

Ideal Gas

(1)

We will now study the ideal gas as an example of how to connect our statistical description to our thermodynamic perspective.

Let's start with a few important assumptions, which we will validate later.

An ideal gas is a simplified model of a gas which has the following assumptions:

- ① particles do not interact w/ each other
- ② the volume density of particles is low
- ③ particles (of a given type*) are indistinguishable.

CQ: what are the properties of an ideal gas?

We can call these properties as they define an ideal gas, but it's more productive (IMO) to call them assumptions of a type of ideal gas model b/c we can then change or relax them in other more complex models.

What do these assumptions tell us?

(2)

- (1) tells us that we can model our gas as a collection of particles in a box.
- (2) tells us that we must be dealing w/ a dilute gas. If we violate (2), we tend to violate (1) b/c the probability of interactions goes up.
- (3) tells us that there will be some counting we have to pay attention to b/c we will initially overcount.

For the time being we will have an additional assumption:

- (4) we only have particles of one type
→ a monatomic ideal gas

CQ: For which gases could the ideal gas be a model? (why?)

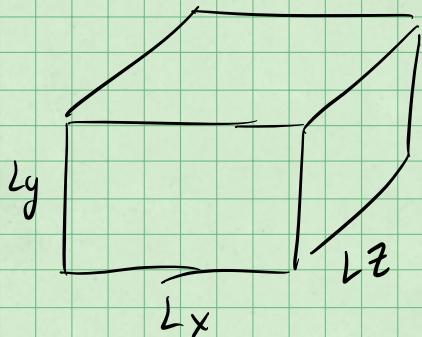
⇒ Essentially, we have a model of dilute Noble Gases: He, Ne, Ar, Kr, Xe, R_d

CQ: T/F
the more
we
violate
(2); the
more we
violate (1)

Let's begin with the most dilute gas,
a single atom gas. From that we will
build up to N atoms and then to
some results for energy, heat capacity,
and few thermodynamic relationships.

(3)

Reminder : Particle In a Box



Schrödinger Equation
(Why no V ? no interactions)

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi$$

To solve this PDE, we need boundary conditions.
We can either use (i) "hard" walls or (ii) periodic
boundary conditions. Our goal is to find E .

Kittel chooses (i) : Hard Walls ($\psi = 0 @ \text{walls}$)

$$\psi(x, y, z) = A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

with $n_x, n_y, n_z = 1, 2, 3, \dots$

We choose (ii) : Periodic B.C.s $\psi(x+L_x, y, z) = \psi(x, y, z)$

$$\psi(\vec{r}) = \frac{1}{V} e^{i \vec{k} \cdot \vec{r}} \quad \vec{k} = n_x \frac{2\pi}{L_x} \hat{x} + n_y \frac{2\pi}{L_y} \hat{y} + n_z \frac{2\pi}{L_z} \hat{z}$$

$n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots$

We seek E in this case. CQ: What are the ⁽⁴⁾ energy eigenfunctions

$$E(k) = \frac{\hbar^2 k^2}{2m} \quad \begin{pmatrix} \text{note: } k \text{ is} \\ \text{not } k_B \\ \text{the Boltzmann} \\ \text{constant} \end{pmatrix}$$

for the Particle in a Box?

The reason we want E is to be able to use the architecture of Boltzmann's partition function to develop our resulting thermodynamic properties. (Maxwell Boltzmann gas)

CQ: What is the partition function?

One-particle partition function

$$Z_1 = \sum_{\vec{k} \text{ states}} e^{-E(\vec{k})/T} = \sum_{\vec{k}} e^{-\frac{\hbar^2 k^2}{2mT}}$$

From prior lecture: $\sum f(\vec{k}) = \frac{V}{(2\pi)^3} \int d^3k f(\vec{k})$
(photons in a box)

CQ: When is it ok to make

Making this change gets us to an analytical tractable solution but also adds an assumption $\Delta E(k)$ should be small

the change from discrete energy states to the continuum?

