Appendix B : Classical Ideal Gas (Microcanonical Ensemble)

System: N non-interacting (indistinguishable) particles

In classical physics, the system is defined by the Hamiltonian:

↙ 6N variables

$$H(p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, p_{2z}, \cdots; q_{1x}, q_{1y}, q_{1z}, q_{2x}, q_{2y}, q_{2z}, \cdots)$$

$$\equiv H(\{p,q\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} = H(\{p\})$$

↑ No potential energy term (non-interacting particles)

$$p_i^2 = p_{ix}^2 + p_{iy}^2 + p_{iz}^2$$

Reasoning

- Want to find W(E,V,N) → S(E,V,N) for given E → Gas Law
- But! In Classical Mechanics, a state is specified by speifying p and q for each particle. But these are continuous variables, which make the counting problem harder to do!
- Invoke the idea of phase space.

Remarks:

- This problem is easier if we use quantum mechanics (particle-in-a-(big)-box). Here, we pretend that we don't know sufficient QM to do the problem. But we will see that we need some QM here.
- What is a "classical ideal gas" anyway?

  From Quantum physics, either Bosons or Fermions!

  "Classical Gases" don't seem to worry about this!

Aim: Allow for a small energy uncertainty ΔE and look for number of states with energy*

$$E < H(\{p\}) < E + \Delta E$$

This is the problem.

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* It is perfectly OK to consider $E - \frac{\Delta E}{2} < H(\{p\}) < E + \frac{\Delta E}{2}$ instead. It really doesn't matter!

Aside: <u>Phase space</u>

1 particle → 6-dimensional phase space (x, y, z, p_x, p_y, p_z)

Specify a state of the particle

⇒ specify all 6 variables

⇒ one point in the 6D phase space for a particle.

<u>N particles</u> → <u>6N-dimensional phase space</u>

$(\vec{r}_1, \cdots, \vec{r}_N ; \vec{p}_1, \cdots, \vec{p}_N)$

<u>One point in 6N-dim phase space</u>

⇒ specifying all "coordinates"

⇒ specifying a microstate of the system

Requiring: $\underbrace{H(\{p,q\}) = E}$ ← some given energy

defines a (6N−1)-dimensional "surface"

constant energy surface

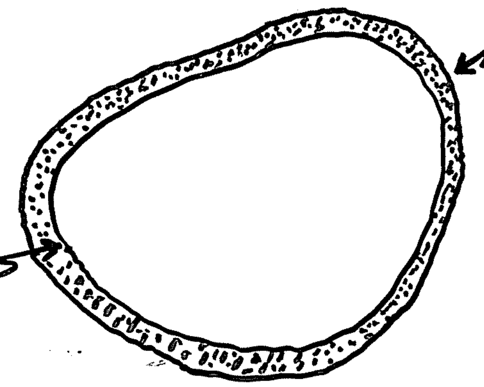
As system <u>evolves in time</u>

⇒ equal access to all states with given energy (on surface)

⇒ Many points (trajectory) in phase space, all with the given energy.

$$E < H(\{p\}) < E + \Delta E$$

Schematically,



Fundamental Postulate (equal probability)

⇒ all points in the volume bounded by the two surfaces are equally visited by the system

⇒ the density ρ of points in phase space is given by

$$\underset{\text{"microcanonical"}}{\rho_{mc}} = \begin{cases} \text{constant} & E \leq H(\{p,q\}) \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

∴ Number of accessible states $W(E, V, N; \Delta E)$ ← allowing a buffer in energy

$$W(E, V, N; \Delta E) \propto \left(\begin{array}{l} \text{Volume of phase space } \underline{\text{between}} \text{ the} \\ \text{constant energy surfaces at} \\ E \quad \text{and} \quad E + \Delta E \end{array} \right)$$

↑ # microstates with energy between E and E+ΔE

Mathematically‡;

$$W(E,V,N;\Delta E)=\frac{1}{\Lambda}\int_V d\vec{r}_1\int_V d\vec{r}_2\cdots\int_V d\vec{r}_N\int d\vec{p}_1\int d\vec{p}_2\cdots\int d\vec{p}_N$$

with the constraint $E \leq H(\{p,q\}) \leq E+\Delta E$

Λ = a constant that gives the correct units

LHS is a number (i.e., no units)

$\boxed{\Lambda = N!\,h^{3N}}$ gives correct answers

$N!$: to correct for over-counting of number of states due to indistinguishability of the N classical particles+

h: Planck constant (something Quantum)

- → makes W dimensionless
- → uncertainty relation
  - → for a particle in one dimension, can't specify x_i and p_{ix} simultaneously, instead $\Delta x_i \cdot \Delta p_{ix} \sim h$

‡ Formally, this number is $W(E,V,N;\Delta E)$ and it is expected to be (something)$\cdot\Delta E$.

