6. Ideal Gas

Read: Chapter 6
DO: Prob 6, 8, 13 (Also Prob 6,10,12 of Chap. 5)

What makes a gas "ideal"? We neglect interactions between particles. A good approximation for a sufficiently dilute gas.

In addition, if gas is really sufficiently dilute, then there is a negligible prob of two particles in the same "orbital" (one-particle state). This is "classical regime", where certain quantum effects can be neglected. Chapter 6 concerns ideal gas in classical regime. Chapter 7 is about quantum gases

Identical Particles

A peculiar feature of QM. Two electrons, or two H atoms must be regarded as indistinguishable. This affects counting of states

① orbital A ② orbital B

Different states for distinguishable particles, not for identical particles

Two Types of identical particles

spin = integer	Boson	Any no. of particles allowed in a single orbital
spin = integer + ½	Fermions	only 0 or 1 allowed in an orbital (empty or full) Pauli Exclusion Princ.

"spin-statistics connection"

Identical Particles

Why is there a connection between spin and statistics?

Spin: The angular momentum of a boson along (any) axis is $J_z = \hbar \cdot \text{integer}$,

while the angular momentum of a fermion is

$$J_z = \hbar \cdot (\text{integer} + \tfrac{1}{2})$$

Recall that the operator that represents a rotation by θ about axis $\hat{n}$ is

$$R(\hat{n}, \theta) = \exp(-i\theta \vec{J}\cdot\hat{n}/\hbar)$$

Thus for a rotation by 4π, $2\vec{J}\cdot\hat{n}/\hbar = \text{integer}$ means that

$$R(\hat{n}, 4\pi) = I$$

A rotation by 4π is represented trivially

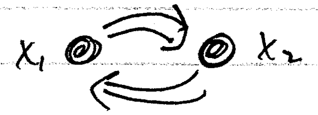
$$\text{But} \quad \vec{J}\cdot\hat{n}/\hbar = \frac{1}{2} \times \begin{cases} \text{even} & (\text{bosons}) \\ \text{odd} & (\text{fermions}) \end{cases}$$

Therefore, since $e^{i\pi\cdot\text{odd}} = -1$

$$R(\hat{n}, 2\pi) = \begin{cases} +I & \text{bosons} \\ -I & \text{fermions} \end{cases}$$

The wave function of a fermion changes sign under a rotation by 2π (!). Does it make sense for a rotation by 2π to be a nontrivial operation? Consider rotating a coffee cup: a 2π rotation twists your arm, a 4π rotation does not

Another way to describe the distinction between a boson and a fermion is to consider the effect of exchanging two particles. If all electrons are indistinguishable, then an operation under which two electrons change places is a symmetry



$$R: \psi(x_1, x_2) \rightarrow \psi(x_2, x_1)$$

– which can be simultaneously diagonalized with the Hamiltonian of the world. Note that $R^2 = I$; therefore eigenvalues of R are ± 1. The eigenstates are

$$\psi_{sym} = \frac{1}{\sqrt{2}}\left(\psi(x_1, x_2) + \psi(x_2, x_1)\right) -$$ symmetric under interchange: bosons

$$\psi_{antisym} = \frac{1}{\sqrt{2}}\left(\psi(x_1, x_2) - \psi(x_2, x_1)\right) -$$ Antisymmetric under interchange: fermions

what is the connection with our earlier proviso that fermions can occupy an orbital at most once?

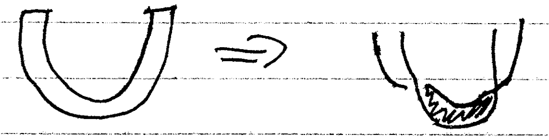
$$\frac{\text{②}}{\quad}\ b$$
$$\frac{\text{①}}{\quad}\ a$$

For a fermion $\psi_{E_a}(x_1)\,\psi_{E_b}(x_2) - \psi_{E_b}(x_1)\,\psi_{E_a}(x_2) = 0$ for $a=b$

If we put 2 indistinguishable particles in the same orbital, the state is symmetric under interchange of the two particles. If we try to antisymmetrize we get zero!