(5) When compared to $k_B T$. That is the energy spacing should be small compared to thermal background.

$$Z_1 = \frac{V}{(2\pi)^3} \int d^3k e^{-\hbar^2 k^2 / 2mc} \quad (5)$$

It's easier to do this integral with Cartesian coordinates.

$$e^{-\hbar^2 k^2 / 2mc} = e^{-\hbar^2 (k_x^2 + k_y^2 + k_z^2) / 2mc}$$

So the partition function becomes,

$$Z_1 = \frac{V}{(2\pi)^3} \left(\int_{-\infty}^{\infty} dk_x e^{-\hbar^2 k_x^2 / 2mc} \right)^3$$

$\underbrace{\hspace{10em}}$
I (the integral)

$$\text{let } u = \hbar k / \sqrt{2mc} \quad du = \hbar / \sqrt{2mc}$$

$$I = \int_{-\infty}^{\infty} dk_x e^{-\hbar^2 k_x^2 / 2mc} = \frac{\sqrt{2mc}}{\hbar} \int_{-\infty}^{\infty} du e^{-u^2}$$

$\underbrace{\hspace{10em}}$
 $\sqrt{\pi}$

Q:
Estimate
the integral

$$I = \frac{\sqrt{2\pi mc}}{\hbar}$$

$$Z_1 = \frac{V}{(2\pi)^3} I^3 = \frac{V}{(2\pi)^3} \frac{(2\pi mc)^{3/2}}{\hbar^3}$$

$$= \sqrt{\left(\frac{mc}{2\pi\hbar^2}\right)^{3/2}} \equiv V n_Q \quad \text{where } n_Q = \left(\frac{mc}{2\pi\hbar^2}\right)^{3/2}$$

$$\text{Units} = \frac{1}{\text{volume}} \quad (Z \text{ is dimensionless})$$

is the quantum
concentration.
(when QM matters)

Q:
Units
of n_Q ?

Aside: as you will prove in HW 5, n_Q is approx. (6)
 equal to the concentration of atoms if they
 were separated by the average de Broglie λ .

Average Energy of a 1 atom gas

CQ: how should
 we compute the
 energy? Why?

$$U_1 = T^2 \frac{\partial}{\partial T} (\ln Z_1)$$

$$= T^2 \frac{\partial}{\partial T} \left(\ln \left[V \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \right] \right)$$

$$= T^2 \left\{ \frac{\partial}{\partial T} \left[\ln V + \frac{3}{2} \ln \left(\frac{mT}{2\pi\hbar^2} \right) \right] \right\}$$

$$= T^2 \left\{ \frac{\partial}{\partial T} \left[\frac{3}{2} \ln(T) + \text{constants} \right] \right\}$$

$$U_1 = \frac{3}{2} T^2 \frac{\partial}{\partial T} \ln T = \frac{3}{2} T^2 \left(\frac{1}{T} \right) = \frac{3}{2} T$$

$$\boxed{U_1 = \frac{3}{2} k_B T}$$

Well known result from
 Equipartition Theorem

$U_i = 1/2 k_B T$ per d.o.f.

What about a gas with N -atoms?

Consider 2 independent systems, at temp T , that can each be described by a partition function.

System 1 : Z_1

CQ: What's $Z(1+2)$?

System 2 : Z_2

$$Z(1+2) = Z_1 Z_2 \text{ for two independent}$$

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systems at the same temp. T . CQs: calc Z

\Rightarrow for N identical, independent

$$\text{systems : } Z_N = (Z_1)^N$$

for zero energy
systems.

1 part; 2 part. dis.

But these systems are distinguishable ones.

CQ: are we over/under counting states for the ideal gas?

(Some painted numbers on each particle, so we
have more unique states than if we can't tell
them apart \Rightarrow ideal gas)

What if the N systems are
indistinguishable?

CQ: calc Z for zero
energy sys. 2 particles
indistinguishable.

For the current case, we assume they are (#3 above).

But for real particles (fermions & bosons), this is definitely
the case!