+ A factor of $\frac{1}{N!}$ appears when we handle a system of N indistinguishable "classical" particles. Here, "classical" means situations where the bosonic or fermionic nature of particles is NOT important.

To proceed, consider

$$W^{<}(E,V,N)=\frac{1}{N!\,h^{3N}}\int_V d\vec{r}_1\int_V d\vec{r}_2\cdots\int_V d\vec{r}_N\int d\vec{p}_1\int d\vec{p}_2\cdots\int d\vec{p}_N$$

with constraint $H=\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m}\leq E$

= Number of microstates with energy less than or equal to E

$$W^{<}(E,V,N)=\frac{V^N}{N!\,h^{3N}}\underbrace{\int d\vec{p}_1\int d\vec{p}_2\cdots\int d\vec{p}_N}_{\text{with constraint }\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m}\leq E}$$

$$=\frac{V^N}{N!\,h^{3N}}\underbrace{\int dp_1\int dp_2\cdots\int dp_{3N}}_{\text{with constraint }\sum_{i=1}^{3N}\frac{p_i^2}{2m}\leq E}$$

change variables $p_i=\sqrt{2m}\,x_i$

$$=\frac{V^N}{N!\,h^{3N}}(2m)^{3N/2}\underbrace{\int dx_1\int dx_2\cdots\int dx_{3N}}_{\text{with constraint }\sum_{i=1}^{3N}x_i^2\leq E}$$

Volume of 3N-dim sphere of radius $\sqrt{E}$

$$=\frac{V^N}{N!\,h^{3N}}(2m)^{3N/2}\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)}E^{3N/2}$$

Note: $W^{<}(E,V,N)\sim E^{3N/2}$ increases rapidly with E and N

- Want to obtain $W(E,V,N;\Delta E)$ from $W^{<}(E,V,N)$

$$W(E,V,N;\Delta E) = W^{<}(E+\Delta E,V,N) - W^{<}(E,V,N)$$

$$= \frac{\partial W^{<}(E,V,N)}{\partial E}\cdot\Delta E \qquad \text{(Taylor expansion)}$$

$$\equiv \underbrace{\mathcal{W}(E,V,N)}\cdot\Delta E \qquad \text{(proportional to } \Delta E\text{)}$$

- does not depend on ΔE
- Density of states
- Units: 1/energy

$$\mathcal{W}(E,V,N) = \frac{\partial W^{<}}{\partial E}$$

$$= \frac{V^N}{N!\,h^{3N}}(2m)^{3N/2}\frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)}\frac{3N}{2}E^{3N/2-1}$$

$$\therefore\ W(E,V,N;\Delta E) = \left[V\left(\frac{2m\pi E}{h^2}\right)^{3/2}\right]^N\frac{1}{N!}\frac{1}{\left(\frac{3N}{2}-1\right)!}\frac{\Delta E}{E}$$

Remarks

- Note that $W(E,V,N;\Delta E) \sim \overbrace{\underbrace{(\text{something})}_{\bullet\ \text{depends on } (E,V,N),\text{ but not } \Delta E}}^{\text{"Density of states"}}\cdot\Delta E$

  (see discussions on p. IV-⑭)

- Note that $W(E,V,N;\Delta E) \sim E^{3N/2-1} \sim E^{3N/2}$

  $\Rightarrow$ rapidly increasing function of E

  (see discussions on p. IV-⑧)

The entropy:

$$S(E,V,N) = k\ln W(E,V,N;\Delta E) \qquad \text{(Ex.)}$$

$$= Nk\ln\left(V\left(\frac{mE}{2\pi\hbar^2}\right)^{3/2}\right) + k\ln\frac{\Delta E}{E} - k\ln N! - k\ln\left(\frac{3N}{2}-1\right)!$$

