G. The Partition Function Z

Define: Z = Partition Function

$$\boxed{Z(T,V,N) \equiv \sum_{\text{all states } i} e^{-\beta E_i} \qquad \text{where } \beta = \frac{1}{kT}}$$

- Z comes from "Zustandssumme", meaning "sum over states".
- It is the quantity that normalizes P_i
- $Z(T,V,N)$

$$\begin{cases} T \text{ comes in from } \beta = \frac{1}{kT} \\ E_i \text{ refers to a } N\text{-particle system} \Rightarrow N \text{ comes in} \\ V \text{ affects } E_i \end{cases}$$

- Z plays the central role in doing stat. mech. calculations

Why?

Key relation → (see later)

$$\boxed{F(T,V,N) = -kT \ln Z(T,V,N) = -\frac{1}{\beta} \ln Z(T,V,N)}$$

Knowing $F(T,V,N)$, other quantities can be obtained by taking derivatives!

$$Z = \underbrace{\sum_{\text{all states } i}}_{\text{sum over states (including states with the same energy)}} e^{-\beta E_i}$$

e.g. A system with 11 states of possibly different energies[+]

state i =	1	2	3	4	5	6	7	8	9	10	11
	↕	↕	↕	↕	↕	↕	↕	↕	↕	↕	↕
energy	E_0	E_1	E_1	E_2	E_2	E_2	E_3	E_3	E_3	E_3	E_3
degeneracy	1	2		3			5				

$$Z = e^{-\beta E_0} + 2e^{-\beta E_1} + 3e^{-\beta E_2} + 5e^{-\beta E_3} = \sum_{i=1}^{11} e^{-\beta E_i}$$

If we want to turn $\sum_{\text{all states}}$ into $\sum_{\text{levels}}$, then

$$Z = \sum_{\text{energy levels}} \underbrace{W_s(E_i)} e^{-\beta E_i}$$

↑ degeneracy of level E_i

↑ number of states with energy E_i

[+] See figure on next page

e.g. 11 states / 4 energy levels

Energy		W(E_i) [Degeneracy]
E_3	7 8 9 10 11	5
E_2	4 5 6	3
E_1	2 3	2
E_0	1	1

$$Z = \underbrace{\sum_{\text{all states } i}}_{\text{over 11 states one-by-one!}} e^{-\beta E_i}$$

$$= \underbrace{\sum_{\text{all energy levels } i}}_{\text{over the 4 different levels}} \overset{\text{but need to include } W(E_i)}{\overbrace{W(E_i)}} e^{-\beta E_i}$$

⌜. A little bit of QM:

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

Schrödinger Equation:

$$\hat{H}_N |i\rangle = E_i |i\rangle$$ "free of representation"

$$\therefore\ Z(T,V,N) = \sum_{\{|i\rangle\}} \langle i| \underbrace{e^{-\beta\hat{H}}|i\rangle}_{e^{-\beta E_i}|i\rangle} \leftarrow$$ sum over diagonal (ii) elements of a matrix

⇓

Trace of a matrix

$$= \underbrace{Tr}_{\text{trace}}\ e^{-\beta\hat{H}}$$ ← free of representation

[An alternative way to write Z] ⌟

$$\therefore\ \boxed{Z(T,V,N) = Tr\ e^{-\beta\hat{H}}}$$

- is an abstract way of writing Z,
- and one can then use any convenient basis to express the trace.

H. Averages

- A is a physical quantity
- Let A take on the value A_i in state i of the system

- $\langle A\rangle$ = Mean (average) value of A

$$= \sum_i A_i P_i = \frac{1}{Z}\sum_i A_i e^{-\beta E_i}$$

over states

Remarks:

- In QM language, an operator $\hat{A}$ is associated with a physical observable, the quantum statistical average is:

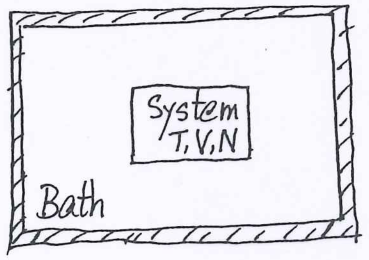
$$\langle A\rangle = \frac{\sum_i \langle i|\hat{A}|i\rangle e^{-\beta E_i}}{Z}$$

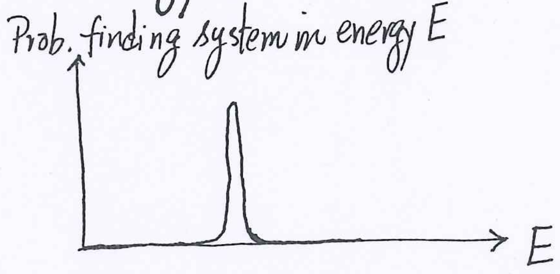
where $|i\rangle$ is a state with energy E_i

- Two kinds of average are involved:
  - $\langle i|\hat{A}|i\rangle$ is the expectation value of quantity $\hat{A}$ given the system is in a state $|i\rangle$ (quantum)
  - $\frac{1}{Z}\sum_i e^{-\beta E_i}(\dots)$ is a statistical mechanical average.

