F. The Density of single-particle states $g(\varepsilon)$

Motivation:

$$n_i = g_i \cdot \left(\begin{matrix} \text{Fermi-Dirac} \\ \text{Bose-Einstein} \end{matrix} > \text{distribution} \right)$$

Take energies as continuously spreading over the energy axis:

$$\underbrace{n(\varepsilon)\,d\varepsilon}_{} = \frac{g(\varepsilon)\,d\varepsilon}{e^{(\varepsilon-\mu)/kT} \pm 1}$$

particles having energies in interval $\varepsilon \to \varepsilon + d\varepsilon$

single-particle states (of the system) in the energy interval $\varepsilon \to \varepsilon + d\varepsilon$

$g(\varepsilon)$ is called the Density of Single-particle states in energy OR simply the Density of States

$\underbrace{g(\varepsilon)\,d\varepsilon}$ is <u>NOT</u> related to temperature

it depends on whether the particles are in 3D, 2D, 1D (dimensionality)

- the particles are free <u>OR</u> trapped in some one-particle potential
- the particles are non-relativistic <u>OR</u> relativistic

[useful in solid state physics, astrophysics, materials science, statistical physics]

We will aim at getting $g(\varepsilon)$ for <u>3D free non-relativistic particles</u>

(but method is general)

> Key idea: It is a result of fitting waves subject to boundary conditions

Let's start with 1D

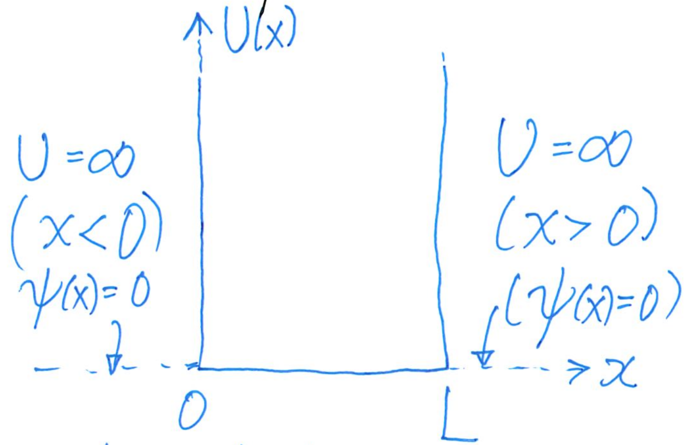
(a) $\underbrace{\text{Non-relativistic}}\ \underbrace{\text{Free}}$ Particles in 1D

s.p. Hamiltonian $\rightarrow$ $$\underbrace{h = \frac{p^2}{2m}}_{\text{and particle can only live in a 1D space of length } L} + \underbrace{U(x)}_{= 0 \text{ (free)}}$$ (single-particle Hamiltonian)

particle can only live in $0 \le x \le L$

$\Downarrow$

1D particle-in-a-box box in QM



In box, Schrödinger Equation is

$$\frac{\hat{p}^2}{2m}\psi = \varepsilon\psi$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = \varepsilon\psi(x) \quad , \quad 0 \le x \le L$$

But $\underbrace{\psi(x) = 0 , \quad x < 0 \ \& \ x > L}$

provide the B.C.'s (and size L enters into solutions)

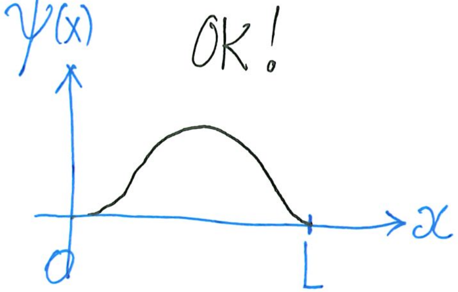
$\psi(x) \sim \sin kx$ works for specific k-values $\left[k = \frac{2\pi}{\lambda} \right]$

wave number ← wavelength

$x=0$ B.C. satisfied

but $x=L$ B.C. requires specific values of k [thus λ, fitting waves]

matter waves



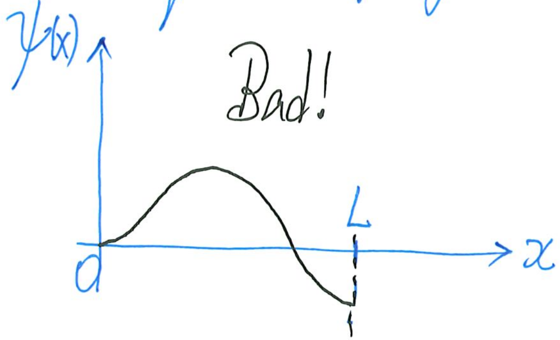
$\lambda = 2L$

$k = \frac{2\pi}{\lambda} = \frac{\pi}{L}$

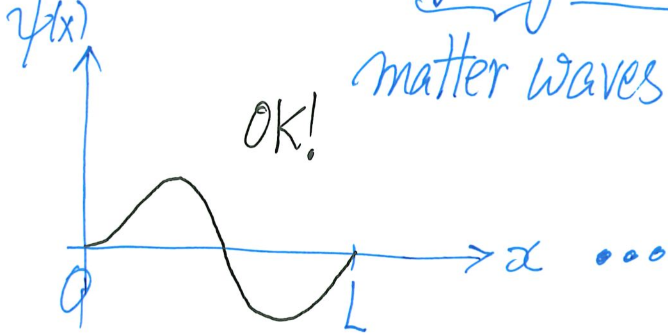
$\mathcal{E}_1 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{(1^2)\hbar^2\pi^2}{2mL^2}$

