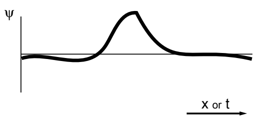
Vibrational Motion

The Wave Equation

In one dimension wave motion can be described by

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \frac{\partial^2 \psi}{\partial x^2}$$

Where ψ is a function that describes the wave (the wave function) and v is the speed of the wave. This equation tells us about how a wave propagates in space and time.



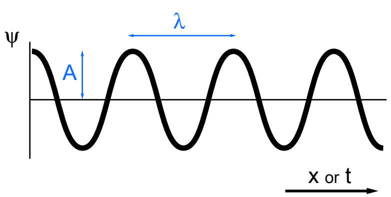
The general solutions to this equation can be expressed as the superposition of two waves propagating in opposite directions.

$$\psi(x,t) = f_1(x - vt) + f_2(x + vt)$$

where f_1 and f_2 are arbitrary functions. The fluctuations in a wave can be perpendicular to the direction of motion (a **transverse** wave), or parallel to the direction of motion (**longitudinal** wave).

Sinusoidal Waves

We can verify that this differential equation really does describe a wave. Let's start with the simplest of waves, a sinusoid.



We can draw two equivalent sine waves, one describing oscillations in position (x), and another describing oscillations in time (t).

The equation for this wave can be written as

$$\psi(x,t) = A \sin(kx - \omega t + \phi)$$

We can vary either time or position in this equation, and we would see a sinusoidal variation in amplitude of the wave function.

Wavelength, λ

The distance between successive peaks.

Amplitude, A

The maximum value of the wave function

Frequency, ν

The number of cycles per second.

Phase, φ

The initial offset of the wave in x at time $t=0$.

Angular Wavenumber,[1,2] k

The number of wavelengths in the distance 2π. $k = 2\pi/\lambda$.

Angular Frequency, ω

The number of cycles per second, measured in radians. $\omega = 2\pi\nu$.

Wave Velocity[3], v

The speed of the wave. $v = \lambda\nu = \omega/k$.

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[1] Thus far we have only considered 1D waves, so we don't have to resort to vectors. In the case of multidimensional waves, $\boldsymbol{k}$ is called the wave vector and also specifies the direction of propagation of the wave.

[2] Don't confuse **angular wavenumber** ($k=2\pi/\lambda$) used when talking about waves, and **wavenumber** used in spectroscopy. In spectroscopy, wavenumber is the number of wavelengths in one unit of length. It is the spatial analogue of frequency and usually expressed in units of cm^{-1}.

[3] There are actually several kinds of wave velocity, here we are talking about the group velocity.

So is this sinusoid a solution to the general wave equation?

Differentiate the wave function with respect to t at fixed x, twice

$$\psi(x,t) = A\sin(kx - \omega t + \phi)$$
$$\frac{\partial^2\psi}{\partial t^2} = -A\omega^2\sin(kx - \omega t + \phi) = -\omega^2\psi(x,t)$$

Repeat the (partial) differentiation of the wave function, but now with respect to x at fixed t:

$$\frac{\partial^2\psi}{\partial x^2} = -Ak^2\sin[kx - \omega t + \phi] = -k^2\psi(x,t)$$

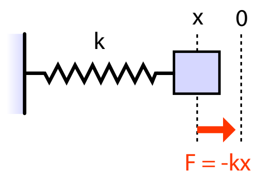
Combining these two equations, making use of the definition of the wave velocity, $v = \omega/k$, gets us back to the linear wave equation.

$$\frac{\partial^2\psi}{\partial t^2} = v^2\frac{\partial^2\psi}{\partial x^2}$$

Simple harmonic motion

One easy example of a wave equation is from simple harmonic motion. SHM is present where there is a restoring force that is proportional to the displacement of the system (e.g a pendulum, springs, molecular vibrations, sound waves, etc).

An Example: Mass and Spring



Consider the forces on the mass when it is displaced from its resting position by a distance x. We know that $F=ma$. The spring also applies a force give by **Hooke's law** proportional to the displacement $F_{\text{restoring}}=-kx$. Here k is the spring constant.

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = -kx$$

Another second order differential equation! Let's tidy up:

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \frac{k}{m}x = 0$$

You will learn how to solve such equations in your mathematics course. We can quote the solution and check it really works:

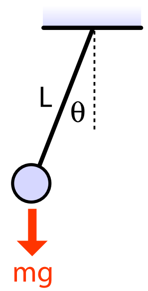
$$x(t) = A\sin(\omega t + \phi)$$

Where ω is the angular frequency $\omega^2=k/m$. If we substitute this into the the differential equation, we can check it is a solution and gives us the result.

$$T = \frac{2\pi}{\omega} = 2\pi\sqrt{\frac{m}{k}}$$

Interestingly, the period is independent of the initial displacement.