I. Mean Energy of System

- fixed temperature, but energy is not fixed





- Very sharp, but not a δ-function (fixed E)
- With a spread ⇒ fluctuations in energy

What is the mean of energy?

$$\langle E\rangle = \frac{1}{Z}\sum_i E_i e^{-\beta E_i} \qquad \left(\sum_i = \sum_{\text{all states } i}\right)$$

$$= -\frac{1}{Z}\left(\frac{\partial}{\partial\beta}\underbrace{\sum_i e^{-\beta E_i}}_{Z}\right)_{V,N}$$

This becomes U in thermodynamics

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

Formula of $\langle E\rangle$ directly from $Z(T,V,N)$

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

This is not difficult to see that $\langle E\rangle = \bar{E}$, where the prob. peaks.

Recall:

Microcanonical Ensemble

fixed E (E, V, N)

$\uparrow$ or U in thermodynamics

In equilibrium with heat bath

"canonical ensemble"

(T, V, N)

fixed T

But physics is physics!

For macroscopic systems, don't expect results to depend on the calculation scheme.

This will be the case if $U=\langle E\rangle$ is very sharp[+], i.e., $\underbrace{\text{very unlikely}}_{\text{tiny chance}}$ to fluctuate away from U by much!

∴ We need to examine the spread in the distribution of E, i.e., ΔE.

- In microcanonical ensemble, no fluctuations in E as E is fixed.

[+] Meaning: If one observes the system, it is almost always in some states at the energy $\bar{E}=\langle E\rangle$. Why? This partition of energy $\bar{E}$ to the system is dominant in the number of microstates. Thus, in equilibrium, we say that a system has an energy U or $\langle E\rangle$ in thermodynamics.

J. Relating $\ln Z$ to thermodynamics: A short cut[+]

Know that

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

$$= kT^2\left(\frac{\partial}{\partial T}\ln Z\right)_{V,N} \qquad \left(\because \beta=\frac{1}{kT}\right)$$

This is what we call the energy E of a system in thermodynamics

- Writing it as E, we have

$$E = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N} \qquad \text{(statistical mechanics)}$$

- Question:

  In thermodynamics, what is the quantity that gives

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

[+] This is the simplest way to connect Z to thermodynamics, assuming a basic knowledge in thermodynamics.

Motivation: $\underbrace{Z(T,V,N)}_{\text{note the variables}}$

- In thermodynamics, T, V, N are the natural variables of Helmholtz free energy $F(T,V,N)$
- Recall: $F = E - TS$ (Legendre Transform)

$$dF = dE - TdS - SdT = -SdT - pdV + \mu dN$$

- Consider

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

$$= \frac{1}{T}(-SdT - pdV + \mu dN) - \frac{(E-TS)}{T^2}dT$$

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

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

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

$$\Rightarrow \boxed{E = kT^2\left(\frac{\partial}{\partial T}\left(\frac{-F}{kT}\right)\right)_{V,N}}$$ from thermodynamics

But from Stat. Mech.

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

Comparing results:

$$-\frac{F}{kT} = \ln Z$$

$$\Rightarrow \boxed{F = -kT\ln Z}$$ Key Result

Explicitly,

$$\boxed{\underset{\substack{\uparrow\\ \text{thermodynamics}\\ \text{(macroscopic)}}}{F(T,V,N)} \ \underset{\substack{\uparrow\\ \text{bridge}}}{=} \ \underbrace{-kT\ln Z(T,V,N)}_{\substack{\text{stat. mech.}\\ \text{(microscopic)}}}}$$

Together with $dF = -SdT - pdV + \mu dN$

$\Rightarrow$ all thermodynamic quantities

Z(T,V,N) gives F(T,V,N), and thus everything.

$$\boxed{F(T,V,N) = -kT \ln Z(T,V,N) = -\frac{1}{\beta}\ln Z}$$

OR
$$Z(T,V,N) = e^{-\beta F(T,V,N)}$$

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

- For given (T,V,N), if we know F(T,V,N), then everything follows immediately!

