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1 Lecture 1: Blackbody Radiation

1.1 What is Physics?

Why do we need quantum mechanics? **The older (classical) theory was wrong!**

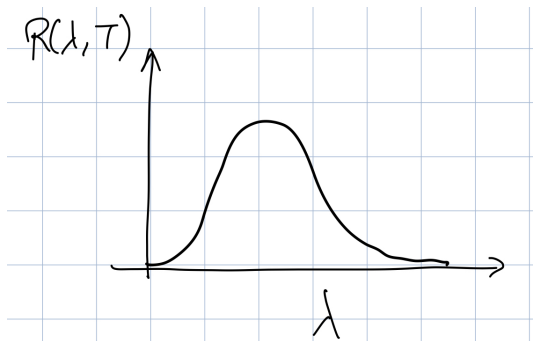
Physics doesn't tell you "why" things work—it tells you "how" things work. The reality is not observable, quantum mechanics "describes" observations rather than helping you "understand" some. By throwing away our philosophical concerns, we instead directly study the mathematics.

1.2 The Potter's Problem: Blackbody Radiation

Take a cube of some solid and heat it up to some temperature T . When you do this, it emits light (it glows). For a long time, no one knew how this phenomenon worked. Here are some observations throw the ages:

- 1792: Wedgewood notes that all objects (at a certain T) glow the same color.
- 1800s: With improvements in spectroscopy, we can now measure the frequency content of light.
- 1859: Kirchoff proposes a model. R is the "emissive power/area", λ is wavelength of the light and T is the temperature.

$$R(\lambda, T)$$



The idea is that there are multiple collisions between the walls and the radiation field. The blackbody (as a perfect absorber) is absorbing all light at all frequencies. It looked something like this. The left-side is near 0 because you have no wave at that wavelength. The right side must be bounded because we want total emissive power to be finite (or do we?).

- 1879: Stefan's Law

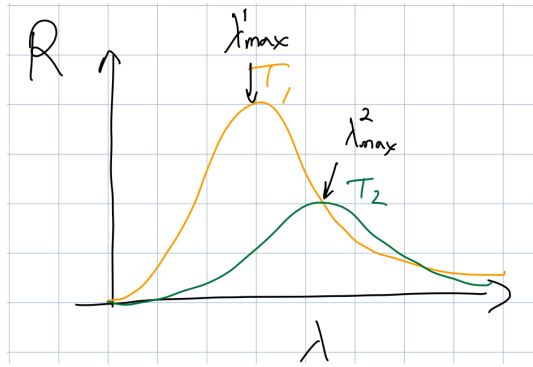
$$\int_0^{\infty} R(\lambda, T) d\lambda = \sigma T^4$$

i.e. the total radiation emitted is proportional to T^4 , which $\sigma \approx 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$

- ????: Wien's Law

$$\lambda_{\max} T \approx 2.898 \times 10^{-3} \text{m} \cdot \text{K}$$

i.e. these curves all have the same constant for the quantity. For example, in the following graph, $T_1 > T_2$.



- ????: Rayleigh-Jeans Law

$$R(\lambda, T) \propto \frac{8\pi k_B T}{\lambda^4}$$

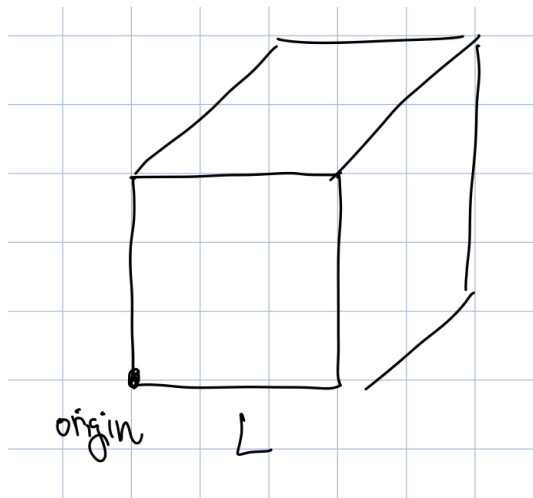
which only works at longer frequencies (the area is unbounded). The original derivation was similar to many observations in astronomy (guess a power law and add fudge factors).

1.3 A Formal Derivation

Let's derive the last law using thermodynamic principles and waves. We will analyze the energy density that the light trapped in the solid produces. The energy of a light wave increases with frequency, which in turn is proportional to the number of wave modes. In other words:

$$\text{Energy} = \text{Number of modes} \times \text{Energy per mode}$$

Suppose our blackbody is a cube of length L .