$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right), \quad 0 \le x \le L$

QM normalization condition



this wavelength is Bad! (not allowed)



$\lambda = L, \quad k = \frac{2\pi}{\lambda} = \frac{2\pi}{L}$

$\mathcal{E}_2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{(2^2)\hbar^2\pi^2}{2mL^2}$

$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right); \quad 0 \le x \le L$

$$\psi_{n_x}(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_x \pi x}{L}\right) = \sqrt{\frac{2}{L}}\sin\left(k_{x,n_x} x\right), \quad n_x = 1, 2, 3, \ldots$$

$$\updownarrow$$

$$\varepsilon_{n_x} = \frac{n_x^2 \pi^2 \hbar^2}{2mL^2} = \frac{\hbar^2 k_{x,n_x}^2}{2m}, \quad n_x = 1, 2, 3, \ldots$$

these are all the single-particle states (1D) (22)

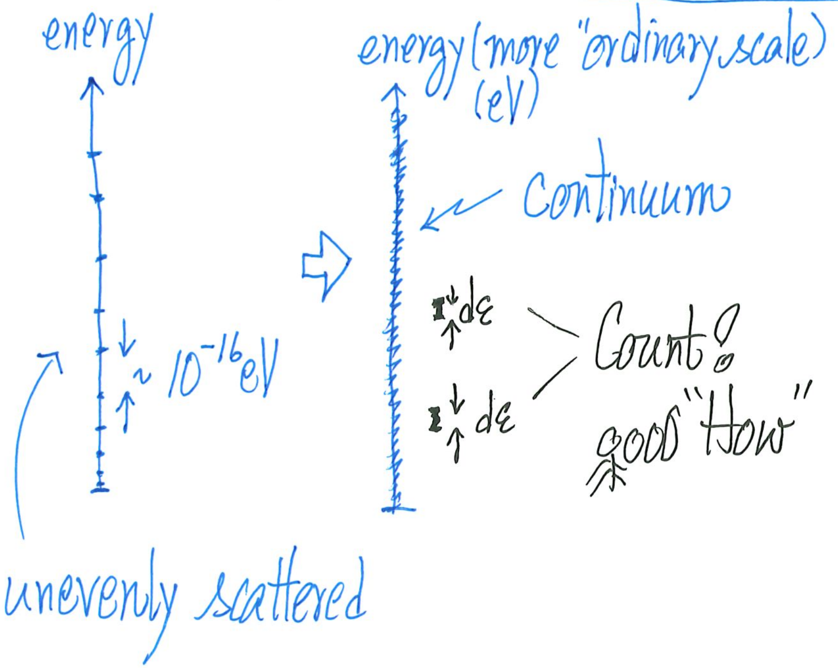
$$\boxed{\text{A number to remember: } \frac{\hbar^2}{m_e} \approx 7.62 \ \underbrace{\text{eV-Å}^2}_{\text{note the unit}}}$$

electron mass → m_e

(23)

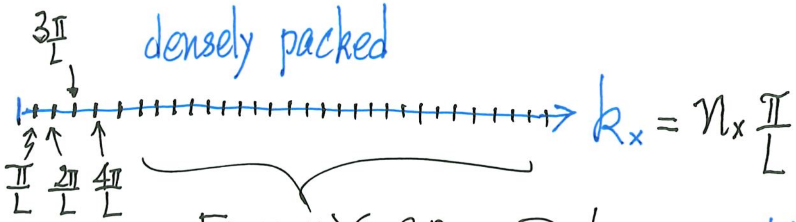
stat. mech. problems

$$\boxed{\text{Here } L \sim \text{cm} \sim 10^8 \text{ Å}}$$



Look at the k_x axis

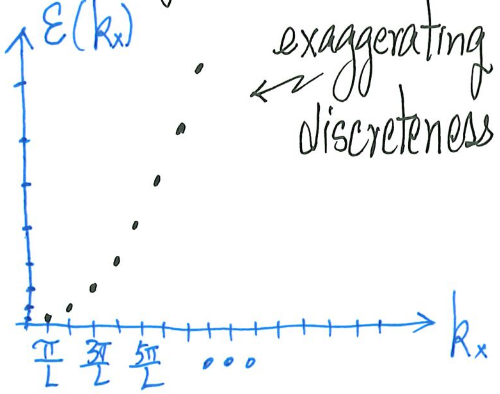
$$k_{x,n_x} = n_x \frac{\pi}{L}; \quad n_x = 1, 2, \ldots$$