$$dF = -S\,dT - p\,dV + \mu\,dN$$

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

- In equilibrium, F is a minimum

Since $F = E - TS$, $\boxed{S = \frac{E-F}{T}}$ ← a short cut of getting S

K. Spread in Energy ΔE / Fluctuations in Energy

$$P_i = \frac{1}{Z}e^{-\beta E_i} \;;\quad \langle E\rangle = \sum_i E_i P_i = \frac{1}{Z}\sum_i E_i e^{-\beta E_i}$$

first moment of distribution

$$\langle(\Delta E)^2\rangle \equiv \sigma_E^2 = \langle(E - \langle E\rangle)^2\rangle \quad \text{(definition)}$$

deviation from mean squared

Variance in energy

$$= \langle E^2 - 2E\underbrace{\langle E\rangle}_{\text{a number}} + \underbrace{\langle E\rangle^2}\rangle$$

$$= \langle E^2\rangle - 2\langle E\rangle^2 + \langle E\rangle^2$$

$$\Rightarrow \boxed{\langle(\Delta E)^2\rangle = \sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2}$$

Spread is measured by the standard deviation σ_E

$$\Delta E \equiv \sigma_E = \sqrt{\langle E^2\rangle - \langle E\rangle^2}$$

↑ already calculated by $\langle E\rangle = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_{V,N}$

∴ Need to get $\langle E^2\rangle$

By definition,

$$\langle E^2 \rangle = \frac{1}{Z}\sum_i E_i^2\, e^{-\beta E_i}$$

$$= \frac{1}{Z}\left[\frac{\partial^2}{\partial\beta^2}\left(\sum_i e^{-\beta E_i}\right)\right]$$

$$\langle E^2 \rangle = \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial \beta^2}\right)_{V,N}$$

a formula of getting $\langle E^2\rangle$ from Z

$$\therefore\ (\Delta E)^2 = \langle E^2\rangle - \langle E\rangle^2$$

$$= \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 \qquad \text{(constant } V, N\text{)}$$

$$= \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)_{N,V}$$

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

$$(*)\rightarrow\ = -\left(\frac{\partial U}{\partial \beta}\right)_{N,V}$$

$$\beta = \frac{1}{kT}\ ;\quad \frac{dT}{d\beta} = -kT^2$$

$$= -\left(\frac{\partial U}{\partial T}\right)_{N,V}\frac{dT}{d\beta}$$

$$(*)\rightarrow\ = kT^2\left(\frac{\partial U}{\partial T}\right)_{N,V}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \text{System's heat capacity at constant volume} \geq 0$$

$$(*)\rightarrow\ = kT^2 C_V$$

Useful in getting $(\Delta U)^2$ or C_V

$$\therefore\ \boxed{(\Delta E)^2 = kT^2 C_V} \Rightarrow \boxed{\Delta E = \sqrt{kT^2 C_V} = \sigma_E}$$

$$\Delta E = \sqrt{k\underset{\uparrow\,\text{intensive}}{T^2}\,C_V} \leftarrow \underbrace{\text{extensive}}_{C_V\sim N} \sim \sqrt{N}$$

Relative energy fluctuation

$$\frac{\Delta E}{\langle E\rangle} = \frac{\sqrt{kT^2 C_V}}{\underset{\nwarrow\,\text{extensive}}{\langle E\rangle}} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

measures how representative $U = \langle E\rangle$ is.

$\therefore\ \dfrac{\Delta E}{\langle E\rangle} \sim \dfrac{1}{\sqrt{N}} \ll 1$ for systems with large N

