

Application C

Classical Ideal Gas

System : Classical Ideal Gas

N non-interacting particles in a Volume V [$6N$ variables]

No interaction terms
(ideal gas)

Microscopic starting point: Hamiltonian[†] $H(\{p, x\}) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} = \sum_{i=1}^N \left(\frac{p_{ix}^2}{2m} + \frac{p_{iy}^2}{2m} + \frac{p_{iz}^2}{2m} \right)$ (C1)

Find $W(E, V, N)$

$3N$ kinetic energy terms

Practically, we introduce a buffer ΔE (or often written as δE) in counting the microstates, i.e. we count

microstates in the energy interval E to $E + \Delta E$

It is a number (so can go into $k \ln[\text{number}]$ for getting S)

This can avoid the roughness in $W(E, V, N)$ [c.f. binning in data]

[†] Monatomic Gas, no other internal motion such as rotation.

Expected this number turns out to be of the form

$$\underbrace{\mathcal{W}(E, V, N)}_{\text{property of system (not depending on } \Delta E)} \cdot \overbrace{\Delta E}^{\text{buffer}} = \# \text{ microstates in interval } E \rightarrow E + \Delta E \quad (C2)$$

(for sufficiently small ΔE)

Definition

$\mathcal{W}(E, V, N)$ is the Density of States⁺ of the N-particle system
(explicitly, Density of N-particle States) (C3)

$\mathcal{W}(E, V, N) \cdot \Delta E$ is a number

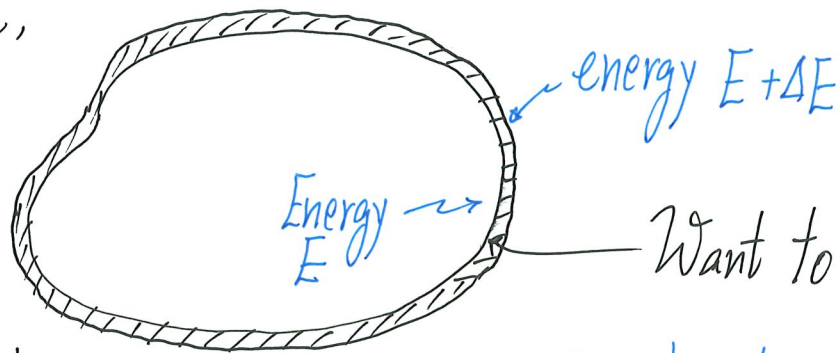
$\mathcal{W}(E, V, N)$ has the unit of "per unit energy"

⁺ Be careful, you will also see a density of states of single-particle system. In long form, this one is density of single-particle States.

Following the discussion on the $6N$ -dim Phase Space

$$W(E, V, N) \cdot \Delta E \propto \left(\text{Volume of Phase Space between two constant-energy surfaces, one at energy } E \text{ and another at } E + \Delta E \right)$$

Schematic,



Want to find the "volume" between two surfaces

Mathematically,

$$W(E, V, N) \cdot \Delta E = \frac{1}{\Lambda} \underbrace{\int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N}_{\text{3N integrals on the coordinates}} \underbrace{\int d\vec{p}_1 \int d\vec{p}_2 \cdots \int d\vec{p}_N}_{\text{3N integrals on the momenta}} \quad (C4)$$

a constant Λ to turn phase space volume into a number (takes care of units) under constraint $E \leq H(\{p, x\}) \leq E + \Delta E$ select that region of phase space

A standard strategy to find $\mathcal{W}(E, V, N)$ is to consider

$$W^{\leq}(E, V, N) = \# \text{ microstates with energy less than or equal to } E$$