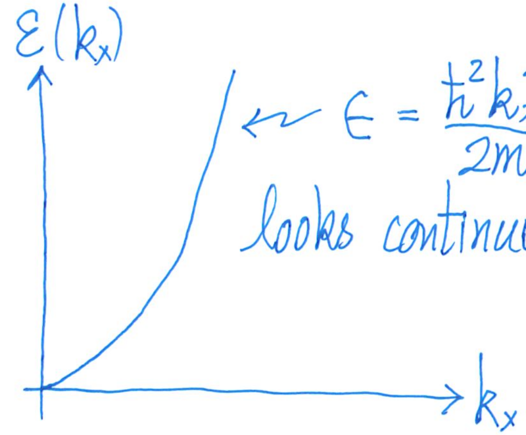
EVENLY SPACED! ← Key idea

$$\boxed{\text{Easier to count in "k-axis" (k-space)!}}$$

Putting the two axes together



$\Rightarrow$ macroscopic L



$\leftarrow \mathcal{E} = \frac{\hbar^2 k_x^2}{2m}$ (quadratic in k_x)

looks continuous

This is called the Dispersion Relation in general

- how $\mathcal{E}$ varies with k_x (or k_y & k_z in 2D, 3D)
- how ω varies with k_x (or k_y, k_z)

e.g. EM waves, elastic waves (string)

In solid state physics, $\mathcal{E}(k_x)$ or $\mathcal{E}(\vec{k})$ is the band structure.

Note that: Each allowed "k-value" occupies $\left(\frac{\pi}{L}\right)$ of k-space. (1D)

Strategy of getting $g(\varepsilon)$

Let $g^<(\varepsilon)$ (this is NOT $g(\varepsilon)$ but related) be the number of s.p. states having energies less than or equal to ε (i.e. from energy zero to energy ε)

$$g^<(\varepsilon+\Delta\varepsilon) - g^<(\varepsilon) = \#\text{ s.p. states with energies in } \varepsilon \to \varepsilon+\Delta\varepsilon$$
$$= g(\varepsilon)\,\Delta\varepsilon$$

$$\therefore \boxed{g(\varepsilon) = \frac{dg^<(\varepsilon)}{d\varepsilon}} \qquad (24)$$

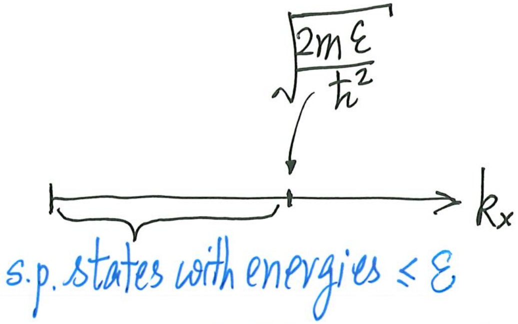
i.e. Find $g^<(\varepsilon)$ first and then take derivative

$g^<(\varepsilon)$ can readily be found by doing the counting in k-space

This approach is good for any spatial dimension.

$g_{1D}(\varepsilon)$

- For a given ε, it sets a value of k_x



$$\varepsilon = \frac{\hbar^2 k_x^2}{2m} \Rightarrow k_x = \sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

and (i) s.p. states with values of k_x smaller than this value have energies smaller than ε [Key idea here!]

(ii) each s.p. state occupies $\left(\frac{\pi}{L}\right)$ of k-space (k_x axis in 1D case)

$$\therefore \quad g_{1D}^{<}(\varepsilon) = \frac{\sqrt{\frac{2m\varepsilon}{\hbar^2}}}{\left(\frac{\pi}{L}\right)}$$

← "k-space" length from $k_x = 0$ to $k_x = \sqrt{\frac{2m\varepsilon}{\hbar^2}}$

← "k-space" occupied by one s.p. state

$$= \frac{L}{\pi}\sqrt{\frac{2m}{\hbar^2}}\sqrt{\varepsilon}$$

(1D) $$\boxed{g_{1D}(\mathcal{E}) = \frac{dg^{<}_{1D}(\mathcal{E})}{d\mathcal{E}} = \frac{L}{2\pi}\sqrt{\frac{2m}{\hbar^2}}\frac{1}{\sqrt{\mathcal{E}}} \sim \frac{1}{\sqrt{\mathcal{E}}}} \quad (25a)$$

- Good for free particles (fermions, bosons, even "classical particles")
- For fermions, e.g. electrons, there is a SPIN factor not included

  Recall: Schrödinger QM needs to introduce spin as an extra variable. Each s.p. state can hold two electrons if their spins are opposite ($m_s = +1/2, -1/2$), there is a spin-degeneracy factor