- Using Stirling's approximation:

$$\ln N! \approx N\ln N - N$$

and ignore $\ln\frac{\Delta E}{E}$ when compared with $\overbrace{N}^{\text{all terms go like } N}$, (Ex.)

except $k\ln\frac{\Delta E}{E}$

$$\boxed{S(E,V,N) = Nk\ln\left(\left(\frac{V}{N}\right)\left(\frac{mE}{3\pi N\hbar^2}\right)^{3/2}\right) + \frac{5}{2}Nk}$$

Key result

"Sackur-Tetrode equation"

Notes:

- Check that $S(E,V,N)$ is <u>extensive</u>, as it should be.
- The $\left(\frac{V}{N}\right)$ term helps in making sure that $S(E,V,N)$ is extensive. [Scale up system, but keeping $\frac{N}{V}$ constant and $\frac{E}{N}$ constant; $S \propto Nk$]
- Tracing the calculation (Ex.), the $N!$ factor in Λ is important as it gives S its extensive character. [If not, one will run into the so-called "Gibbs paradox".]

Calculate the temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{Nk}{\frac{V}{N}\left(\frac{mE}{3\pi N\hbar^2}\right)^{3/2}} \cdot \frac{V}{N}\left(\frac{m}{3\pi N\hbar^2}\right)^{3/2} \frac{3}{2} E^{1/2}$$

$$= \frac{3}{2}\frac{Nk}{E}$$

OR $\boxed{E = \frac{3}{2} NkT}$ a familiar result† for classical ideal gas

† Note how this result depends on the factor $\sim E^{3N/2}$ in $W(E,V,N)$. What is that "3"? What is that "2"?

The Pressure

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

OR $\boxed{pV = NkT}$ again a familiar result†

- We derived the ideal gas law from the postulate of equal a priori probabilities and Boltzmann's relation. And an expression that one can evaluate S.
- A by-product is that we can identify the "k" in $S = k \ln W$ to be the Boltzmann's constant, which appears in the ideal gas law and is related to the gas constant R.
- We will do this problem again, after we know how to treat systems in equilibrium with a heat bath at temperature T, i.e., (T,V,N) instead of (E,V,N).

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† Note: How this result depends on the factor V^N in $W(E,V,N)$?

Note: Calculate the chemical potential μ for classical ideal gas.

If we have kept h instead of using $\hbar$, the end result is:

$$S(E,V,N) = Nk\ln\left[\left(\frac{V}{N}\right)\left(\frac{4\pi m E}{3h^2 N}\right)^{3/2}\right] + \frac{5}{2}Nk \qquad (*)$$

[• In the process, we kept terms that are extensive (goes like N) and ignored those that are not.]

Knowing $E = \frac{3}{2}NkT$, we could substitute it into (*) and find

$$S = Nk\ln\left[\left(\frac{V}{N}\right)\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3\right] + \frac{5}{2}Nk$$

$$\therefore \frac{h}{\sqrt{2\pi mkT}} \text{ must be } \underline{\text{a length}} \equiv \underset{\text{thermal de Broglie wavelength}}{\lambda_{th}} \ \overset{\text{notation in some books}}{(=\lambda_{dB})}$$

$$= Nk\ln\left[\left(\frac{V}{N}\right)\frac{1}{\lambda_{th}^3}\right] + \frac{5}{2}Nk$$

What is a Classical Ideal Gas anyway?

$$S = Nk\ln\left[\left(\frac{V}{N}\right)\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3\right] + \frac{5}{2}Nk \qquad (*)$$

- A tricky, yet non-trivial answer is: A gas that the answer (*) works!
- S must be >0
- When $\frac{V}{N}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3 \gg 1$, $S>0$ (OK!)
  - high T, $\frac{N}{V}$ = number density should be small (dilute)

  [but the physics is actually deeper!]
- What if $\frac{V}{N}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3 \ll 1$? (*) becomes negative ⇒ Invalid!

(Same gas that is a classical ideal gas at high T ceases to be one at low T)

<u>Quantum behavior (Quantum Gas) comes in when</u>

$$\frac{V}{N}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3 \ll 1$$

Must then consider whether particles are fermions or bosons.