Let's find the waves that are stable in the cube. First, we write the wave equation.

$$\nabla^2 \Psi(\mathbf{r}, t) = \frac{1}{c^2} \frac{\partial}{\partial t^2} \Psi(\mathbf{r}, t)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In addition, we need boundary conditions—consider a standing wave in 1-d. At the ends it is fixed at 0. For 3-d this is:

$$\Psi(x = 0, y, z, t) = \Psi(x = L, y, z, t) = 0, \forall y, z, t$$

$$\Psi(x, y = 0, z, t) = \Psi(x, y = L, z, t) = 0, \forall x, z, t$$

$$\Psi(x, y, z = 0, t) = \Psi(x, y, z = L, t) = 0, \forall x, y, t$$

The solution is:

$$\Psi(\mathbf{r}, t) = A(t) \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

where $k_i = \frac{n_i \pi}{L}$ for $n_i \in \mathbb{N}$. n_i is the number of nodes along the i th axis. Each tuple of n_i is a valid mode (configuration) of the wave.

This looks like:

$$\Psi(\mathbf{r}, t) = A(t)B(x, y, z)$$

So we are modulating the space component of the wave with some $A(t)$ that changes over the time. This is true for any standing wave.

2 Lecture 2: Blackbody Radiation

2.1 Formal Blackbody Radiation, continued

To use our DE solution, we need a few partials:

$$\begin{aligned}\nabla^2\Psi(\mathbf{r}, t) &= \left(A(t) \sin(k_y y) \sin(k_z z) \frac{\partial^2 \sin(k_x x)}{\partial x^2} \right) + \dots \\ &= -k_x^2 (A(t) \sin(k_x x) \sin(k_y y) \sin(k_z z)) + \dots \\ &= -\left(n_x^2 + n_y^2 + n_z^2\right) \frac{\pi^2}{L^2} A(t) B(x, y, z)\end{aligned}$$

Another one, letting $A(t) = A_0 \cos \omega t + \phi$.

$$\frac{\partial^2 \Psi(\mathbf{r}, t)}{\partial t^2} = -\omega^2 A(t) B(x, y, z)$$

Let's plug our solution back into the wave equation.

$$\begin{aligned}\nabla^2 \Psi(x, y, z, t) &= \frac{1}{c^2} \frac{\partial^2 \Psi(x, y, z, t)}{\partial t^2} \\ -\left(n_x^2 + n_y^2 + n_z^2\right) \frac{\pi^2}{L^2} A(t) B(x, y, z) &= \frac{-\omega^2}{c^2} A(t) B(x, y, z) \\ \omega^2 &= \frac{c^2 \pi^2}{L^2} \left(n_x^2 + n_y^2 + n_z^2\right)\end{aligned}$$

This equation relates the angular frequency of the wave to its mode configurations. To find the number of modes for a given wavelength we define notion of density of states:

$$g(\omega) = \frac{dN(\omega)}{d\omega}$$

We choose to work with densities since ω is a continuous quantity. Differentiating both sides yields:

$$N(\omega) = \int_0^\omega g(\omega) d\omega$$

This quantity will encapsulate all (n_x, n_y, n_z) such that:

$$n_x^2 + n_y^2 + n_z^2 \leq \frac{\omega^2 L^2}{c^2 \pi^2}$$

(because we are looking at frequencies less than ω). Note that this looks like a sphere equation (with $n_i \geq 0$). The volume of this first octant is

$$N(\omega) = \frac{1}{8} \left(\frac{4}{3} \pi \frac{\omega^3 L^3}{c^3 \pi^3} \right) = \frac{\omega^3 L^3}{6c^3 \pi^3}$$

Let $V = L^3$ be the volume of the blackbody. Converting from angular to linear frequency:

$$\begin{aligned}N(f) &= \frac{(2\pi f)^3 V}{6c^3 \pi^2} = \frac{4\pi f^3 V}{3c^3} \\ g(f) &= \frac{dN(f)}{df} = \frac{4\pi f^2 V}{c^3}\end{aligned}$$