Consider this QM system: 2 particles (1,2) in
one of two different states (a,b)

$$\Psi_a(\vec{r}_1) \Psi_b(\vec{r}_2) \text{ or } \Psi_a(\vec{r}_2) \Psi_b(\vec{r}_1)$$

You can't distinguish the particles so that the
total wave function is the superposition of both
states

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\Psi_a(\vec{r}_1) \Psi_b(\vec{r}_2) \pm \Psi_a(\vec{r}_2) \Psi_b(\vec{r}_1)]$$

+ for bosons and - for fermions (comes back in h.6)

CQ: how many ways can you place N particles in N different quantum states? (8)

For N particles and N different states there are $N!$ ways of arranging them.

$$\rightarrow Z_N = (Z_1)^N \text{ overcounts by } N!$$

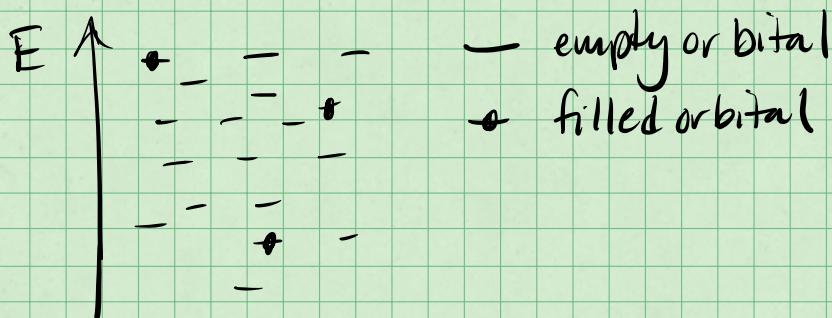
So the appropriate correction to this is,

$$Z_N = \frac{(Z_1)^N}{N!} \text{ indistinguishable particles in this classical limit}$$

CQ: When is this valid? $n = N/V$ compared to n_Q

We have a dilute gas where single particle quantum states are sparsely populated.

$$\text{Thus, } n = N/V \ll n_Q$$



Summary:

$$N \text{ identical, distinguishable} \quad Z_N = (Z_1)^N$$

$$N \text{ identical, indistinguishable} \quad Z_N = (Z_1)^N / N!$$

"

Classical

" in QM

latter in Ch. 6.

Results from the Ideal Gas Model

(9)

With $Z_1 = \sqrt{n_Q}$ and $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$,

Partition Function: $Z_N = (Z_1)^N / N!$

$$\ln(Z_N) : \quad \ln(Z_N) = N \ln Z_1 - \ln(N!) \quad \text{(Q: } \ln(N!) \approx ? \text{)}$$

b/c appears
in all calculations

$$= N \ln \left[\sqrt{\left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2}} \right] - (N \ln N - N)$$

$$\ln(Z_N) = N \ln \left[\frac{V}{N} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \right] + N$$

① Average Energy

$$U = \tau^2 \frac{d}{d\tau} (\ln Z_N) = \tau^2 \frac{d}{d\tau} \left(\frac{3}{2} N \ln(\tau) + \text{consts} \right)$$

$$= \tau^2 \frac{3}{2} N / \tau = \frac{3}{2} N \tau = \frac{3}{2} N k_B T$$

$$\boxed{U = \frac{3}{2} N \tau = \frac{3}{2} N k_B T}$$

② Heat Capacity at const. vol.

$$\boxed{C_V = \left(\frac{\partial U}{\partial \tau} \right)_{N,V} = \frac{3}{2} N}$$

③ Equation of State

(Q: what's E.o.S. for ideal gas?)

We will start from the Helmholtz free

energy b/c we consider the whole system (10)
at a given volume, temp, & particle #.

This setup "defines" the canonical ensemble,
which is a general statement of the specific
analysis we have done on the M-B gas.

$$F = -T \ln Z_N = -NT \ln \left[\frac{V}{N} \left(\frac{mC}{2\pi k^2} \right)^{3/2} \right] - NT$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = - \frac{\partial}{\partial V} \left[-NT \ln V + \text{constants} \right]$$

$$P = NT/V \quad \text{or} \quad \boxed{PV = NT} \quad \begin{array}{l} \text{Eq. of State} \\ \text{for Ideal Gas} \end{array}$$