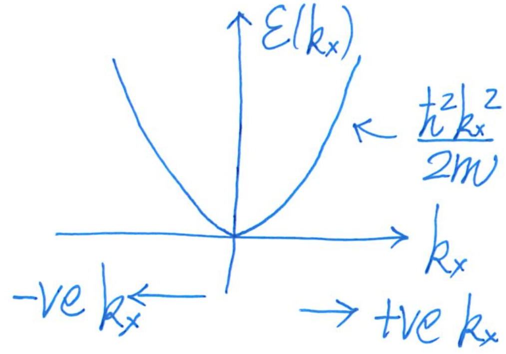
$$g_s = 2$$

so that
$$\boxed{g_{1D}(\mathcal{E}) = \frac{L}{2\pi}\cdot g_s \cdot \sqrt{\frac{2m}{\hbar^2}}\frac{1}{\sqrt{\mathcal{E}}}} \quad (25)$$

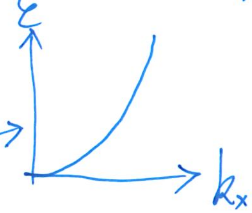
- For bosons of "spin-1", $g_s = 3$

Further Remark

- Very often, you see the $\mathcal{E}(k_x)$ being drawn as with both +ve and -ve values of k_x



- But what we want to count is



- If you include negative k_x-values in counting, remember to divide number by 2

$$g_{1D}^{<}(\mathcal{E}) = \frac{\left[2\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\right]}{\left(\frac{\pi}{L}\right)} \times \frac{1}{2}$$

"k-space" from $-\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}$ to $+\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}$

divide number by 2

$$= \frac{L}{\pi}\sqrt{\frac{2m}{\hbar^2}}\sqrt{\mathcal{E}} \quad \text{(same expression)}$$

and $$g_{1D}(\mathcal{E}) = \frac{L}{2\pi}\sqrt{\frac{2m}{\hbar^2}}\frac{1}{\sqrt{\mathcal{E}}} \quad \text{(same expression)}$$

(b) <u>Non-relatistic Free Particles in 2D</u>

Particle-in-a-2D Box ($L \times L$ in size)

$$\left[\frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m}\right]\psi(x,y) = \varepsilon\,\psi(x,y) \quad \text{in box}$$

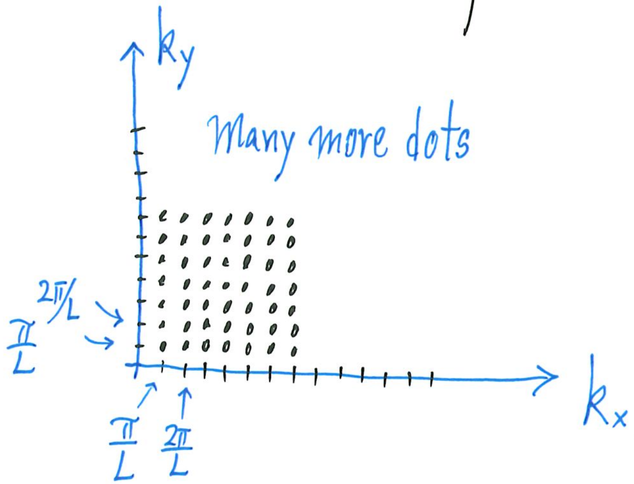
$\because U = 0$ (in box)

[$\psi(x,y) = 0$ as $U = \infty$ (outside box)]

$$\boxed{\begin{aligned} &\psi_{n_x,n_y}(x,y) = \frac{2}{L^2}\sin\left(\frac{n_x \pi x}{L}\right)\sin\left(\frac{n_y \pi y}{L}\right) = \frac{2}{L^2}\sin(k_{x,n_x} x)\sin(k_{y,n_y} y) \quad \text{in box} \\ &\updownarrow \qquad k_{x,n_x} = n_x\frac{\pi}{L}\ ;\ k_{y,n_y} = n_y\frac{\pi}{L} \qquad n_x = 1,2,\ldots\ ;\ n_y = 1,2,\ldots \\ &\varepsilon_{n_x,n_y} = \frac{(n_x^2+n_y^2)\pi^2\hbar^2}{2mL^2} = \frac{\hbar^2}{2m}\left(k_{x,n_x}^2 + k_{y,n_y}^2\right) \end{aligned}} \qquad (26)$$

These are all the 2D single-particle states (2D)

Look at the "k-space" (k_x and k_y axes)



- Each s.p. state is specified by (n_x, n_y) and thus a (k_x, k_y) dot
- Each dot specifies a s.p. state
- $\boxed{\text{Each s.p. state occupies a "k-space" of } \left(\frac{\pi}{L}\right)^2}$ (27)