$\nearrow$
 • a number
 • an increasing function of E

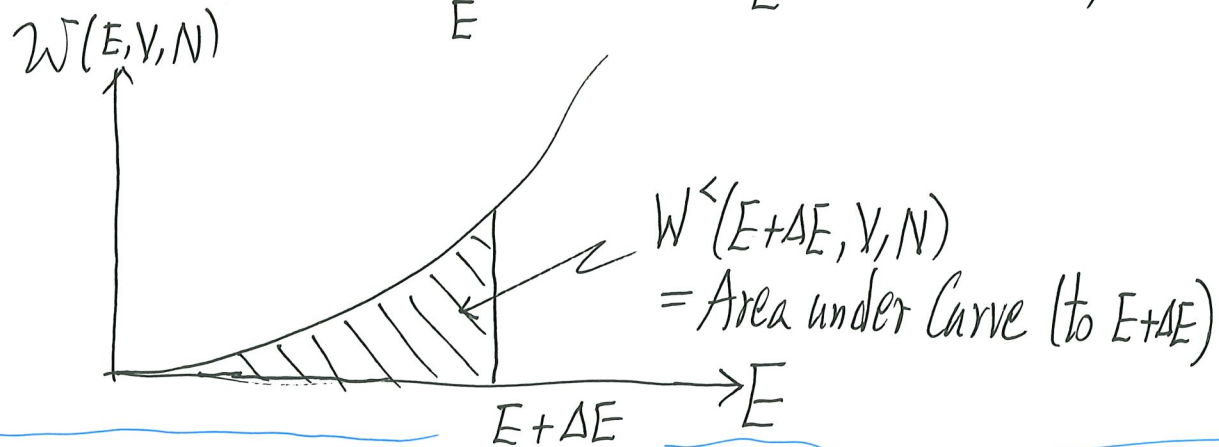
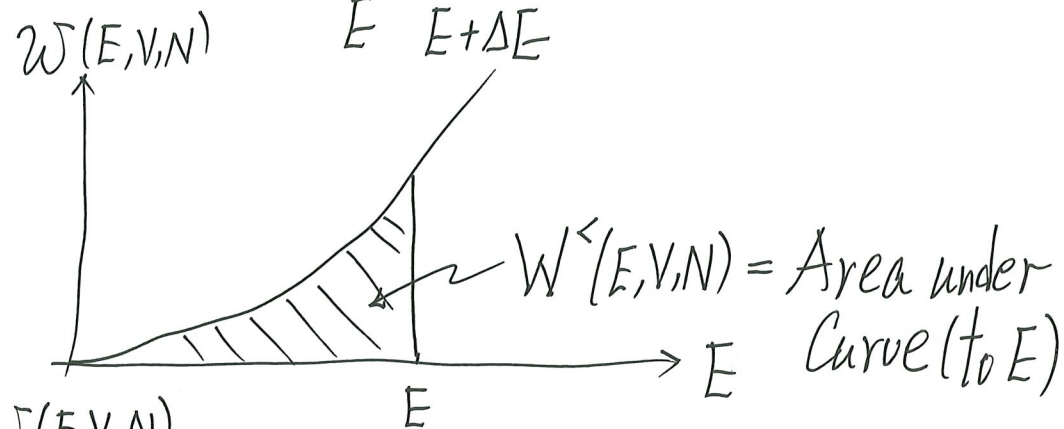
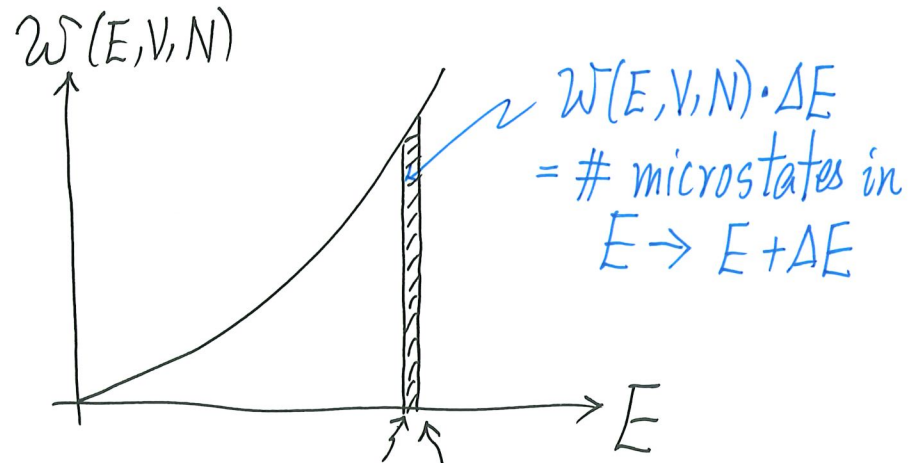
all microstates with energies up to E