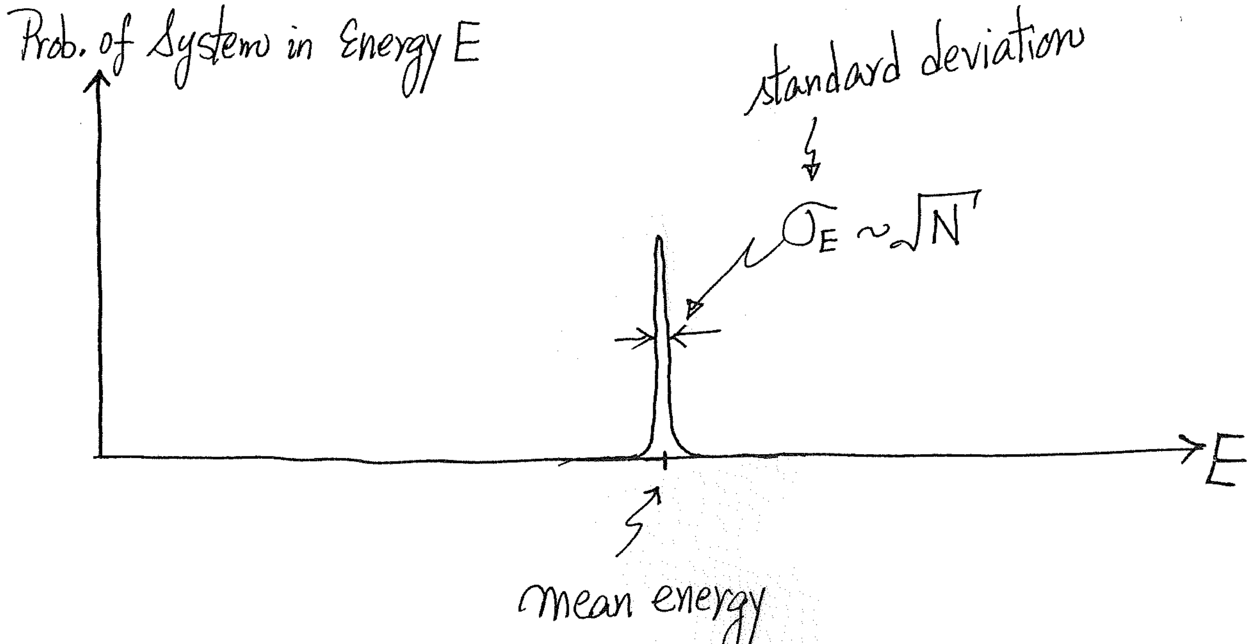
For macroscopic systems ($N \sim 10^{23}$) where we can talk about thermodynamics, $\dfrac{\Delta E}{E} \ll 1$

$\Rightarrow$ system is highly unlikely to have E fluctuates far away from $\langle E\rangle$ or U (in thermodynamics language)

$\Rightarrow$ system, although formally does not have a fixed E, behaves as if it has a definite U.

$\therefore$ For macroscopic system ($N \gg 1$), talking about a fixed U (microcanonical) or a highly representative $\langle E\rangle$ (canonical) leads to the same results (as it should be).

Picture:



$\langle E\rangle$ is extensive $\propto N$

$$\frac{\sigma_E}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

×

Remark

$$(\Delta E)^2 = \underbrace{kT^2 C_V = \langle E^2\rangle - \langle E\rangle^2}_{\text{provides a way to calculate } C_V \text{ by numerical simulations}}$$

↳ Easier to get $\langle E\rangle$ and $\langle E^2\rangle$ from simulation data

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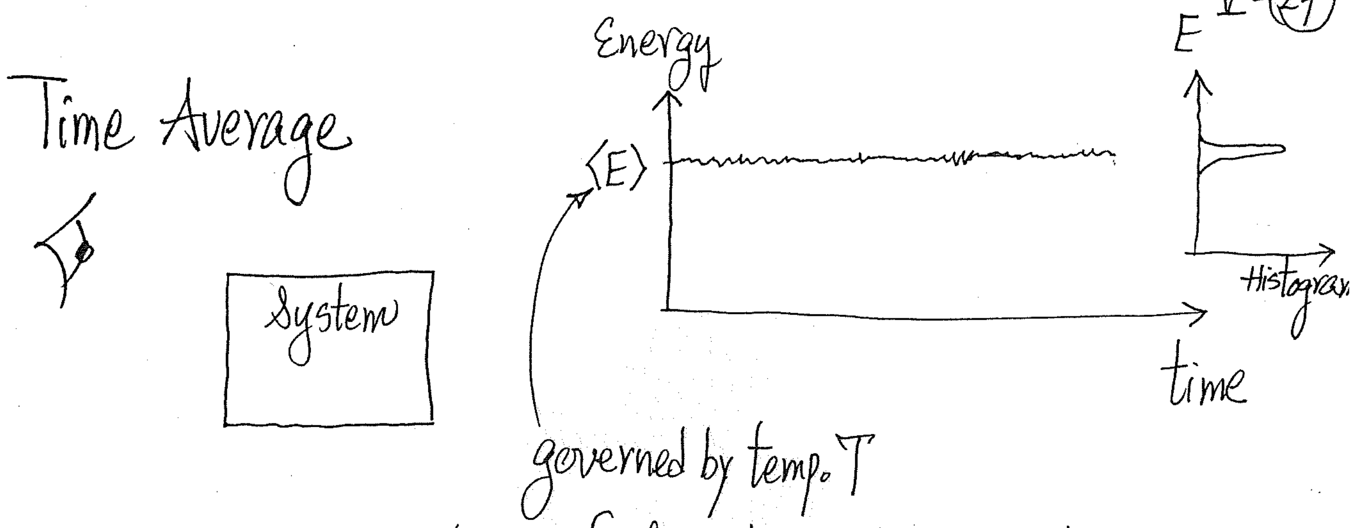
L. Canonical Ensemble