However, this is slightly incomplete. This assumes a certain polarization of the electric field. However, there are two degrees of freedom in which this field can polarize, so the amount of states is actually double. This means:

$$g(f) = \frac{8\pi f^2 V}{c^3}$$

In classical statistical mechanics, the equipartition each mode of a system is excited with energy equal to $k_B T$ (??), so the total energy for frequency f to $f + df$ is:

$$g(f) df \cdot k_B T = \frac{8\pi}{c^3} f^2 V k_B T df$$

This means the energy density (by volume) is:

$$d\kappa = \frac{8\pi}{c^3} f^2 k_B T df$$

and note since $f = \frac{c}{\lambda}$, $df = -\frac{c}{\lambda^2} d\lambda$ and:

$$\rho(\lambda, T) := \frac{d\kappa}{d\lambda} = \frac{8\pi}{\lambda^4} k_B T$$

where we dropped the negative sign (it just changes the order of integration). Note that our R is proportional to this density (the outward rate is just constant). We have produced the Rayleigh-Jean law (which is inaccurate!).

2.2 The Quantum Calculation

To solve our ultraviolet catastrophe, Planck postulated that light waves cannot have arbitrary energy values. Instead, for a fixed frequency f , he proposed that energy is quantized in discrete packets as

$$E_n = nhf$$

where hf is a quanta and $n \in \mathbb{N}$. He then calculated the expected energy of a wave as:

$$\bar{E} = \sum_{n=0}^{\infty} nhf \frac{\exp\left(-\frac{nhf}{k_B T}\right)}{\sum_{m=0}^{\infty} \exp\left(-\frac{mhf}{k_B T}\right)}$$

where the fraction term is the Boltzmann factor normalized to a probability. Can we simplify this? Let $x = \exp\left(-\frac{hf}{k_B T}\right)$.

$$\begin{aligned} \bar{E} &= hf \sum_{n=0}^{\infty} n \frac{x^n}{\sum_{m=0}^{\infty} x^m} \\ &= hf \frac{1 + x \sum_{n=0}^{\infty} (n+1)x^n}{\left(\frac{1}{1-x}\right)} \\ &= hf(1-x) \left(0 + x \frac{d \sum_{n=0}^{\infty} x^{n+1}}{dx}\right) \\ &= hf(1-x) \left(x \frac{d \frac{x}{1-x}}{dx}\right) \\ &= hf x(1-x) \left(\frac{(1-x) + x}{(1-x)^2}\right) \\ &= hf \frac{x}{1-x} \\ &= hf \frac{1}{x^{-1} - 1} \\ &= hf \frac{1}{\exp\left(\frac{hf}{k_B T}\right) - 1} \end{aligned}$$

Then, our energy is:

$$\frac{g(f) df}{V} \bar{E} = \frac{8\pi h f^3}{c^3} \frac{1}{e^{\frac{hf}{k_B T}} - 1} df$$

By converting from f to λ , the correct formula is:

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

Quantum mechanics is all about things that can be *quantized*. How far can we take this idea? Planck successfully applied it to energy radiated from a blackbody. What about an atom? Bohr applied this concept to the model of the Hydrogen atom, as we will soon see.

3 Lecture 3: Matter as a wave

3.1 Everything is a wave (in Quantum Mechanics)

Whether we analyze something as a particle versus wave is really a question of system size versus wavelength. For example, for the de Broglie wavelength (for an electron orbital), angular momentum is quantized, so:

$$\lambda_{dB} = \frac{h}{p} \text{ nm}$$

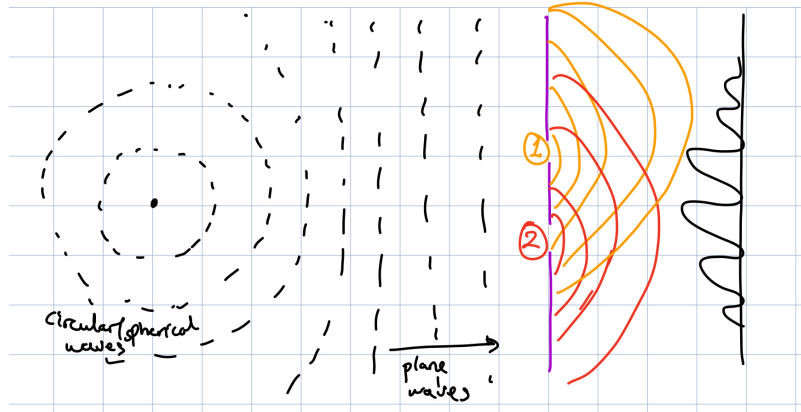
versus the size of an atom is on the order of an angstrom, much smaller.