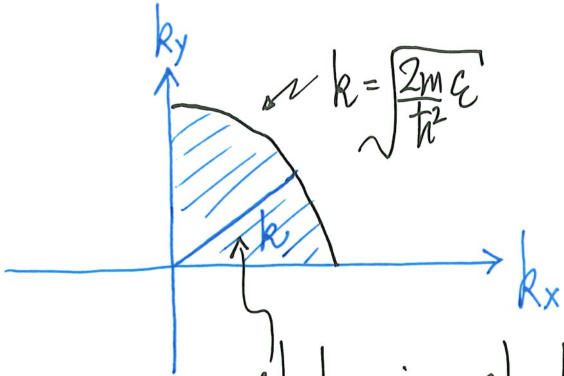
Key idea

- Evenly spaced!
- Easier to count in k-space

For a given energy ε, it sets a value of $k = \sqrt{k_x^2 + k_y^2}$

$$\varepsilon = \frac{\hbar^2}{2m}(k_x^2 + k_y^2) \Rightarrow k = \sqrt{\frac{2m}{\hbar^2}\varepsilon}$$

and s.p. states of k-values smaller than this value have energies smaller than ε



Given ε, $k = \sqrt{\frac{2m}{\hbar^2}\varepsilon}$ sets boundary in k-space for s.p. states having energies smaller than ε

states in shaded region (1/4 of a circle of radius k) have energies less than ε

$$g^{<}_{2D}(\varepsilon) = \frac{\pi\left(\sqrt{\frac{2m}{\hbar^2}\varepsilon}\right)^2 \cdot \frac{1}{4}}{\left(\frac{\pi}{L}\right)^2}$$

← "k-space" of k-values less than $\sqrt{\frac{2m\varepsilon}{\hbar^2}}$

← "k-space" occupied by one s.p. state

$$= \frac{A}{4\pi}\left(\frac{2m}{\hbar^2}\right)\cdot\varepsilon$$

$A = L \times L$ = Area of 2D system

$$\therefore \boxed{g_{2D}(\varepsilon) = \frac{A}{4\pi}\left(\frac{2m}{\hbar^2}\right)} \quad (28)$$

(doesn't depend on ε, or goes like ε^0)

Remark: Important in understanding the Quantum Hall effect in 2D electron gas.

(c) Non-relativistic Free Particles in 3D

Particle-in-a-3D Box ($L \times L \times L \equiv V$ in size)

$$\frac{1}{2m}\left[\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right]\psi(x,y,z) = \varepsilon\, \psi(x,y,z) \quad \text{in box}, \quad \psi = 0 \text{ outside box}$$

$$\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi x}{L}\right) \quad \text{in box}$$

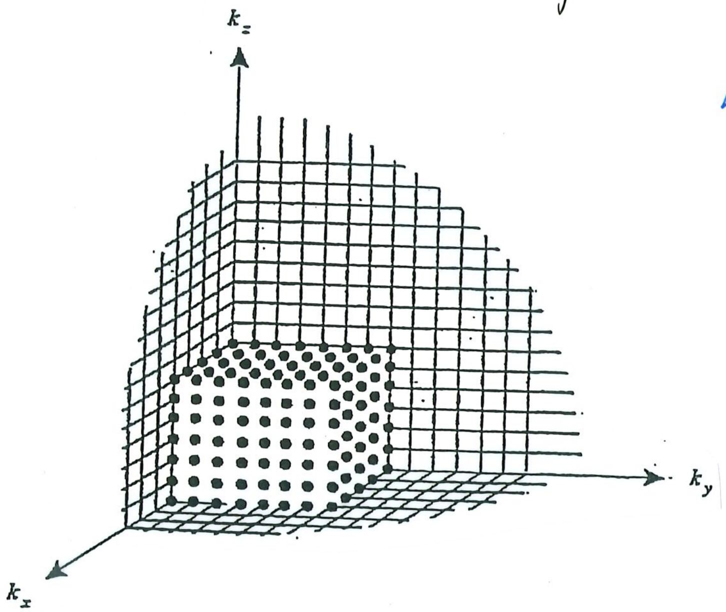
$$= \left(\frac{2}{L}\right)^{3/2} \sin(k_{x,n_x} x) \sin(k_{y,n_y} y) \sin(k_{z,n_z} z) \quad \text{in box}$$

with $k_{x,n_x} = n_x \frac{\pi}{L}$; $k_{y,n_y} = n_y \frac{\pi}{L}$; $k_{z,n_z} = n_z \frac{\pi}{L}$, $n_x = 1, 2, \ldots$ $n_y = 1, 2, \ldots$ $n_z = 1, 2, \ldots$ (29)

$$\varepsilon_{n_x,n_y,n_z} = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2 \hbar^2}{2mL^2} = \frac{\hbar^2}{2m}\left(k_{x,n_x}^2 + k_{y,n_y}^2 + k_{z,n_z}^2\right)$$

These are all the 3D single-particle states (3D)

Look at the "k-space" (k_x, k_y, k_z axes)



Evenly spaced! Easier to count in k-space.