So, the "connection between spin and statistics" says that symmetry under interchange $\leftrightarrow$ invariance under 2π rotation
antisymmetry " " $\leftrightarrow$ $(-I)$ " "

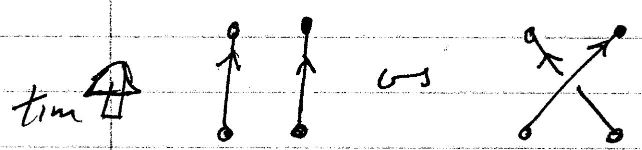
Why are these two things related? For a hint, follow Feynman and take off your belt.



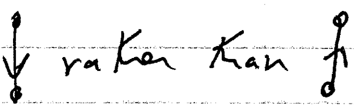
When we interchange the two ends of the belt, the belt acquires a twist by 2π.

In a sense, an interchange and a 2π twist are the same thing!

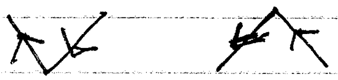
To make the connection less impressionistic, think of a process in spacetime:



And suppose there are antiparticles, which we can represent as world lines oriented backward in time

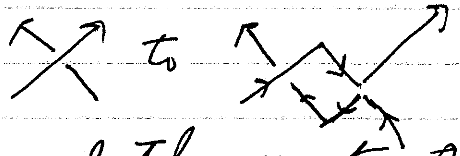


Furthermore, particles can be created and annihilated in pairs:

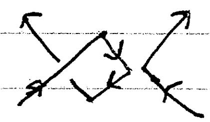


(loosely, the world line turns backward in time)

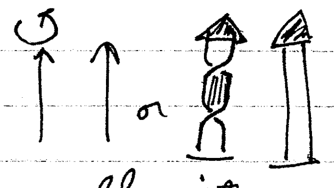
We can deform this exchange history



But then – we annihilate a pair and immediately recreate it; no one knows the difference if we never annihilate it at all in which case:



which we deform to



(Check this by making a loop in a belt and then pulling it taught!) We assign ±1 to exchange and to rotation by 2π, and we can not change $+1$ to -1 continuously. So a (-1) for 2π rot $\Leftrightarrow$ a (-1) for exchange!

But distinction makes no difference for $n/n_Q \ll 1$ — many more orbitals than particles $\Longrightarrow$ no orbital likely to be doubly occupied anyway

"classical regime"

(Note: we can treat each orbital as a separate system — in thermal & diffusive contact with res.)

Fermions: Fermi Dirac Distribution

$E=0,\ N=0$
$E=\epsilon,\ N=1$

$$\mathcal{Z} = 1 + e^{(\mu-\epsilon)/\tau}$$

— for a single orbital

what is expectation value for no. of particles in orbital?

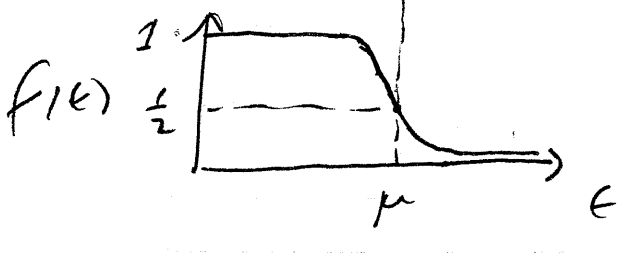
"Distribution function"

$$f(\epsilon) = \langle N \rangle_\epsilon = \frac{e^{(\mu-\epsilon)/\tau}}{1+e^{\mu-\epsilon/\tau}}$$

(Determines how available particles are distributed among orbitals)

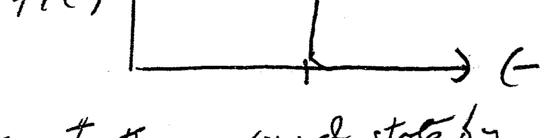
$$\boxed{f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau}+1}}$$

Fermi-Dirac Distribution (1926)



μ is the energy at which orbital is half full

$\tau \to 0$



Becomes a sharp step at $\epsilon=\mu$ (= Fermi energy)

Ground state (minimizes energy for given Number of particles)

[we construct the ground state by filling low-lying states until we run out of particles.]