(C5)

$$\begin{aligned}
 W^{\leq}(E + \Delta E, V, N) - W^{\leq}(E, V, N) &= \# \text{ microstates with energies between } E \text{ to } E + \Delta E \\
 &= \frac{W^{\leq}(E + \Delta E, V, N) - W^{\leq}(E, V, N)}{\Delta E} \cdot \Delta E \\
 &= \frac{\partial W^{\leq}(E)}{\partial E} \cdot \Delta E \\
 &= \mathcal{W}(E, V, N) \cdot \Delta E
 \end{aligned}$$

← (see pictures)

Aside: $\mathcal{W}(E, V, N)$ and $W^*(E, V, N)$



If we know $W^*(E, V, N)$, it is like knowing the area under a curve, i.e. the integration.

$W^*(E)$ is integration of $\mathcal{W}(E)$

So $\mathcal{W}(E)$ is the derivative of $W^*(E)$

$$\mathcal{W}(E) = \frac{\partial W^*}{\partial E}$$

$$\therefore \boxed{\mathcal{W}(E, V, N) = \frac{\partial W^k(E, V, N)}{\partial E}} \quad (C6)$$

(i) Find $W^k(E, V, N)$, (ii) take derivative w.r.t. E to get $\mathcal{W}(E, V, N)$

[Key: General Strategy. Good for Density of N -particle states AND Density of single-particle states]

Mathematically,
$$W^k(E, V, N) = \frac{1}{\Lambda} \underbrace{\int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N \int d\vec{p}_1 \int d\vec{p}_2 \cdots \int d\vec{p}_N}_{\text{under constraint } H(\{p, x\}) \leq E \text{ (or } \sum_{i=1}^{3N} \frac{p_i^2}{2m} \leq E)} \quad (C7)$$

[3N k.e. terms]

Let's do the $6N$ constrained integrals

• Constraint unrelated to $\{\vec{r}_1, \dots, \vec{r}_N\}$, $\int_{\text{all space}} d\vec{r}_1 = V$, $\int d\vec{r}_i = V, \dots$

volume of system

$$\therefore \int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_N = V^N \quad (\text{classical ideal gas})$$

The momenta integrals : $\underbrace{\int d\vec{p}_1 \int d\vec{p}_2 \cdots \int d\vec{p}_N}_{\sum_{i=1}^{3N} \frac{p_i^2}{2m} \leq E} = \underbrace{\int dp_1 \int dp_2 \cdots \int dp_{3N}}_{\sum_{i=1}^{3N} p_i^2 \leq 2mE}$

is the volume (V_{3N}) of a $3N$ -dimensional "sphere" of radius $\sqrt{2mE}$ $\sum_{i=1}^{3N} p_i^2 \leq (\sqrt{2mE})^2$ (+)

Aside : Volume of a D -dim. sphere of radius R

$$V_D(R) = \frac{\pi^{D/2}}{\Gamma(\frac{D}{2} + 1)} \cdot R^D \quad (C8)$$

where $\Gamma(n)$ is the Gamma Function with the property $\Gamma(n+1) = n\Gamma(n)$ and $\Gamma(1/2) = \sqrt{\pi}$
 [the Γ -function generalizes $n!$ to real numbers, e.g. $5/2!$]

* If there were 2 terms, $p_1^2 + p_2^2 \leq (\sqrt{2mE})^2$, it is the area of a circle of radius $\sqrt{2mE}$. If there were 3 terms, $p_1^2 + p_2^2 + p_3^2 \leq (\sqrt{2mE})^2$ is the volume of a sphere of radius $(\sqrt{2mE})$. Here, we have $3N$ terms.