Each allowed (k_x, k_y, k_z) [a dot] is a s.p. state

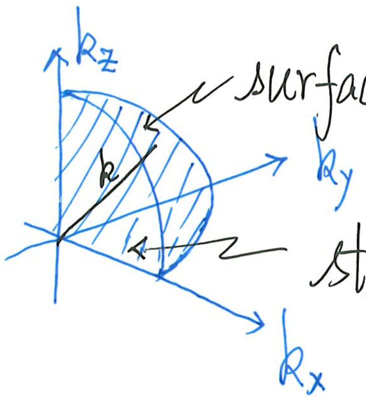
$$\boxed{\text{Each s.p. state occupies a k-space of } \left(\frac{\pi}{L}\right)^3 = \frac{\pi^3}{V}}$$

(Key idea) (30)

For a given energy ε, it sets a value of $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$

$$\varepsilon = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \Rightarrow k = \sqrt{\frac{2m}{\hbar^2}\varepsilon}$$

and s.p. states of k-values smaller than this value have energies smaller than ε.



surface with $k = \sqrt{\frac{2m}{\hbar^2}\varepsilon}$

states in shaded region ($\frac{1}{8}$ of a sphere of radius k) have energies less than ε

$$g^{<}_{3D}(\varepsilon) = \frac{\frac{4\pi}{3}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{3/2}\cdot\frac{1}{8}}{\left(\frac{\pi}{L}\right)^3}$$

k-space of k-values less than $\sqrt{\frac{2m\varepsilon}{\hbar^2}}$

k-space occupied by one s.p. state

\# s.p. states with energies less than or equal to ε

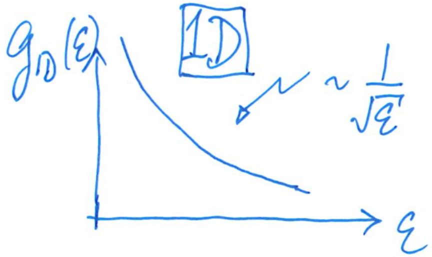
$$= \frac{V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\cdot\varepsilon^{3/2}$$

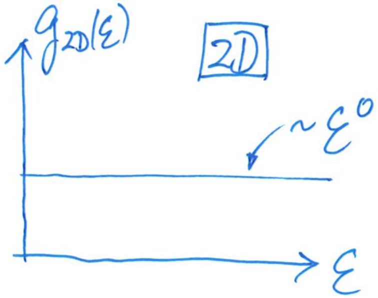
$$\therefore \boxed{g_{3D}(\varepsilon) = \frac{dg^{<}_{3D}(\varepsilon)}{d\varepsilon} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\cdot\varepsilon^{1/2} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\cdot\sqrt{\varepsilon}} \quad (31)$$

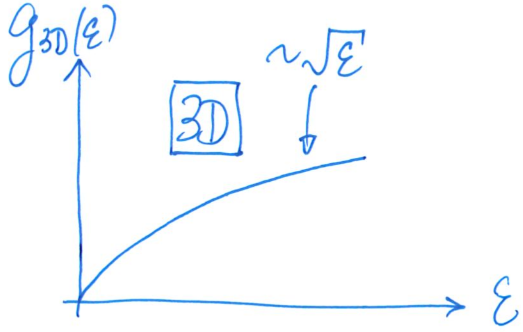
most important result for discussing 3D ideal Fermi/Bose gas, and solid states

Remarks

(i)







Two factors: Dimension AND Dispersion Relation ($\varepsilon = \frac{\hbar^2 k^2}{2m}$ here)

<u>Exercises</u>: How about d-dimension?

(ii) Spin-degeneracy factor $g_s = (2s+1)$ spin-½ : $g_s = 2$; spin-1 : $g_s = 3$

$$\boxed{g_{3D}(\varepsilon) = g_s \cdot \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \varepsilon^{1/2}} \qquad (32)$$

(iii) $g_{3D}(\varepsilon) \propto V$ makes sense!

V increases $\rightarrow$ bigger box $\rightarrow$ $\varepsilon \sim \frac{1}{L^2}$ $\Rightarrow$ energies more closely spaced $\Rightarrow$ $g(\varepsilon)$ increases

(iv) Buy one Get one free!

[This discussion requires the physics of waves]

Debye Model: $D(\omega) \sim \omega^2$ for low normal-mode frequencies' oscillators

Here is why! low $\omega \rightarrow$ long wavelengths

lattice vibrations & long wavelengths $\sim$ sound waves[+] $\underbrace{\omega = v_s \cdot \overset{\text{wave number}}{k}}_{\text{dispersion relation}}$

Given ω, it sets a $k = \omega / v_s$ that normal modes with k-values less than k have angular frequences less than ω

$$D^{<}_{3D}(\omega) = \frac{\frac{4\pi}{3} \frac{\omega^3}{v_s^3} \cdot 1/8}{\pi^3/V} \sim \frac{V}{v_s^3} \frac{1}{\pi^2} \cdot \omega^3$$

$$D_{3D}(\omega) \sim \frac{V}{v_s^3} \cdot \frac{1}{\pi^2} \cdot \omega^2$$ (this is what actual $D(\omega)$ shows in 3D)

[+] If you are not happy with this hand-waving argument, consult a solid state physics book.