Bosons: Bose-Einstein Distribution

one orbital

N particles ⇒ $E = N\epsilon$

Gibbs sum $\mathcal{Z} = \sum_{N=0}^{\infty} e^{N(\mu-\epsilon)/\tau}$

$$\left(\sum x^N = \frac{1}{1-x}\right) \qquad = \frac{1}{1-e^{(\mu-\epsilon)/\tau}}$$

(Need $x<1$; $\mu-\epsilon<0$)

$$f(\epsilon) = \langle N\rangle_\epsilon = \frac{1}{\mathcal{Z}}\sum N e^{N(\mu-\epsilon)/\tau}$$

$$= \frac{1}{\mathcal{Z}}\lambda\frac{d}{d\lambda}\mathcal{Z}$$

$\lambda = e^{\mu/\tau}$ = "absolute activity"

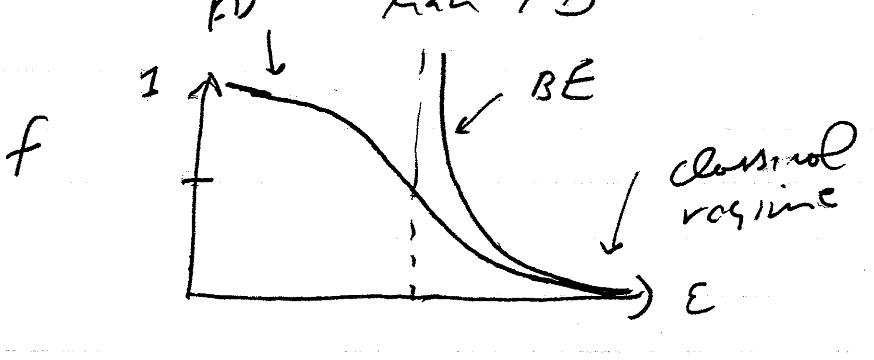
$$\mathcal{Z} = \frac{1}{1-\lambda e^{-\epsilon/\tau}}$$

$$f(\epsilon) = \frac{\lambda e^{-\epsilon/\tau}}{1-\lambda e^{-\epsilon/\tau}} = \frac{1}{e^{(\epsilon-\mu)/\tau}-1}$$

$$\boxed{f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau}-1}}$$

Bose-Einstein distribution (1924)

signif different than FD



Classical for $f \ll 1$ or

$$f \cong e^{(\mu-\epsilon)/\tau} = \lambda e^{-\epsilon/\tau}$$

We'll investigate consequences of this classical distribution. (Rederive properties of ideal gas previously discussed in chapter 3.)

Recover the results of Chap. 3 with new method

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"Classical" Ideal Gas

Now consider many orbitals. We relate μ (or activity λ) to concentration

$$N \equiv \langle N \rangle = \sum_{\substack{\cancel{\text{states}}\ s \\ \text{orbitals}}} \underbrace{\lambda e^{-\epsilon_s/\tau}}_{}$$

$f(\epsilon_s)$ – exp. no. of particles in state s

(~~That is~~ – sum over orbitals – one-particle states)

We did $\sum_s e^{-\epsilon_s/\tau}$ back in chapter 3 (Partition function for a single particle)

$$= Z_1 = n_Q V \qquad n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$$

So $N = \lambda n_Q V$ or $\lambda \equiv e^{\mu/\tau} = n/n_Q$

(and consistency – classical regime – requires $n/n_Q \ll 1$

Thus $\mu = \tau \log n/n_Q$ as found in chapter 5 (from $\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$)

Free energy

Since $\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \tau\left[\log N - \log(V n_Q)\right]$

$$F = \tau\, N\left(\log\left(\frac{N}{V n_Q}\right) - 1\right) + \text{const}$$

$$= \tau N\left(\log\left(\frac{n}{n_Q}\right) - 1\right)$$

(set const = 0) – because F = 0 for N = 0

Pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N} = \frac{\tau N}{V}$$

This time FD/BE distribution keeps track of indistinguishability!