Example: 3D sphere

$$V_3(R) = \frac{\pi^{3/2}}{\Gamma(\frac{3}{2}+1)} \cdot R^3 = \frac{\pi^{3/2}}{\frac{3}{2} \Gamma(\frac{3}{2})} \cdot R^3 = \frac{\pi^{3/2}}{\frac{3}{2} \cdot \frac{1}{2} \Gamma(\frac{1}{2})} R^3$$

$$= \frac{\pi^{3/2}}{\frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi}} = \frac{4}{3} \pi R^3 \quad (\text{it works!})$$

[Try proving it by induction]

$$\therefore \underbrace{\int dp_1 \cdots \int dp_{3N}}_{\sum_{i=1}^{3N} p_i^2 \leq 2mE} = V_{3N}(\sqrt{2mE}) = \frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2}+1)} \cdot (2mE)^{3N/2}$$

$$= (2m)^{3N/2} \frac{\pi^{3N/2}}{(\frac{3N}{2})!} E^{3N/2}$$

(Done!
We did another
 $3N$ (3×10^{23}) integrals!)

$$\therefore W^k(E, V, N) = \frac{1}{\Lambda} V^N (2\pi m)^{3N/2} \frac{1}{(\frac{3N}{2})!} E^{3N/2}$$

[Note: E, V, N are all there on RHS. $W^k(E, V, N) \sim E^{\frac{3N}{2}} \sim E^N$ shows how W^k or $2S$ or W increases rapidly with E and N .

What about the constant Δ ?

$\Delta = N! h^{3N}$ gives the correct answer (h = Planck's constant (1900))

$$(i) \quad \underbrace{\int d\vec{r}_1 \int d\vec{p}_1 \int d\vec{r}_2 \int d\vec{p}_2 \cdots \int d\vec{r}_N \int d\vec{p}_N}_{\text{a big } 6N \text{ Phase Space Volume}} = \underbrace{\int dx_1 \int dp_1}_{\text{product of } (\int dx_i \int dp_i) \text{'s}} \underbrace{\int dx_2 \int dp_2}_{\text{'s}} \cdots \underbrace{\int dx_{3N} \int dp_{3N}}_{\text{'s}}$$

this has the unit of $(x \cdot p)^{3N}$ [NOT a number]

So, need a constant corresponding to phase space volume per microstate

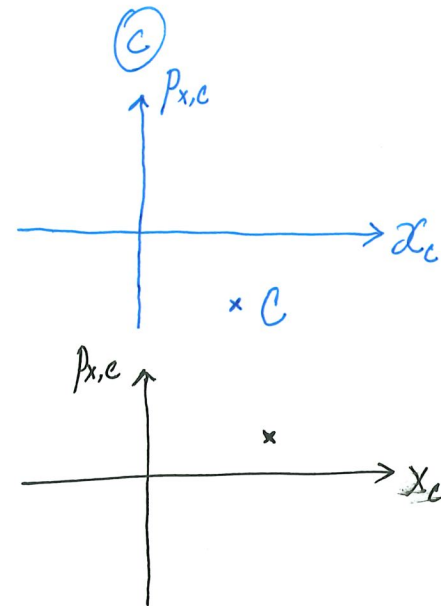
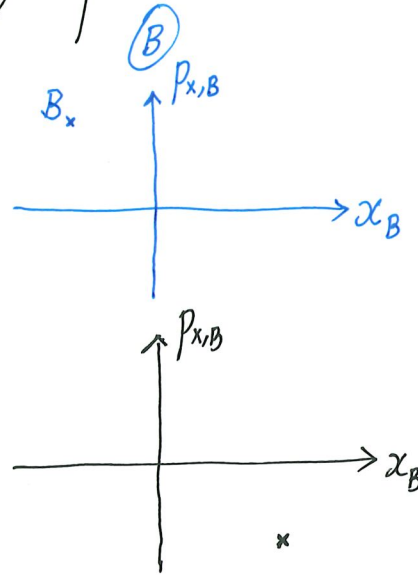
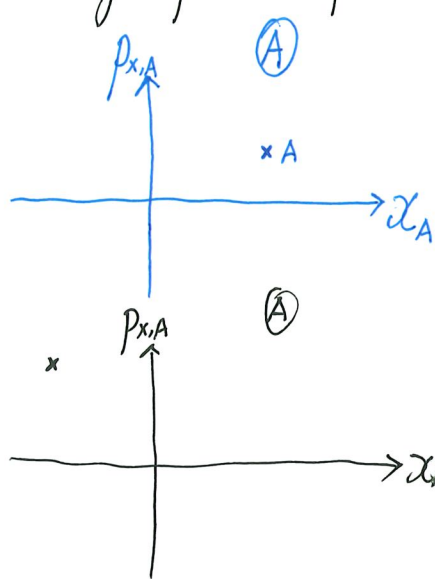
$$\underbrace{\frac{1}{h^{3N}}}_{\text{becomes a number}} \int d\vec{r}_1 \int d\vec{p}_1 \cdots \int d\vec{r}_N \int d\vec{p}_N$$