What does it mean?

Recall: Quantum Physics

de Broglie wavelength $\lambda \sim \frac{h}{p}$

p = momentum

E = energy of a particle $\sim \frac{3}{2}kT \sim \frac{p^2}{2m}$

$\therefore\ p \sim \sqrt{mkT}$

Thus, $\lambda \sim \frac{h}{p} \sim \frac{h}{\sqrt{mkT}}$ ← This factor appears in our classical ideal gas S

Define: $\lambda_{th} \equiv \frac{h}{\sqrt{2\pi mkT}} = \lambda_{th}(T)$

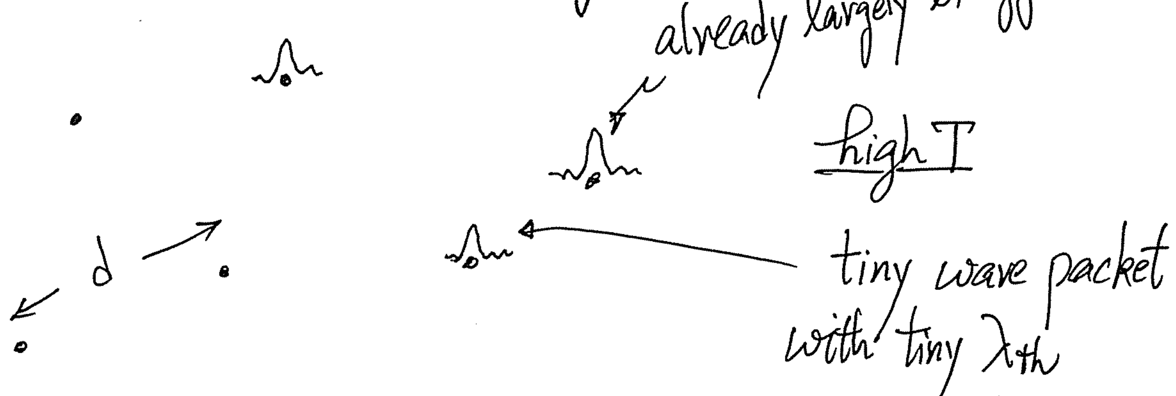
= thermal de Broglie wavelength

[a measure of how important quantum effect is]

$$\lambda_{th} \sim \frac{1}{\sqrt{mkT}} \qquad \underbrace{\text{lighter mass \& low } T}_{\text{quantum effect is important}}$$

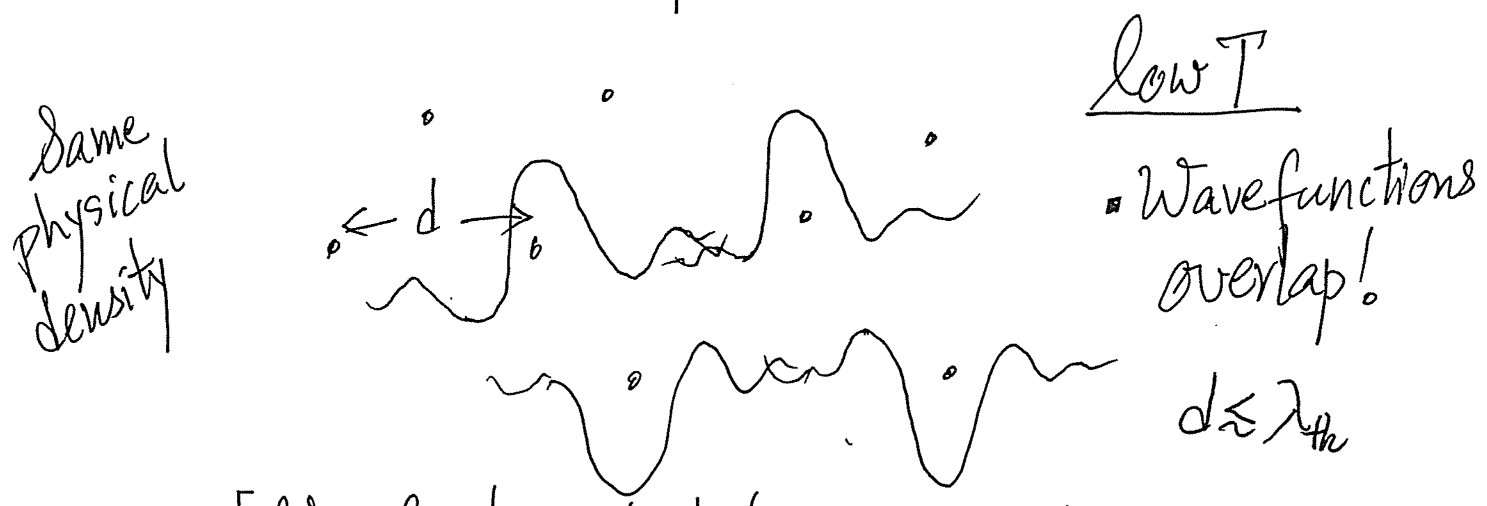
- λ_{th} is one length in the problem
- Another length: $\left(\frac{V}{N}\right)^{1/3} = \underbrace{\left(\frac{\text{Volume}}{\text{Particle}}\right)^{1/3}}_{\text{roughly it is the average separation between particles}} = d$