An Example: Simple Pendulum



The equation of motion for a simple pendulum is given by

$$ma = -mg\sin\theta$$

We can approximate for small angles with

$$\sin\theta \approx \theta$$

So the equation of motion becomes

$$ma = -mg\theta$$

The easiest way to solve this is to convert a to an angular form (a=αL)

$$m\alpha L = -mg\theta$$

Giving us the second order differential equation

$$\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2} + \frac{g}{L}\theta = 0$$

Just as in the previous example, we can substitute in a sinusoidal solution to show that this gives a period of oscillation of

$$T = 2\pi\sqrt{\frac{L}{g}}$$

Energy in Simple Harmonic Motion

Potential Energy

$$\begin{aligned} V(t) &= \tfrac{1}{2}kx^2 \\ x(t) &= A\sin(\omega t + \phi) \\ V(t) &= \tfrac{1}{2}kA^2\sin^2(\omega t + \phi) \end{aligned}$$

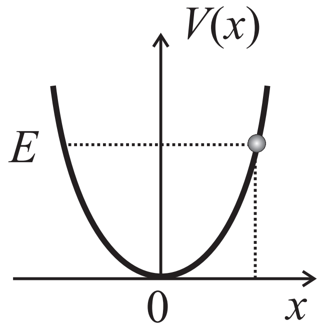
Kinetic Energy

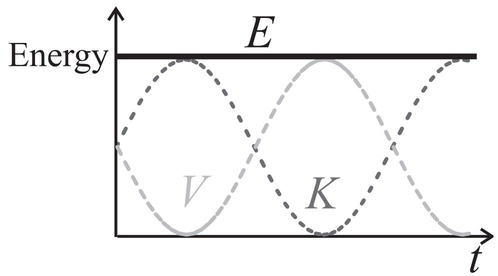
$$\begin{aligned} K(t) &= \tfrac{1}{2}mv^2 \\ v(t) &= A\omega\cos(\omega t + \phi) \\ K(t) &= \tfrac{1}{2}mA^2\omega^2\cos^2(\omega t + \phi) \\ K(t) &= \tfrac{1}{2}kA^2\cos^2(\omega t + \phi) \end{aligned}$$

Total Energy

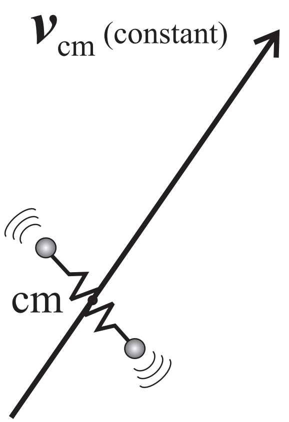
$$\begin{aligned} E &= K + V \\ E &= \tfrac{1}{2}kA^2\left[\sin^2(\omega t + \phi) + \cos^2(\omega t + \phi)\right] = \tfrac{1}{2}kA^2 \end{aligned}$$

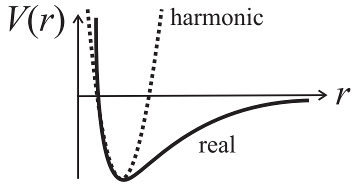
The vibrational frequency of a harmonic oscillator is independent of the total energy.

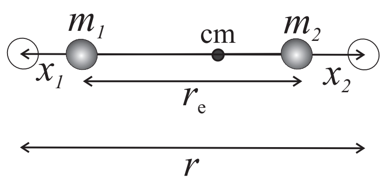




Vibration Motion of a Diatomic Molecule



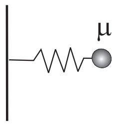




In the absence of external forces, the motion of the centre of mass (CM) of a molecule can be treated separately from the relative motion of the two atoms. The relative motion describes the time-dependent changes in bond length of the molecule

In this case, we have an analogous system to a mass on a spring. The only difference here is that we must again use the relative or **reduced mass**, μ, of the system rather than the actual mass, as we are only considering the internal motion.

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} \qquad \omega = \sqrt{\frac{k}{\mu}}$$



μ is the reduced mass of the oscillator and ω is the angular frequency.

An Example: Vibrational Frequency of HBr

Treating HBr as a simple harmonic oscillator with force constant 412 Nm^{-1}, calculate the expected vibrational wavelength of the molecule. [3.76 μm] (The actual vibrational wavenumber is 2649.7 cm^{-1} = 3.77 μm). Not bad for just SHM.