Conventional Notation: $pV = Nk_B T$

Aside: Chemists define $n = N/N_A$ the # of moles $N = nN_A$

$$pV = nN_A k_B T \quad \text{with} \quad k_B N_A = R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$pV = nRT \quad \xrightarrow{\text{not what Kittel uses}} \quad n = N/V \quad \begin{array}{l} \text{# density} \\ \text{# density} \end{array}$$

(4) The entropy

Q: how might you expect
the entropy to increase?

$$\sigma = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = - \frac{\partial}{\partial T} \left\{ -NT \ln \left[\frac{V}{N} \left(\frac{mC}{2\pi k^2} \right)^{3/2} \right] - NT \right\}$$

$$= N \ln \left[\frac{V}{N} \left(\frac{mC}{2\pi k^2} \right)^{3/2} \right] + NT \frac{3}{2} \frac{1}{T} + N$$

$$\sigma = N \ln \left[\frac{V}{N} \left(\frac{m\tau}{2\pi k^2} \right)^{3/2} \right] + \frac{5}{2} N$$

(1)

$V \uparrow \Rightarrow \sigma \uparrow$ $\tau \uparrow \Rightarrow \sigma \uparrow$ CQ: What about as $N \uparrow$?
 as $N \uparrow$ it depends! b/c
 as $N \uparrow$ $n = N/V$ goes up (the particles are more densely packed). We have to be careful not to approach n_Q !

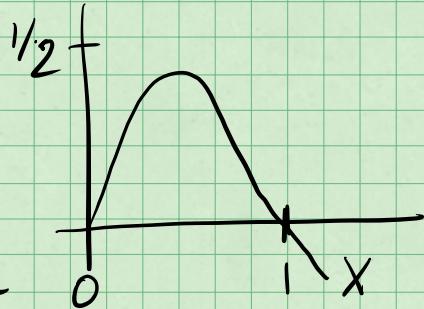
Let's recast the equation above in terms of $n + n_Q$:

$$\sigma = N \ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} N$$

Sackur-Tetrode Equation

$$\sigma = N \left[\ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right] \quad \text{note for us, } n \ll n_Q$$

Aside: Graph of $x \ln(1/x)$



This was an introduction to the analysis of a gas. Later, you will study gases of fermions and bosons (Ch 6)

Van der Waals Gas

(12)

Let's study another slightly more complex gas using the same arch.techno. This will help us see how general this process is.

The Van der Waals gas is really the next most complex gas that still uses M-B. like particles.

Two new assumptions:

- (1) particles have a finite size, and
- (2) particles have weak interactions

CQ: Van der Waals Gas (sign of A & B?)

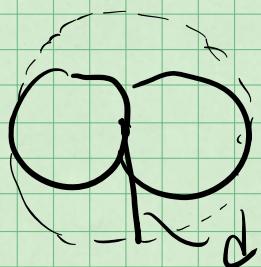
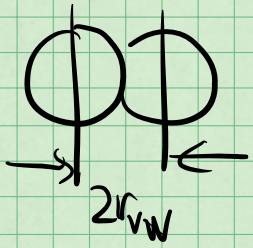
These assumptions will lead to changes to Z,

Ideal Gas: $Z_i = VN_Q$ $N_Q = \left(\frac{mT}{2\pi k h^2}\right)^{3/2}$

(1) Not all of V is available anymore

With hard spheres the closest that two particles can get is $2r_{vw}$ apart (center to center)





Let $d = 2r_{VW}$

(13)

This effectively excludes a volume of radius d for each pair of particles,

$$b_2 = \frac{4}{3}\pi d^3$$

so on avg. for 1 particle

$$b = b_2/2 = \frac{2}{3}\pi d^3$$

is excluded so that for N particles,

$V \rightarrow V - Nb$ and thus,

$$Z_1 = VN_Q \rightarrow Z_1 = (V - Nb)N_Q$$

(2) An additional interaction energy, E_{VW}

$Z_1 = VN_Q$ ideal gas

$Z_1 = (V - Nb)N_Q$ account for particle vol.

Now with pairwise interactions each particle has an additional energy term,

$E_{VW} \leftarrow$ which we will develop.