(v) Buy one get another free!

We saw $Z = \frac{1}{N!} z^N$ in classical ideal gas with $z = \frac{1}{h^3}\int d\vec{x}\int d\vec{p}\, e^{-\vec{p}^2/2mkT}$

$$= \frac{V}{h^3}\int d\vec{p}\, e^{-\vec{p}^2/2mkT}$$

For classical ideal gas, the particles are Non-interacting.

Expect z = s.p. partition function $= \sum_{\text{all s.p. states } i} e^{-\varepsilon_i/kT}$

Treating s.p. energies as continuous:

$$z = \int_0^\infty g(\varepsilon)\, e^{-\varepsilon/kT} d\varepsilon = \underbrace{\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon}_{\text{Is this the same as } \frac{V}{h^3}\int d\vec{p}\, e^{-\vec{p}^2/2m}\text{ ?}} \left(= \frac{V}{h^3}\left(\sqrt{2\pi mkT}\right)^3 \right)$$

$$Z = \frac{V}{h^3}\int d\vec{p}\; e^{-\vec{p}^2/2mkT} = \frac{V}{h^3}\int_0^\infty 4\pi p^2 e^{-p^2/2mkT}\,dp$$ (use spherical coordinates)

[free particle $\Rightarrow$ $\varepsilon = p^2/2m$ $\Rightarrow$ $d\varepsilon = \frac{2p}{2m}dp$ and $p = \sqrt{2m\varepsilon}$]

$$Z = \frac{V}{h^3}\, 2\pi \int_0^\infty p\, e^{-\varepsilon/kT}\, 2p\,dp = \frac{V}{h^3}\, 2\pi \int_0^\infty \sqrt{2m\varepsilon}\, e^{-\varepsilon/kT}\, 2m\, d\varepsilon$$

$$= V\cdot\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/kT}\, d\varepsilon$$

$$= \frac{V}{4\pi^2}\cdot\frac{8\pi^3}{h^3}(2m)^{3/2}\int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/kT}\, d\varepsilon$$

$$= \underbrace{\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}}\int_0^\infty \underbrace{\varepsilon^{1/2}}\, e^{-\varepsilon/kT}\, d\varepsilon^{\dagger} = \int_0^\infty g(\varepsilon)\, e^{-\varepsilon/kT}\, d\varepsilon$$

This also justifies the factor $\frac{1}{h^{3N}}$ in evaluating Z by integrating $6N$-dim. phase space!

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† The integral can be readily done by using Gamma Function (see Essential Math Skills).

G. Equations for the Physics of Ideal Quantum Gases

Putting together $g(\varepsilon)d\varepsilon$ and $f_{FD}(\varepsilon)$ $[f_{BE}(\varepsilon)]$

Using Ideal Fermi Gas in 3D as an example

$$\boxed{\begin{aligned} N &= \sum_{\text{cells } i} n_i = \sum_{\text{cells } i} g_i \cdot f_{FD}(\varepsilon_i) \quad \text{[general, any dimensions]} \\ E &= \sum_{\text{cells } i} \varepsilon_i n_i = \sum_{\text{cells } i} \varepsilon_i g_i f_{FD}(\varepsilon_i) \quad \text{[general, any dimensions]} \end{aligned}} \qquad (33)$$

$f_{FD}(\varepsilon)$ contains the thermodynamic factors (T, μ, fermionic nature)

$g(\varepsilon)$ contains dimensionality and dispersion relation

3D non-relativistic particles: $$g_{3D}(\varepsilon) = g_s \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2} \qquad (32)$$

$$\boxed{\begin{aligned} N &= g_s \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\mu)/kT}+1}\,d\varepsilon \qquad (34) \\ E &= g_s \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{(\varepsilon-\mu)/kT}+1}\,d\varepsilon \qquad (35) \end{aligned}}$$

The equations that govern the Physics of a 3D Ideal Fermi Gas

sodium  gold  electron physics is governed by the same eqns!

$$\underbrace{\frac{N}{V}}_{} = 2.65 \times 10^{22}/\text{cm}^3 \qquad \underbrace{\frac{N}{V}}_{} = 5.90 \times 10^{22}/\text{cm}^3$$

\# conduction electrons per unit volume of solid

$\therefore$ We can set up the equations for studying 3D, 2D, 1D ideal Fermi (Bose) Gases

Ex: Write down the general Equations (c.f. Eq.(33)) for Ideal Bose Gas

Ex: Write down the governing equations (c.f. Eq.(34), Eq.(35)) for 3D Ideal Bose Gas

H. Ideal Quantum Gases AIN'T CLASSICAL Ideal Gas

Classical Ideal Gas (non-interacting particles) $\quad pV = NkT$

Ideal Fermi/Bose Gas (also non-interacting particles) $\quad pV \overset{?}{=} NkT$ OR NOT?