- Time averge Vs $\underbrace{\text{Ensemble average}}_{\text{properly choose members of the collection}}$
- When an ensemble is constructed according to $P_i = \frac{1}{Z} e^{-E_i/kT}$ (i.e. choosing a state of energy E_i as member based on P_i), the ensemble is called the canonical ensemble.

Note: Microcanonical: Members are all of the Same Energy

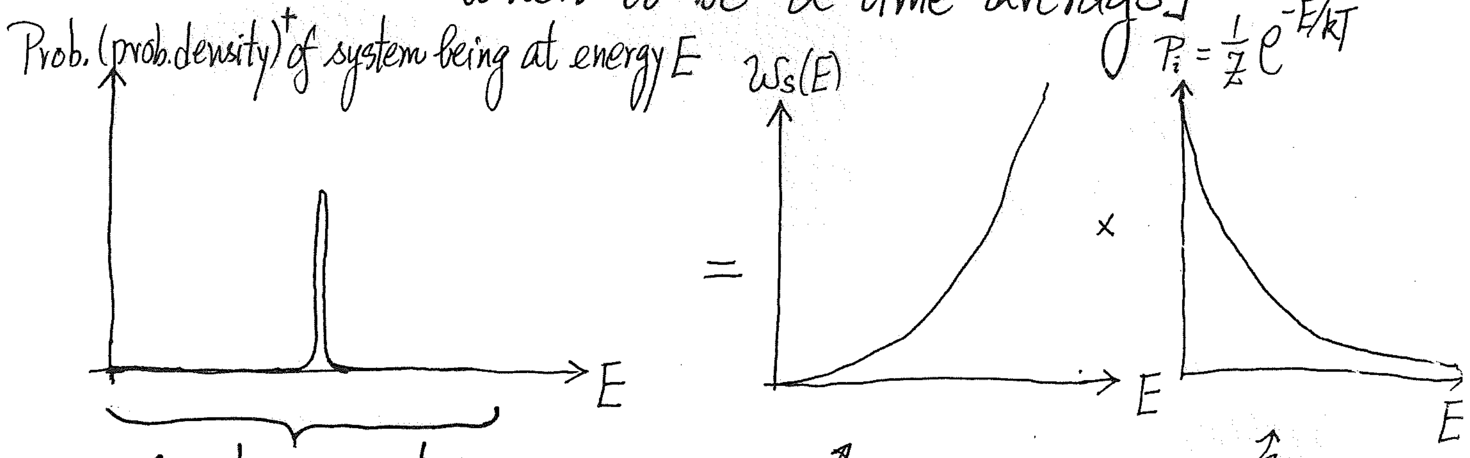
Canonical: Members cover different energies
Many members with $\langle E\rangle$
A few deviate from $\langle E\rangle$

Time Average



Energy of System : { Spend most time at ⟨E⟩
Sometimes deviate from ⟨E⟩

[Quantities taken to be a time average]



Can be viewed as...