Δ carries h^{3N}

$$(ii) \quad \frac{1}{\Lambda} = \frac{1}{N! h^{3N}}$$

↑ correct over counting as N particles are indistinguishable in ideal gas

single-particle phase space μ -space



included in integrals

also included in integrals

there are other four cases $[3! = 6 \text{ cases}]$ all included in integrals

$\therefore \frac{1}{N!}$ serves to take care of the indistinguishability of the N particles

$$W^{\leftarrow}(E, V, N) = \frac{1}{h^{3N} N!} V^N (2\pi m)^{3N/2} \frac{1}{\left(\frac{3N}{2}\right)!} E^{\frac{3N}{2}} = \frac{1}{N!} V^N \left(\frac{m}{2\pi\hbar^2}\right)^{3N/2} \frac{1}{\left(\frac{3N}{2}\right)!} E^{\frac{3N}{2}} \quad (C9)$$

$$\omega(E, V, N) = \frac{\partial W^{\leftarrow}}{\partial E} = \frac{1}{N!} V^N \left(\frac{m}{2\pi\hbar^2}\right)^{3N/2} \frac{1}{\left(\frac{3N}{2}-1\right)!} \frac{E^{\frac{3N}{2}}}{E} = \frac{1}{N!} V^N \left(\frac{mE}{2\pi\hbar^2}\right)^{3N/2} \frac{1}{\left(\frac{3N}{2}-1\right)!} \frac{1}{E} \quad (C10)$$

Density of States
(basically also $\sim E^N$)

this is a number

$$S(E, V, N) = k \ln [W(E, V, N) \cdot \Delta E]$$

[other terms $\sim N$]
ignore!

looks like there
should be a ΔE
on this side,
but that term
is negligible

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

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

$$= Nk \ln \left[\frac{V}{N} \left(\frac{mE}{2\pi\hbar^2}\right)^{3/2} \right] - \frac{3Nk}{2} \ln \frac{3N}{2} + \frac{5}{2} Nk$$

ignore "1"

Aside: For those who are "too theoretical" (can skip and move on to next page)

(i) ignore $-k \ln\left(\frac{E}{\Delta E}\right)$ term?

May worry about $\frac{E}{\Delta E}$ is huge!

OK! Let's say $\frac{E}{\Delta E} \sim 10^{40}$
that's huge

$$\ln[10^{40}] = \underbrace{94.4}_{\text{not big!}}$$

All other terms have N in front.

Also imply value of ΔE is irrelevant.

(ii) Choice of ΔE ?

$$\text{Using } \Delta E_1: S(E, V, N; \Delta E_1) = \dots - \overbrace{k \ln\left(\frac{E}{\Delta E_1}\right)}^{\sim Nk}$$

$$\text{Using } \Delta E_2: S(E, V, N; \Delta E_2) = \dots - k \ln\left(\frac{E}{\Delta E_2}\right)$$

$$\text{Difference} = -k \ln\left(\frac{\Delta E_2}{\Delta E_1}\right)$$

order 1

where S is extensive ($\sim Nk$)

$\therefore$ Choice of ΔE 's is irrelevant

$\hookrightarrow$ as long as $\left(\frac{\# \text{ microstates in } E \rightarrow E + \Delta E}{E \rightarrow E + \Delta E}\right) = \mathcal{W}(E, V, N) \cdot \Delta E$ works

$$S(E, V, N) = Nk \ln \left[\frac{V}{N} \left(\frac{mE}{3\pi\hbar^2 N} \right)^{3/2} \right] + \frac{5}{2} Nk \quad (C11)$$

$\downarrow$ Nk $\uparrow$ $\left(\frac{V}{N} \right)$ and $\frac{E}{N}$ are intensive $\uparrow$ Nk