- Physics is often related to comparison (OR competition) between two scales (two lengths)



$\lambda_{th} \sim \frac{h}{\sqrt{2\pi mkT}}$

$(d \gg \lambda_{th})$ [particles don't care about whether they are bosons/fermions, as their wavefunctions (packets) don't overlap]



[Wavefunctions tend to overlap and form superpositions, thus a quantum state of the whole system!]

(Fermi Gas, Bose Gas)

Fermi Gas: Bloch's states in metals → Electrons ($10^{23}/\text{cm}^3$) at room temp.

Bose Gas → Liquid Helium (~1K)

[This is what cold atoms/molecules want to achieve.]

$$\left(\frac{V}{N}\right)^{1/3} \gg \frac{h}{\sqrt{2\pi mkT}}$$ Classical gas

$$\left(\frac{V}{N}\right)^{1/3} \ll \frac{h}{\sqrt{2\pi mkT}}$$ Quantum Gas

(Fermi Gas[+] / Bose Gas)

- Make good physical sense!
- Inspect what one can tune experimentally.

"Controllable Quantum Gases" is a hot research topic.

Ultracold atoms/molecules

At CUHK: Experiments (Prof. D.J. Wang)
Theory (Prof. Q. Zhou, Prof. C.K. Law)

[+] Daily-Life example: Electrons in a metal. Electrons ⇒ m small. electron # density $\sim 10^{24}/\text{cm}^3 \Rightarrow \left(\frac{V}{N}\right)^{1/3}$ is tiny
$\left(\frac{V}{N}\right)^{1/3} < \frac{h}{\sqrt{2\pi mkT}}$ even at room temp. ∴ Must treat electrons as Fermi Gas.

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

Carrying out the derivative gives

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{4\pi m E}{3Nh^2}\right)^{3/2}\right] \qquad \text{(Ex.)}$$

- Putting $\frac{E}{N} = \frac{3}{2}kT$, we have

$$\mu = -kT \ln\left[\frac{V}{N}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^{3}\right]$$

- For a classical gas, note that $\mu < 0$.
- Recall that $dE = TdS - pdV + \mu dN$, an interpretation of the chemical potential μ is:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$ → i.e. add one particle to the system, what would you do to the energy E in order to keep the entropy S unchanged?

Say, if you don't do anything to E, with one more particle to share E, W will increase and thus S increases (changes!). In order to keep S unchanged, you need to take some energy out of the system, thus $\Delta E < 0$ and hence $\mu < 0$.