doesn't depend on temperature

temperature dependent

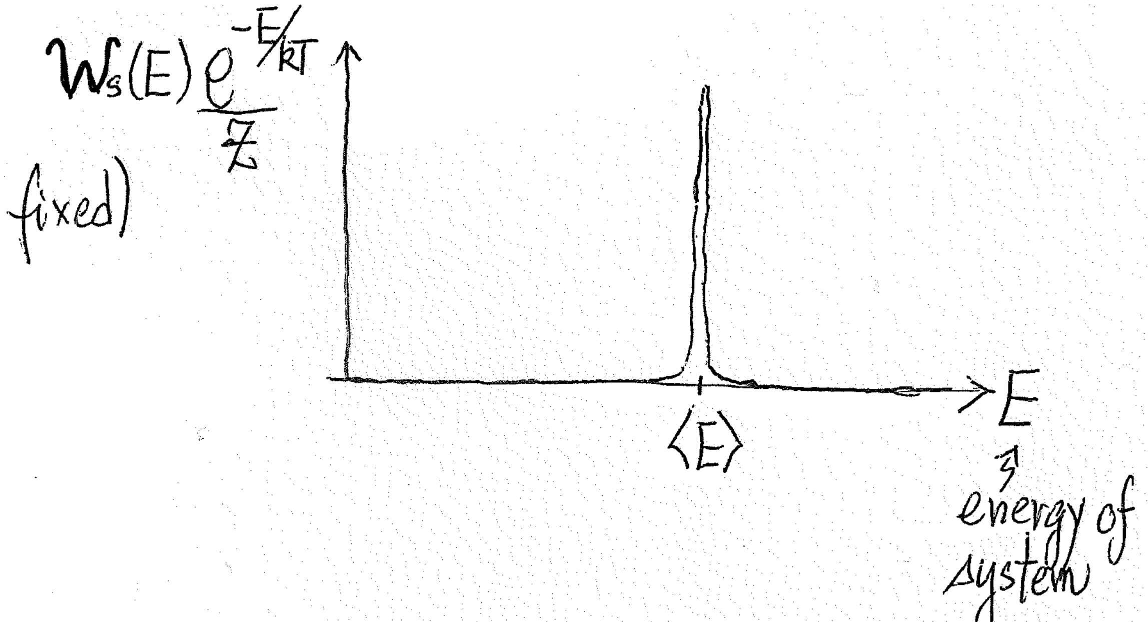
- Go through every state of any energy
- Accept a state of energy E as a member based on the probability $\frac{1}{Z} e^{-E/kT}$
- Collection forms canonical ensemble

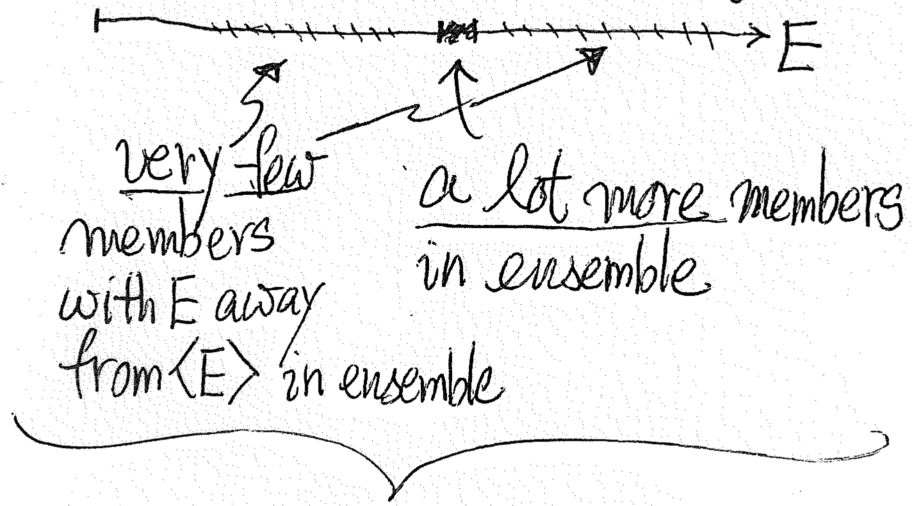
Time average is replaced by ensemble average

\+ The prob. density is invoked when E is taken as a continuous variable

- Canonical ensemble

(T is fixed)





Importance Sampling

- Contrast with only including members with a fixed energy E in microcanonical ensemble.

Importance Sampling

- Members (systems) of different energies are unevenly represented in the ensemble
- Members of energy E have a weight $\propto W_s(E)\, e^{-E/kT}$ in ensemble
- Useful in numerical studies of systems that cannot be solved analytically

How to sample states as required?

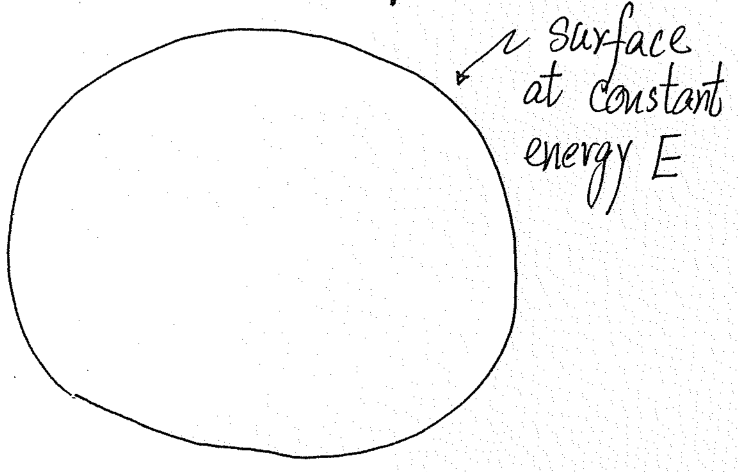
[Metropolis' Monte Carlo method[†]]

Remark

The term "Canonical Ensemble" is now often used to refer to the calculation scheme based on $Z(T,V,N)$ for a system of N particles and Volume V at equilibrium at a temperature T.