$\therefore S$ is extensive as required! [Note: $\frac{1}{N!}$ in $\frac{1}{\Lambda}$ works here]

without it, S will not be extensive.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V, N} = Nk \frac{\partial}{\partial E} \ln(\mathcal{B} E^{3/2}) = \frac{Nk}{\mathcal{B} E^{3/2}} \cdot \mathcal{B} \frac{3}{2} E^{1/2} = \frac{3}{2} \frac{Nk}{E} \quad (C12)$$

$\left[\frac{1}{T} = \frac{3}{2} \frac{Nk}{E} \right]$, thus higher E means higher T (ideal gas)

$$\Rightarrow \boxed{E = \frac{3}{2} NkT}$$

(C13) well known result for ideal gas $U = \frac{3}{2} NkT$
 (derived from $H(\{p, x\})$ using Boltzmann's Formula!)

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = Nk \frac{\partial}{\partial V} \ln(AV) = \frac{Nk}{AV} \cdot A = \frac{Nk}{V} \quad (C14)$$

$$\therefore p = \frac{NkT}{V} \quad (\text{pressure derived})$$

$$\Rightarrow \boxed{pV = NkT} \quad (C15) \quad (\text{derived from } H(\{p, x\})!)$$

$$p = \frac{Nk}{V} \cdot \frac{2E}{3Nk} = \frac{2}{3} \left(\frac{E}{V} \right) = \frac{2}{3} (\text{energy density})$$

$$\text{or } \boxed{pV = \frac{2}{3} E} \quad (C15)$$

Remark: Applying the method to classical ideal gas also confirms that the "k" in $S = k \ln W$ is the same k that appears in ideal gas law $pV = NkT$ and $E = \frac{3}{2} NkT$ ($U = \frac{3}{2} NkT$).

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N} \right)_{E,V} \quad (\text{be careful! there are three } N\text{'s in } S \text{ to "d"})$$

$$\Rightarrow \boxed{\mu = -kT \ln \left[\frac{V}{N} \left(\frac{mE}{3\pi\hbar^2 N} \right)^{3/2} \right]} \quad (C16) \quad (Ex.)$$

Chemical potential
(intensive)

negative
for classical

ideal gas as this argument is big in ideal gas

ALL Done!

• Rich physics follows!

The equation of $S(E, V, N)$ is called the Sackur-Tetrode Equation [Eq. (C11)] (1911-1912). An early triumph of Stat. Mech.

Comments(a) Getting a physical sense of μ

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

< 0 for classical ideal gas

Why so?

$$dE = TdS - pdV + \mu dN \quad \text{Central Equation}$$

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

it says μ is how the energy E would change when a particle is added to the system under the condition of keeping S constant

good

Add N , usually more microstates and thus usually S increases. To keep S constant, need to take energy OUT to keep W constant, thus μ is negative.

(b) When is a gas a classical ideal gas?

And More Importantly, when is a gas NOT a classical ideal gas?

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

When $\frac{V}{N} \left(\frac{m E}{3\pi \hbar^2 N} \right)^{3/2} \gg 1$, then $S > 0$ safely!

$$[E = \frac{3}{2} NkT] \quad \frac{V}{N} \left(\frac{m k T}{2\pi \hbar^2} \right)^{3/2} \gg 1$$

$\frac{V}{N}$ big is good (volume per particle big) $\Rightarrow$ dilute gas
 $T^{3/2}$ (high temperature)

Condition for a gas of particles to behave as classical ideal gas

A wonderful warning flag!

When $\frac{V}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \ll 1$, $\ln[]$ negative

then S could become negative!
(violating 3rd law)

⇒ a gas of particles ceases to behave as a classical ideal gas
when $\frac{V}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} < 1$ (C17)

What is it then?