However for a human

$$\lambda_{dB} = 10^{-36} \text{ m}$$

versus the size of a human is on the order of a meter.

Waves can interfere. Suppose you have a light wavefront like this.



We will focus on the case of a plane wave since the mathematics is simpler. We use complex exponentials to represent the waves. The electric field is:

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi)}$$

The amplitude is a vector (direction for which direction the wave wiggles in). The phase $\delta = (\mathbf{k} \cdot \mathbf{r} - \omega t + \phi)$ can be decomposed. \mathbf{k} is the spatial frequency and ω is the time frequency. Then ϕ is the wave phase at $(\mathbf{r}, t) = (\mathbf{0}, 0)$. We can get the total electric field by using simple superposition principle.

$$\begin{aligned} \mathbf{E}_{tot} &= \mathbf{E}_1 + \mathbf{E}_2 \\ &= \mathbf{E}_{01} e^{i\delta_1} + \mathbf{E}_{02} e^{i\delta_2} \end{aligned}$$

In practice, we measure a scalar quantity intensity I ,

$$\begin{aligned} I &\sim |\mathbf{E}|^2 = \mathbf{E} \cdot \mathbf{E}^* \\ &= E_{01}^2 + E_{02}^2 + \mathbf{E}_{01} \cdot \mathbf{E}_{02} \left(e^{i(\delta_2 - \delta_1)} + e^{-i(\delta_2 - \delta_1)} \right) \\ &= E_{01}^2 + E_{02}^2 + 2\mathbf{E}_{01} \cdot \mathbf{E}_{02} \cos(\delta_2 - \delta_1) \end{aligned}$$

However, they did the same experiment with electrons and got the same result. Matter must itself be a wave!

3.2 The Wavefunction

Now we want a wave description of matter. The \mathbf{E} is not sufficient for these purposes. We will use Ψ as this "wavefunction." Some weird properties of Ψ is:

- Ψ is a wave amplitude.
- It is not physical and cannot directly be measured.
- This function contains all the information about your system.

Max Born in 1926 gave the following interpretation to Ψ .

Theorem 3.1 (Born Rule)

If the wavefunction of a system is $|\Psi|^2$ is a probability (spatial) density to find the "particle" around \mathbf{r}, t .

With repeated measurements, the long-time probability for finding the particle within a cube $d\mathbf{r}$ becomes:

$$P(\mathbf{r}, t) d\mathbf{r} = |\Psi(\mathbf{r}, t)|^2 d\mathbf{r}$$

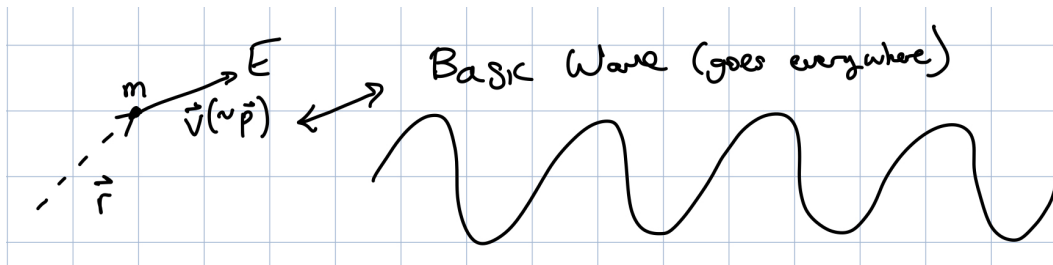
Theorem 3.2 (Superposition)

If Ψ_1, Ψ_2 are allowed waves (solutions), then:

$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

is also a viable solution, $\{c_1, c_2\} \in \mathbb{C}$.

Think about your favorite particle. It looks something like this:



Unfortunately this basic wave spills everywhere in space. This is how our physics translates:

$$E = hf = \hbar\omega$$

$$p = \frac{h}{\lambda} = \hbar k$$

where $\hbar = \frac{h}{2\pi}$ and $k = \frac{2\pi}{\lambda}$.

Consider a 1-D particle with some x direction momentum p_x .

$$\Psi = Ae^{i(kx - \omega(k)t)}$$

$$\Psi = Ae^{i(p_x x - E(p_x)t)}$$

Thus simply by derivative rules, the "momentum operator" p_x is:

$$-i\hbar \frac{\partial}{\partial x} \Psi = p_x \Psi$$

$$i\hbar \frac{\partial}{\partial t} \Psi = E \Psi$$

In 3-D, we have (using dot products):

$$\mathbf{p} = \hbar \mathbf{k}$$

which means that the operator looks like:

$$-i\hbar \nabla \Psi = \mathbf{p} \Psi$$

4 Lecture 4: Wave Packets

4.1 Aside: The Fourier Transform

First let us define the Discrete Fourier Transform.