- Look at Ideal Fermi Gas as an example

We derived the optimal (most probable) $(n_1, n_2, \ldots, n_i, \ldots)$ as

$$\frac{n_i}{g_i} = \frac{1}{e^{(\varepsilon_i-\mu)/kT}+1} \qquad \left(\text{should say } \frac{n_i^{op}}{g_i}\right)$$

Follow the microcanonical ensemble approach, the Entropy of the ideal Fermi Gas is

$$S_F = k \ln W_{FD}(\{n_i^{op}\}) = k \sum_{\text{cells } i} \ln \frac{g_i!}{n_i!\,(g_i-n_i)!}$$

$$= k \sum_i \left[g_i \ln g_i - n_i \ln n_i - (g_i-n_i)\ln(g_i-n_i) \right] \qquad \text{(Stirling Formula)}$$

$$S_F = k\sum_i\left[g_i \ln\left(\frac{1}{1-\frac{n_i}{g_i}}\right) + n_i \ln\left(\frac{g_i}{n_i}-1\right)\right]$$

(we know $\frac{n_i}{g_i}$)

$$= k\sum_i\left[g_i \ln\left(\frac{1}{1-\frac{1}{e^{(\varepsilon_i-\mu)/kT}+1}}\right) + n_i \ln\left(e^{(\varepsilon_i-\mu)/kT}\right)\right]$$

$$= k\sum_i g_i \ln\left(1+e^{-(\varepsilon_i-\mu)/kT}\right) + k\sum_i \frac{n_i(\varepsilon_i-\mu)}{kT}$$

$$\left\{\begin{array}{l}\sum_i n_i\varepsilon_i = E \\ \sum_i n_i\mu = \mu\sum_i n_i \\ \quad = \mu N\end{array}\right.$$

$$= k\sum_i g_i \ln\left(1+e^{-(\varepsilon_i-\mu)/kT}\right) + \frac{E-\mu N}{T} \qquad (36)$$

$\leftarrow$ Good for 1D, 2D, 3D (Fermi Gas Entropy)

$$\therefore\quad E - TS_F - \mu N = -kT\sum_i g_i \ln\left(1+e^{-(\varepsilon_i-\mu)/kT}\right)$$

Recall Euler Equation (Ch. VII) in thermodynamics $E = TS - pV + \mu N$

$\Rightarrow E - TS - \mu N = -pV$

$$\therefore\ F = E - TS_F = \mu N - kT \sum_{\text{cells } i} g_i \ln\left(1 + e^{-(\varepsilon_i - \mu)/kT}\right) \quad (37)$$

Helmholtz free energy (Fermi Gas)

and

$$\boxed{pV = kT \sum_{\text{cells } i} g_i \ln\left(1 + e^{-(\varepsilon_i - \mu)/kT}\right)} \quad (38)$$

1D, 2D, 3D Fermi Gas

Key Points

- The result says that $pV \neq kTN$ for ideal Fermi Gas
- Instead, we have

$$pV = kT\left(\sum_{\text{cells } i} g_i \frac{1}{e^{(\varepsilon_i-\mu)/kT}+1}\right) \cdot \frac{\sum_{\text{cells } i} g_i \ln\left(1+e^{-(\varepsilon_i-\mu)/kT}\right)}{\sum_{\text{cells } i} g_i \frac{1}{e^{(\varepsilon_i-\mu)/kT}+1}}$$

$$\Rightarrow pV = kT\,N \cdot \left[\frac{\sum_{\text{cells } i} g_i \ln\left(1+e^{-(\varepsilon_i-\mu)/kT}\right)}{\sum_{\text{cells } i} g_i \frac{1}{e^{(\varepsilon_i-\mu)/kT}+1}}\right] = kTN \cdot \left[\text{correction terms}\right] \quad (39)$$

- Due to the Pauli Exclusion rule [used in counting $W_{FD}(\{n_i\})$], a collection of non-interacting fermions behave in a way different from a classical non-interacting (ideal) gas!

The 3D version of Eq.(38) is $pV = kT \int_0^{\infty} \frac{g_s V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2} \ln\left(1+e^{-(\varepsilon-\mu)/kT}\right) d\varepsilon$ (40)

$\boxed{\text{Eqs. (34), (35), (40) cover all 3D Ideal Fermi Gas Physics!}}$

$\boxed{\text{Eqs. (33), (38) cover all Ideal Fermi Gas Physics (any dimension)!}}$

Exercise: Derive the analogous equations (see Eqs. (38), (39)) for ideal Bose Gas