It becomes a Quantum (still non-interacting) Gas!

$$\underbrace{\frac{V}{N}}_{(\text{length})^3} \underbrace{\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}}_{\frac{1}{(\text{length})^3}} < 1$$

$\left(\frac{V}{N}\right)^{1/3} \approx \text{separation between particles}$

What is this length?

$$\left(\frac{2\pi mkT}{\hbar^2}\right)^{3/2} \equiv \frac{1}{\lambda_T^3}$$

(C18) $\lambda_T \equiv \frac{\hbar}{\sqrt{2\pi mkT}}$ is a length!

called the thermal de Broglie wavelength

- This is a quantum property ($\hbar$ is there)

Recall: $\lambda_{dB} = \frac{\hbar}{p}$

de Broglie wavelength

momentum p

$$\sim \frac{\hbar}{\sqrt{mkT}}$$

Thermal Physics

per particle

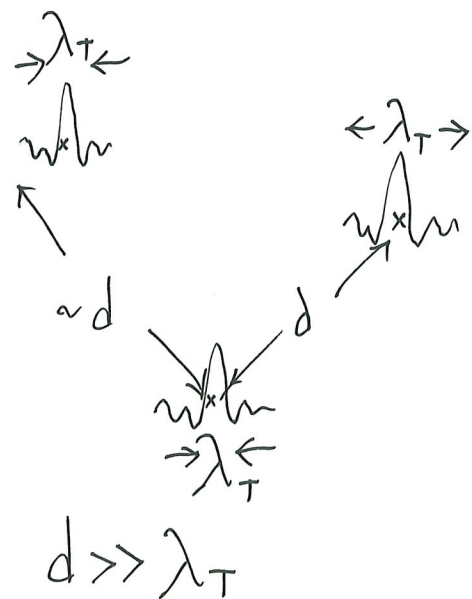
$$E = \frac{p^2}{2m} \Rightarrow p = \sqrt{2mE}$$

per particle

but $E \sim kT$

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

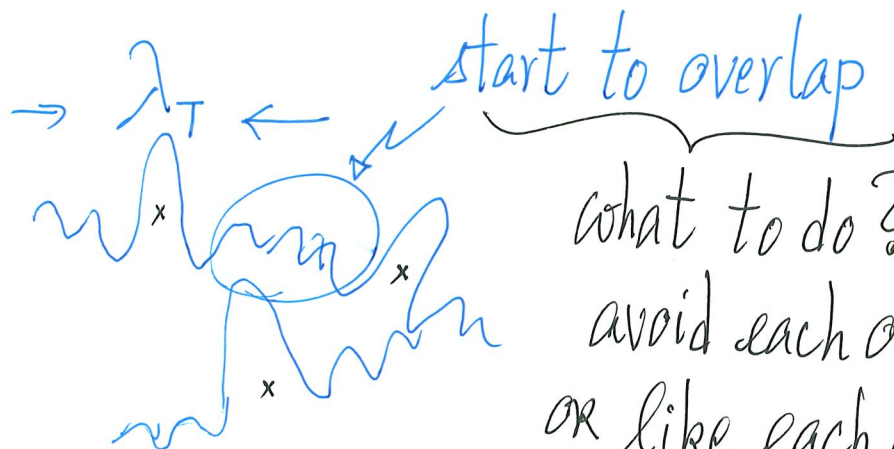
Picture: $\left(\frac{V}{N}\right)^{1/3} \equiv d \approx \lambda_T$
 Classical Ideal Gas



Particles don't meet (not come close to each other)

Don't need to consider whether particles are fermions or bosons!

Quantum Nature becomes important



what to do?

avoid each other (fermions)
 or like each other (bosons)?

∴ Fermions or bosons Matter!

Can be achieved by:

• Denser and/or low temperature

System becomes

• Ideal Fermi Gas

or

• Ideal Bose Gas

(Bose-Einstein Condensation when $d \approx \lambda_T$)

Lessons to Learn...

- The microcanonical ensemble approach is a valid theory
- Not only does it give the known classical ideal gas results from microscopic (Hamiltonian) starting, but also point to when new (quantum) physics will enter!

Exercise: Buy one get many free...

Consider $3N$ independent and distinguishable harmonic oscillators

$$H(\{p, x\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i=1}^{3N} \frac{1}{2} m \omega^2 x_i^2$$

Follow the same steps: $W^*(E) \rightarrow W(E) \rightarrow S = k \ln[W(E) \cdot \Delta E]$
 $\rightarrow \frac{1}{T} = \frac{\partial S}{\partial E} \dots$ (Ex.)

At the end, you will see $\underbrace{E = 3N kT}$ and thus $\underbrace{C_v = 3Nk}$

which is the high temperature regime of the Einstein's model
 (∴ no consideration of oscillator's discrete allowed energies here)