Theorem 4.1 (Discrete Fourier Transform)

Suppose you have a periodic function f such that $f(x + 2\pi) = f(x)$ for all x . If we want to write

$$f(x) = \frac{1}{2}A_0 + \sum_{n=1}^{\infty} (A_n \cos(nx) + B_n \sin(nx))$$

We can do so by setting:

$$A_n = \frac{1}{\pi} \int f(x) \cos(nx) dx$$

$$B_n = \frac{1}{\pi} \int f(x) \sin(nx) dx$$

How can we show this? Just like with a cartesian vector space, we can use inner products to project onto a basis of functions. What is the inner product for functions? It is the integral of the ordinary product:

$$\langle f(x), g(x) \rangle = \frac{1}{\pi} \int f(x)g(x) dx$$

Thus:

$$A_m = \langle f(x), \cos(mx) \rangle$$

$$B_m = \langle f(x), \sin(mx) \rangle$$

Now, suppose you want to decompose your function as:

$$f(x) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} c_n e^{inx}$$

Then (by a similar projection argument):

$$c_m = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{\pi} f(x) e^{-imx} dx$$

Definition 4.1 (Kronecker Delta)

The kronecker delta δ_{mn} is the indicator:

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{otherwise} \end{cases}$$

Thus we must have,

Theorem 4.2

The basis functions e^{inx} are orthonormal, i.e.

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i(n-m)x} dx = \delta_{mn}$$

Theorem 4.3 (Continuous Fourier Transform)

If you wish to write:

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{ikx} dx$$

(where $g(k)$ is the continuous fourier transform of $f(x)$), then we have:

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx$$

We call these fourier transforms unitary transforms since they change basis but do not lose information. Let us now explore the continuous version of the delta, the Dirac delta. Plugging in the Fourier transform into the synthesis equation:

$$\begin{aligned} f(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \left(\int_{-\infty}^{\infty} f(x') e^{-ikx'} dx' \right) e^{ikx} dk \\ &= \int_{-\infty}^{\infty} f(x') \delta(x - x') dx \end{aligned}$$

where we define:

Definition 4.2 (Dirac Delta)

The dirac delta distribution is defined as:

$$\delta(y) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{iky} dk$$

Some wacky properties:

- $\delta(x - x') = 0$ if $x \neq x'$
- $\int_{\text{region including } 0} \delta(x) dx = 1$ otherwise

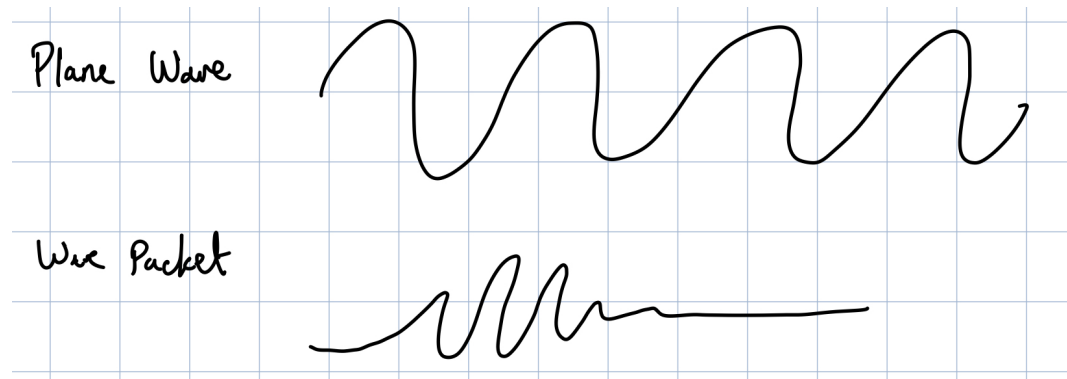
Notice something interesting, a single frequency, a single δ is infinitely thin! But if you take up more frequencies in the frequency domain, add together more and more δ s, the time and space components of the wave will be thinner!