Each State $E_s(k)$ will have this new energy added to it so,

$$E_s(k) \Rightarrow E_s(k) + E_{vw}$$

(14)

CQ: how does this change the partition function?

$$\begin{aligned} Z_1 &= \sum_{\text{states}} e^{-[E_s(k) + E_{vw}]/\tau} \\ &= \sum_{\text{states}} e^{-E_s(k)/\tau} e^{-E_{vw}/\tau} \\ &= e^{-E_{vw}/\tau} \left(\sum_{\text{states}} e^{-E_s(k)/\tau} \right) \end{aligned}$$

$\underbrace{\quad}_{\text{old partition function, } (V-nb')N_Q}$

$$Z_1 = (V-nb')N_Q e^{-E_{vw}/\tau}$$

We need to find E_{vw} given some model of the interaction.

Let's assume that between any pair of particles the model is,

$$U(r) = \begin{cases} \infty & r < d \\ -\epsilon (d/r)^6 & r \geq d \end{cases}$$

The particles are hard spheres with a "Lennard-Jones-like" interaction 15

Any given particle will interact with the "mean field" of all the others,

" $\phi = \sum$ all interactions" for a particle density of N/V , yes I realize this is not $(\sqrt{N}n)^2$

$$\phi = \iiint d^3r u(r) \frac{N}{V}$$

Space
"outside"
particle

$$= \int_0^{4\pi} d\Omega \int_d^\infty u(r) \frac{N}{V} r^2 dr$$

$$= \frac{4\pi N}{V} \int_d^\infty \left[-\epsilon \left(\frac{d}{r} \right)^6 \right] r^2 dr$$

$$= -\frac{4\pi EN}{V} d^6 \int_d^\infty \frac{dr}{r^4} = -\frac{4\pi}{3} d^3 \frac{NE}{V}$$

This is more commonly written as,

$$\phi = -2a N/V \quad \text{with } a = \epsilon \frac{2\pi d^3}{3} = \epsilon b$$

Now this energy, ϕ , is shared between one particle and all its "effective partners" so that the average interaction energy any one particle experiences is,

$$E_{vw} = \phi/2$$

Thus,

$$Z_1 = (V - Nb) n_Q e^{-\phi/2\tau}$$

Recall $Z_N = (Z_1)^N / N!$ still.

To compute Thermodynamic Quantities, we need $\ln(Z_N)$,

$$\ln(Z_N) = N \ln(Z_1) - \ln N!$$

$$= N \ln(V - Nb) + N \ln(n_Q) + N \ln(e^{-\phi/2\tau}) - \ln N!$$

$$= N \ln(V - Nb) + N \ln(n_Q) - \frac{N\phi}{2\tau} - \ln N!$$

With $\phi = -\frac{2aN}{V}$,

$$\ln(Z_N) = N \ln(V - Nb) + N \ln(n_Q) + \frac{N^2 a}{V \tau} - \ln N!$$

① Equation of State

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$$P = T \frac{\partial}{\partial V} \ln Z_N$$

$$P = T \left[\frac{N}{V-Nb} - \frac{N^2 a}{V^2 T} \right] = \frac{N T}{V-Nb} - \frac{N^2 a}{V^2}$$

$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = N k T$$

Note from CQ

$$A = N^2 a / V^2 > 0$$

$$B = -Nb < 0$$

② Average energy

$$U = T^2 \frac{\partial}{\partial T} \ln Z_N$$

$$U = T^2 \frac{\partial}{\partial T} \left[\frac{N^2 a}{V T} + \frac{3}{2} N \ln T + \text{"constants"} \right]$$

$$U = T^2 \left[-\frac{N^2 a}{V T^2} + \frac{3}{2} N \frac{1}{T} \right] = \frac{3}{2} N T - \frac{N^2 a}{V}$$

$$U = \underbrace{\frac{3}{2} N k_B T}_{\text{ideal}} - \underbrace{\left(\frac{N}{V} \right) (Nb) \varepsilon}_{\text{correction based on interactions}}$$

③ heat capacity @ constant volume

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V} = \frac{3}{2} N \quad \text{same as ideal gas}$$