[†] N. Metropolis, "Equations of state calculations by fast computing machines", J. Chem. Phys. 21, 1087 (1953).

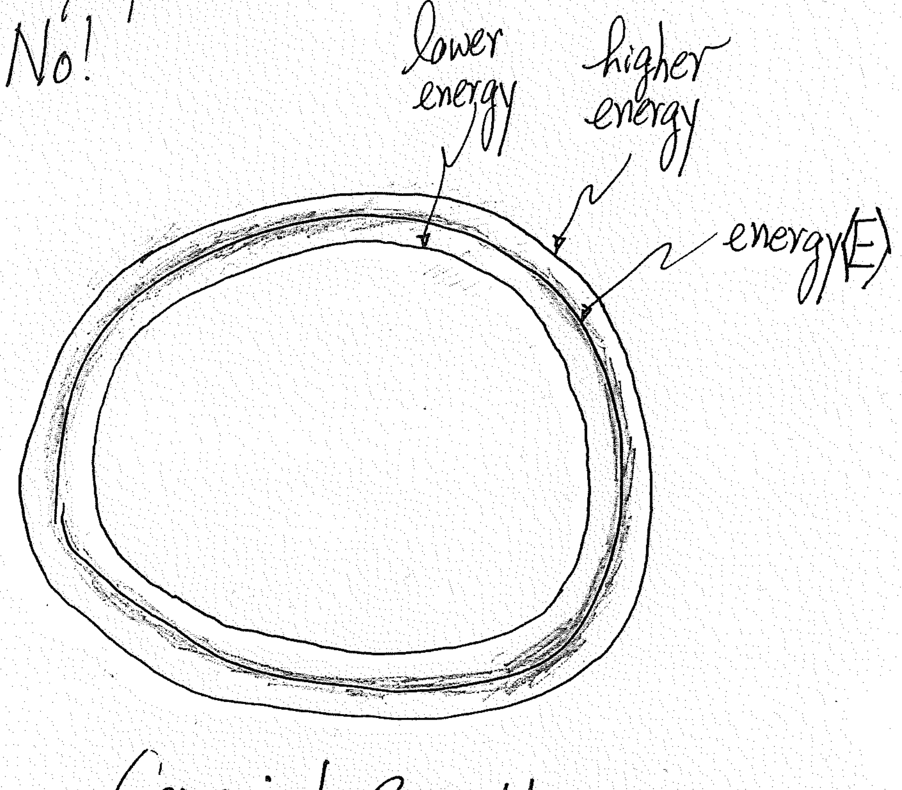
Phase space pictures



Microcanonical Ensemble (E, V, N)

[Only states at energy E are included and they are evenly represented]

higher/lower energy? No!



Canonical Ensemble

- States at different energies are included based on $\frac{1}{Z} e^{-E/kT}$

M. Does Gibbs entropy formula work?

- We saw $S = -k\sum_i P_i \ln P_i$ (Gibbs entropy formula)

  works in microcanonical ensemble where $P_i = \frac{1}{W}$

  It gives $S = k\ln W$ (microcanonical)

- We know that in canonical ensemble,

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

  Recall $F = E - TS$

  $\therefore\ S = \frac{E}{T} - \frac{F}{T} = \frac{E}{T} + k\ln Z$

- Question:
  - We have $P_i = \frac{1}{Z} e^{-\frac{E_i}{kT}}$ as the probability of having a state of energy E_i as a member in the canonical ensemble given (T,V,N)
  - $\boxed{\text{Does } -k\sum_i P_i \ln P_i \text{ give } S\ ?}$

    over all states i

Check: $\ln P_i = -\frac{E_i}{kT} - \ln Z$

$$-k\sum_i P_i \ln P_i = \frac{1}{T}\sum_i E_i P_i + k\ln Z$$
$$= \frac{\langle E\rangle}{T} + k\ln Z$$
$$= \frac{\langle E\rangle}{T} - \frac{F}{T} = \underbrace{S}_{\text{entropy}}$$

$\therefore\ S = -k\sum_i P_i \ln P_i$ works!