Cf $F = -\tau \log Z$

$= -\tau \log\left[\frac{1}{N!} Z_1^N\right]$

$= -\tau\left[N \log(n_Q V) - \log N!\right]$

(We derive p, U, σ from F, repeating derivations in Chap. 3)

This is ideal gas law

$$pV = N\tau \quad \text{or} \quad = \underbrace{Nk_B}T$$

(called R for one mole
$N = N_{avogadro}$ — gas const.)

Energy

$$U = -\tau^2\left[\frac{\partial}{\partial\tau}\left(F/\tau\right)\right]_{V,N}$$

$$F/\tau = N\left(\log(n/n_Q) - 1\right) \qquad n_Q \sim c\tau^{3/2}$$

$$= -\tfrac{3}{2}N\log\tau + \tau\text{-independent}$$

$$U = -\tau^2\left(-\tfrac{3}{2}N\right)\frac{1}{\tau} = \tfrac{3}{2}N\tau$$

Entropy

$$\sigma = -\left(\frac{\partial F}{\partial\tau}\right)_{V,N}$$

$$= -N\log\left(n/n_Q - 1\right) + \tfrac{3}{2}N$$

$$= N\left(\log(n_Q/n) + 5/2\right)$$

(Sackur-Tetrode)

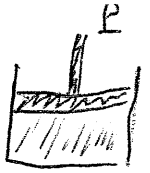
Heat Capacity

Constant volume: $C_V = \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_{V,N}$

$$\sigma \sim \tfrac{3}{2}N\log\tau \Rightarrow C_V = \tfrac{3}{2}N$$

Constant pressure:

$$C_p = \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_{p,N} \qquad \text{use } \tau d\sigma = dU + pdV$$



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then --

$$\tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p = \left(\frac{\partial U}{\partial \tau}\right)_p + p\left(\frac{\partial V}{\partial \tau}\right)_p$$

use $U = \frac{3}{2}N\tau$ and $V = N\tau/p$

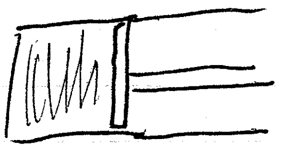
$$= \frac{3}{2}N + N = \frac{5}{2}N \nwarrow$$ larger than C_V
Need more heat to do work to expand the gas

Ideal Gas Thermodynamics

We'll consider 3 cases:

1. Isothermal - constant τ
2. Adiabatic (isentropic) - constant σ] Reversible (quasistatic)
3. Free expansion - Irreversible (far from equilibrium in intermediate stages)

1. Isothermal Expansion



Let gas expand (reversibly) at constant τ, from initial volume V_i to final volume V_f.

How do entropy and pressure change?

Ideal gas law: $pV = N\tau$
since N, τ fixed

$$\boxed{p_f/p_i = V_i/V_f}$$

(expansion lowers pressure)

(6.7)

Entropy: $\sigma = N\left[\log\left(\frac{n_Q V}{N}\right) + 5/2\right]$

$n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$ = constant at constant τ

$$\boxed{\sigma_f - \sigma_i = N\log(V_f/V_i)}$$

The entropy increases, because there are more accessible states in a larger volume

work done by the gas (against the piston)

$$W = \int p\,dV = \int_{V_i}^{V_f} \frac{N\tau}{V}dV = N\tau\log(V_f/V_i)$$

Note that $\boxed{W = \tau\Delta\sigma}$. Why?

This is integral of thermodynamic identity

$$\int dU = \int(\tau d\sigma - p\,dV)$$

$$\Rightarrow \quad \boxed{\Delta U = \tau\Delta\sigma - W} \quad \text{(at constant } \tau)$$

For ideal gas $U = \frac{3}{2}N\tau$, so $\Delta U = 0$ if N and τ do not change

Thus $W = \tau\Delta\sigma$

Since U does not change, the energy to do the work must be supplied by the reservoir — heat flows from reservoir to gas as it expands (reversibly and isothermally)

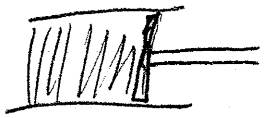
The amount of heat flow is $\boxed{Q = \tau \Delta \sigma}$

The thermodynamic identity may be written as

$$dU = \underset{\substack{\uparrow \\ \text{heat flow} \\ \text{into system}}}{dQ} - \underset{\substack{\uparrow \\ \text{work} \\ \text{done by} \\ \text{system}}}{dW} \qquad (N \text{ fixed})$$