4.2 Wave Packets and Normalization

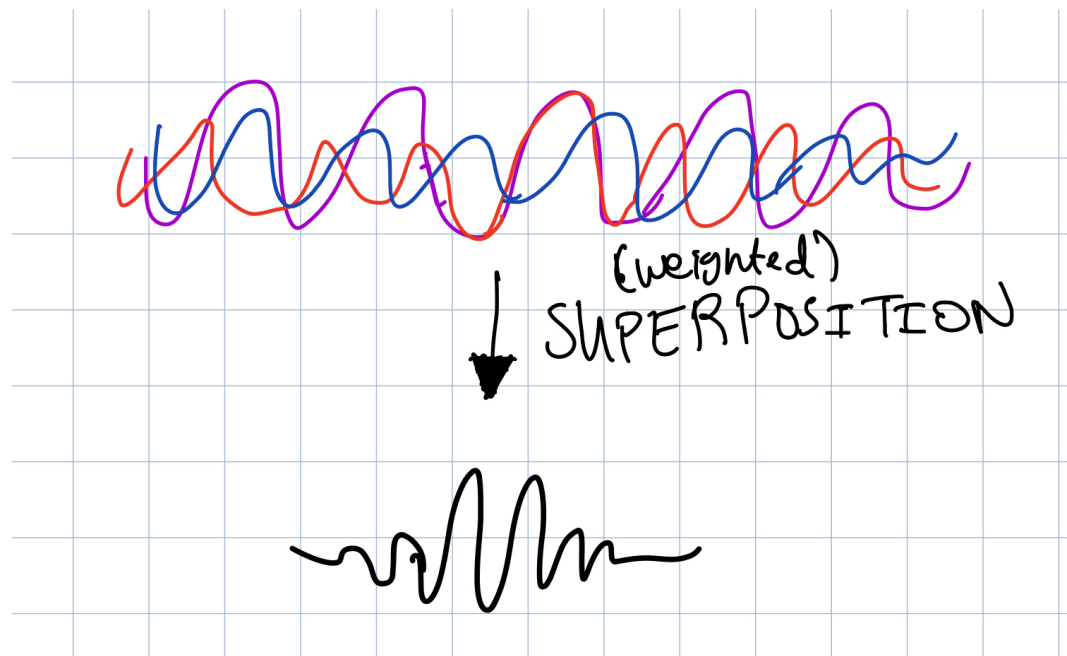
By probability density laws,

$$\int \mathbb{R}^3 |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1$$

but for this basic wave that spans all of space, this diverges! (Or the wavefunction is zero everywhere). Instead we have wave packets that are much more localized.



Suppose we have some waves indexed by j : $A_j e^{i(k_j x - \omega t)}$. We want to pick them and add them up to get this localized shape.



For a 1-D wavepacket, the wave function is as follows (our index j has become continuous p_x).

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{\frac{i(p_x x - E t)}{\hbar}} \phi(p_x) dp_x$$

Let us assume $\phi(p_x)$ is a sharp (non-delta) function that is centered p_0 and has half-max width $2\delta p_x$.

Let

$$\beta(p_x) = p_x x - E(p_x) t$$

Then

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{\frac{i\beta(p_x)}{\hbar}} \phi(p_x) dp_x$$

In the vicinity of p_0 is the only place where the integral does not vanish. Furthermore, we also do not want the exponential to rapidly oscillate (this will kill the integral) so we only get nonzero components in places where $\beta(p_x)$ doesn't vary much. Thus we look for the stationary phase condition

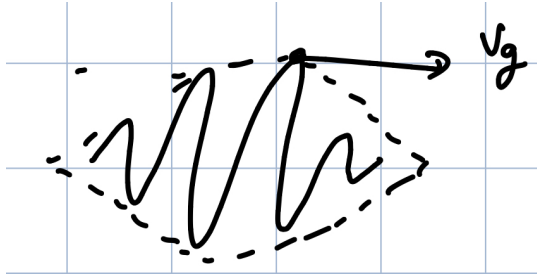
$$\left. \frac{d\beta(p_x)}{dp_x} \right|_{p_x=p_0} = 0$$

So, doing this yields:

$$x - t \frac{d}{dp_x} E(p_x) = 0$$

$$\frac{x}{t} = \frac{dE(p_x)}{dp_x}$$

where this quantity is defined as the group velocity v_g . This is how fast the highest amplitude part of the wave packet moves:



We can also find the phase velocity, the velocity of each component. Each component is:

$$e^{i(k_0 x - \omega(k_0) t)}$$

$$k_0 x - \omega(k_0) t = 0$$

$$v_p = \frac{x}{t} = \frac{E(p_0)}{p_0}$$