- In fact, the Gibbs Entropy formula works for any ensemble when members of the ensemble are selected according to a probability P_i

N. Canonical Ensemble : Recipe

$$Z = \sum_{\text{all states } i} e^{-E_i/kT} = Z(T,V,N)$$ normalizes $P_i = \frac{1}{Z} e^{-E_i/kT}$

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

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{U}{T} + k \ln Z$$

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta}(\beta F)$$

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

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

$$S = -k \sum_i P_i \ln P_i$$ a general expression for entropy

$$Z = \mathrm{Tr}\, e^{-\beta H}$$ a general way to write Z [free of representation]

O. Remarks:

- When is the scheme good?

Ans.: Always good! (if we are sufficiently careful!)

$$Z = \sum_{\text{all states } i} e^{-E_i/kT}$$

of N-particle system

sum includes $\underbrace{\text{all states that are allowed by physics!}}_{\substack{\text{must be very careful in deciding} \\ \text{the states to be included in the sum}}}$

- Easiest case: $\underbrace{\text{Distinguishable}}_{\substack{\text{easier to count} \\ \text{the states to include} \\ \text{in } \sum_i}}$ $\underbrace{\text{Non-interacting}}_{\substack{\text{easier to} \\ \text{get } E_i}}$ Particles

[readily handled by anlytical ways]

- Slightly harder case: Indistinguishable Non-interacting Particles

Indistinguishable ⇑ much harder to list the states to be included in the sum

Non-interacting ⇑ easier to get E_i ⇑ can consider single-particle states

(a) if quantum nature of particles is not important, then easier, but still need to include factors like $\frac{1}{N!}$ (as in our previous discussion on classical ideal gas)

(b) if we need to consider the particles as fermions or bosons, then harder.

$\sum_{\text{states } i}$ $\xrightarrow{\text{bosons}}$ $\sum_i$ "such that the N-particle states i in the sum are symmetrical w.r.t. interchanging two particles"

$\sum_{\text{states } i}$ $\xrightarrow{\text{fermions}}$ $\sum_i$ "such that the N-particle state i in the sum are anti-symmetrical w.r.t. interchanging two particles"

[this is what $\sum_i$ really means!] (interacting case)

Non-interacting ⇒ can consider single-particle states and then N-particle state is formed by putting N particles into single-particle states

Recall: Occupation numbers

$$\{n_1, n_2, n_3, \ldots, n_i \ldots\}$$

n_1: # particles in single-particle state #1

n_2: … #2

n_3: … #3

n_i: # particles in single-particle state #i

$\sum_{\substack{\text{N-particle}\\ \text{states } i}}$ $\xrightarrow{\text{Bosons}}$ $\sum_{\substack{\text{ways of putting N particles into single-particle states}\\ \text{and there is no restriction on \# particles in a state}}} = \sum_{\substack{\text{all strings of occupation numbers } \{n_i\}\\ \text{with } \sum_i n_i = N \text{ and } n_i = 0,1,2,\ldots}}$

$\sum_{\substack{\text{N-particle}\\ \text{states } i}}$ $\xrightarrow{\text{Fermions}}$ $\sum_{\substack{\text{ways of putting N particles into single-particle states}\\ \text{and each single-particle state can at most be occupied}\\ \text{by one particle}}} = \sum_{\substack{\text{all strings of occupation numbers } \{n_i\}\\ \text{with } \sum_i n_i = N \text{ and } n_i = 0,1}}$

- It is not easy to list all these ways or strings!
- The difficulty leads us to find another way to handle non-interacting bosons/fermions

- Interesting (but hard-to-solve) cases

Interacting Particles [Possibility of phase transitions]

Ways out...

- Many-body physics
- Approximations (Mean-field theories for example)
- Numerical Methods (e.g. Monte Carlo Simulation)

Summary (Learning Outcomes)

Students should be able to:

- state the condition of fixed (T,V,N) is studied
- argue that $P_i \propto W_B(E_0-E_i)$
- derive that $P_i \propto e^{-E_i/kT}$ and state clearly the meaning of P_i
- normalize P_i and show $Z=\sum_{\text{all states } i} e^{-E_i/kT}$
- take averages using P_i
- obtain $\langle E\rangle$ and ΔU from Z
- show $\frac{\Delta U}{\langle E\rangle} \sim \frac{1}{\sqrt{N}}$ and argue that for macroscopic systems $(N \gg 1)$, fixing T and fixing U do not lead to different behaviour
- Apply $S=-k\sum_i P_i \ln P_i$
- show $F(T,V,N)=-kT\ln Z(T,V,N)$
- obtain S, p, μ from F
- state clearly what canonical ensemble is about and contrast it with microcanonical ensemble
- solve problems, after practicing, using the canonical ensemble calculation scheme.