Summary on Classical Ideal Gas Calculation

$$W(E,V,N;\Delta E) = \frac{1}{N!\,h^{3N}} \int_{E\le H(\{p,q\})\le E+\Delta E} d^3x_1 \cdots d^3x_N\, d^3p_1 \cdots d^3p_N$$

$$= \mathcal{W}(E,V,N)\cdot\Delta E$$

$$= \left[V\left(\frac{mE}{2\pi\hbar^2}\right)^{3/2}\right]^N \frac{1}{N!}\,\frac{1}{\left(\frac{3N}{2}-1\right)!}\,\frac{\Delta E}{E}$$

$$\sim E^{\frac{3N}{2}-1} \leftarrow \text{(rapidly increasing with } E \text{ \& } N)$$

$$\mathcal{W}(E,V,N) = \frac{\partial W^<(E,V,N)}{\partial E} \quad \text{and} \quad W^<(E,V,N) \sim E^{3N/2}$$

Sackür-Tetrode Equation

$$S(E,V,N) = Nk\ln\left[\left(\frac{V}{N}\right)\left(\frac{mE}{3\pi\hbar^2 N}\right)^{3/2}\right] + \frac{5}{2}Nk \quad \text{(extensive)}$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \Rightarrow E = \frac{3}{2}NkT \quad \text{"equipartition theorem"}$$

$$\frac{p}{T} = \frac{\partial S}{\partial V} \Rightarrow pV = NkT$$

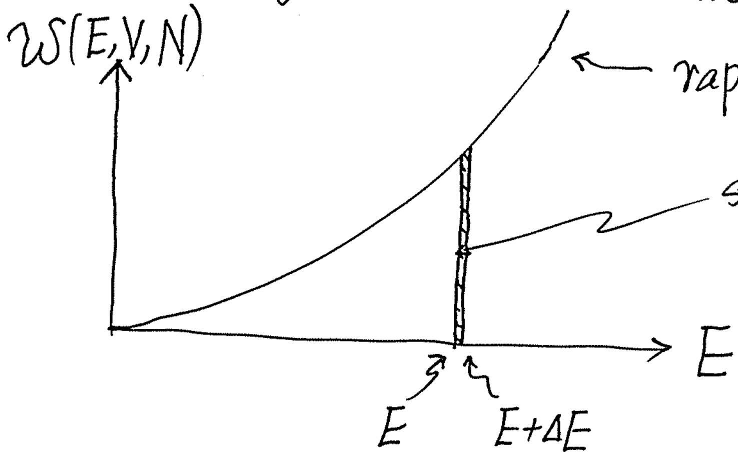
Expressing S in terms of T:

$$S = Nk\ln\left[\underbrace{\left(\frac{V}{N}\right)\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}}\right] + \frac{5}{2}Nk = Nk\ln\left[\left(\frac{V}{N}\right)\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3\right] + \frac{5}{2}Nk$$

- comparison between average separation of particles and thermal de Broglie wavelength
- signals when quantum nature of particles becomes important

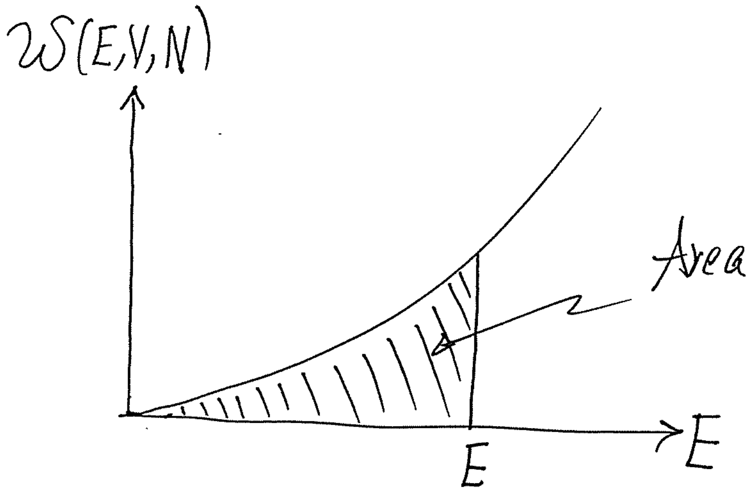
Pictures: $W(E,V,N;\Delta E)$, $W^<(E,V,N)$ and $\mathcal{W}(E,V,N)$

$$\underbrace{\mathcal{W}(E,V,N)}_{\text{Density of States [Units: } \frac{1}{\text{energy}}]}\cdot\Delta E = \#\text{ microstates in interval } E \text{ to } E+\Delta E$$



← rapid increase with E

shaded area is $\mathcal{W}(E,V,N)\Delta E = W(E,V,N;\Delta E)$



Area $= W^<(E,V,N)$
$= \#$ microstates with energy less than or equal to E