It just expresses conservation of energy (the "First Law of Thermodynamics")

2. Isentropic Expansion



Now consider expansion of a gas that is insulated (rather than in contact with a reservoir) – so there is no heat flow: $dQ = 0$

As gas expands $\tau d\sigma = 0$, so entropy is unchanged. (As discussed previously, slow change in closed system preserves σ)

We have $\sigma = N\left[\log \dfrac{V\tau^{3/2}}{N} + \text{constant}\right]$

So $\sigma = \text{constant}$ (and $N = \text{constant}$) $\Rightarrow$

$$\boxed{V\tau^{3/2} = \text{constant}}$$

(Warning: true for a monatomic gas. If gas molecules have internal degrees of freedom – rotation and vibration – this is modified.)

So $$\boxed{\tau_f/\tau_i = \left(V_i/V_f\right)^{2/3}}$$

(slow) Expansion refrigerates the (ideal) gas

Pressure: also falls

use $p = N\tau/V$

$$p_f/p_i = \left(V_i/V_f\right)^{5/3}$$

Work Done:

$$\int_{V_i}^{V_f} p\,dV = p_i \int_{V_i}^{V_f} dV \left(V_i/V\right)^{5/3} = -\tfrac{3}{2} p_i V_i \left(\frac{V_i}{V}\right)^{2/3}\Bigg|_{V_i}^{V_f}$$

$$= -3/2\, p_i V_i \left(\left(V_i/V_f\right)^{2/3} - 1\right)$$

$$= -3/2 \left(p_f V_f - p_i V_i\right)$$

$$\boxed{W = -3/2\, N\left(\tau_f - \tau_i\right)}$$

or $(pV)\,V^{2/3} = \text{const}$

$$\Rightarrow \left[d(pV) + \tfrac{2}{3}(pV)\frac{dV}{V}\right]V^{2/3} = 0$$

$$\Rightarrow p\,dV = -3/2\, d(pV)$$

The energy to do the work now comes from the internal energy of the gas

$$\Delta U = -W \quad , \text{ where } U = \tfrac{3}{2} N\tau$$

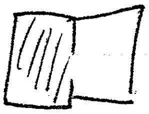
Reversibility

We can undo the isothermal or isentropic expansion by doing work on the system (pushing the piston quasistatically).

In isothermal case, heat is then lost to the reservoir. In isentropic case, the work heats the gas up. It returns to original configuration.

isothermal	ΔQ = Work done on gas	Reverses heat flow during isothermal expansion
isentropic	ΔU = work done on gas	Reverses cooling of gas during isentropic expansion

3. Free Expansion



Now just open a valve and let the gas expand into a larger box. Box is insulated (In practice, free expansion is so rapid that there is no *time* for heat flow.) Now no work is done against piston. So

$$\Delta W = 0 \qquad \Delta Q = 0$$

and hence (conservation of energy)

$$\Delta U = 0$$

Since gas is ideal, $U = \frac{3}{2} N\tau$, the temperature (of ideal gas) is unchanged, and pressure falls in accord with $pV = N\tau$.

Better to say $\tau d\sigma$ is not the heat flow pdV is not the work done

But the *entropy* changes (increases). Important point: thermodynamic identity $dU = \tau d\sigma - p dV$ does not apply — this applies to *reversible* processes, for it concerns difference between two *equilibrium* configs of the system. In *irreversible* process like free expansion, equilibrium is *not* maintained during the expansion.

From $\sigma = N[\log(\tau^{3/2}V/N) + \text{const}]$

we have

$$\sigma_f - \sigma_i = N \log(V_f/V_i)$$

as for isothermal (reversible) expansion. But *now*, the increase occurs without any flow of heat from a reservoir.

We could now compress the gas isothermally, and return it to original configuration. But this requires that heat flow into the reservoir, so that its entropy increases.

Alternatively, we can compress the gas isentropically. But then it does not return to original configuration. (It is hotter now)

Either way, the free expansion has increased the entropy of the world ($\mathcal{S} + \mathcal{R}$). The genie will not go back in the bottle.