac{\partial}{\partial T}\overbrace{\left(\frac{-F}{kT}\right)}^{\text{this is what we are looking for!}}\right)_{V,N}$$

$$\therefore \quad \boxed{F(T,V,N) = -kT \ln Z(T,V,N)}$$

macroscopic
(thermodynamics)

microscopic (need all N-particle states)
(statistical mechanics)

Since $dF = -S\,dT - p\,dV + \mu\,dN$ (thermodynamics, Legendre Transform of U)

it follows that once we obtain $F(T,V,N)$ from $-kT\ln Z(T,V,N)$, then

$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \; ; \quad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} \; ; \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\left(\frac{\partial \ln Z}{\partial N}\right)_{T,V}}$$

$\because$ $F = U - TS = \langle E\rangle - TS$, a short cut to the entropy S is

$$S = \frac{\langle E\rangle - F}{T} \qquad \text{with } \langle E\rangle = -\left(\frac{\partial}{\partial\beta}\ln Z\right)_{V,N} \text{ and } F = -kT\ln Z$$

This calculation scheme, $Z = \sum_i e^{-E_i/kT} \rightarrow F(T,V,N) = -kT\ln Z(T,V,N) \longrightarrow$ take derivatives to get $\langle E\rangle$, S, P, μ, is called the Canonical Ensemble Approach.