Specific Heat of Insulating Solids

Dulong - Petit Law

Heat capacity is given by -

$$C = 3k_B \quad \text{per atom}$$

$$C = 3R \quad \text{per mole}$$

Material	C/R
Aluminum	2.91
Antimony	3.03
Copper	2.94
Gold	3.05
Silver	2.99
Diamond	0.735

This law holds fairly well at room temperature for many materials (exception being Diamond)

At low temperature this law deviates from the experimental behavior for all materials

Einstein's Treatment of Specific Heat

Quantum mechanical treatment of vibrations was essential

Einstein further assumed that every atom is in an identical harmonic well and has an oscillation frequency ω [Einstein freq.]

In one dimension, the eigenstates of a simple harmonic oscillator -

$$E_n = \hbar\omega(n + 1/2)$$

$$C = 3k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

Thus, the high temperature limit $k_B T \gg \hbar\omega$ for specific heat in the three-dimensional case is - $C = 3k_B$

which is in agreement with Dulong – Petit law of specific heat

Coupled Oscillators

Considering small-angle approximation

$$\sin \theta_1 = \frac{x_1}{l} \; ; \sin \theta_o = \frac{x_o}{l}$$

Equation of motion

Total force on Mass-1

$$m\ddot{x}_1 = -mg\,\frac{x_1}{l} - k(x_1 - x_0)$$
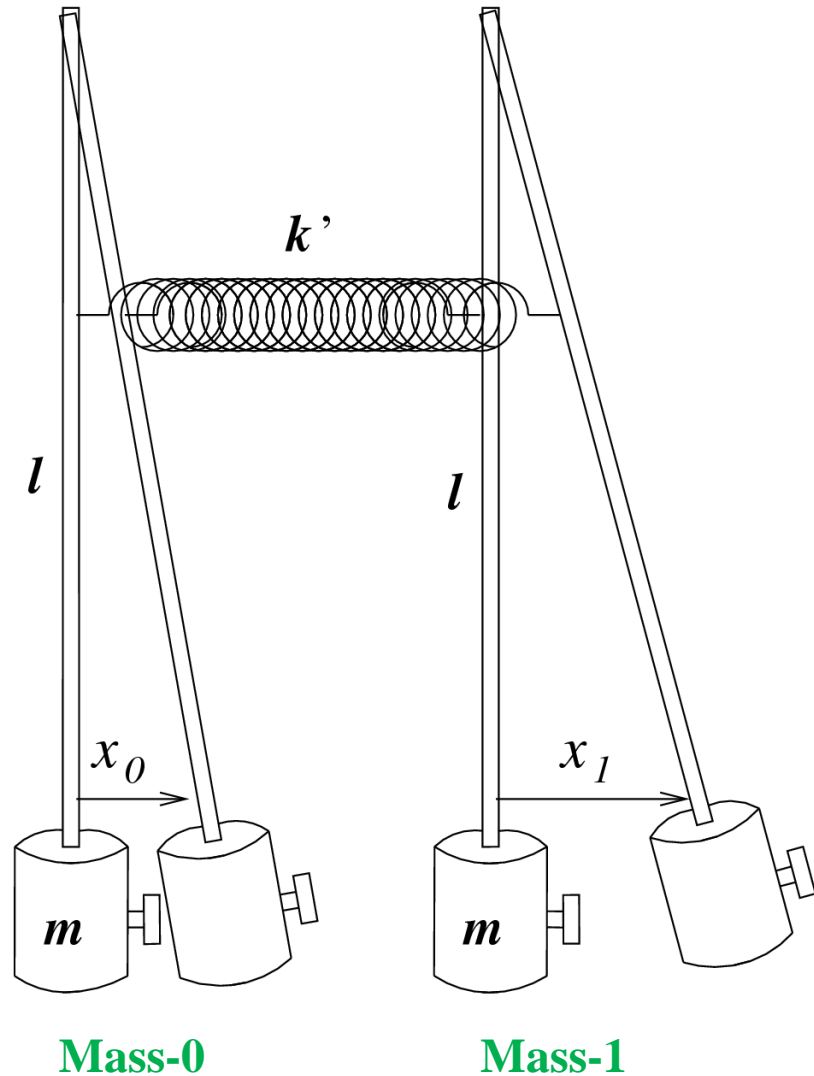
Total force on Mass-0

$$m\ddot{x}_0 = -mg\,\frac{x_0}{l} - k(x_0 - x_1)$$

SHM term   **Coupling term**

Normal Co-ordinates

$$x_1 + x_0 = q_1$$

$$x_1 - x_0 = q_2$$

Which gives a set of linear differential equations with constant coefficients in which each equation contains only one dependent variable (our Simple Harmonic equations in q_1 and q_2 only)

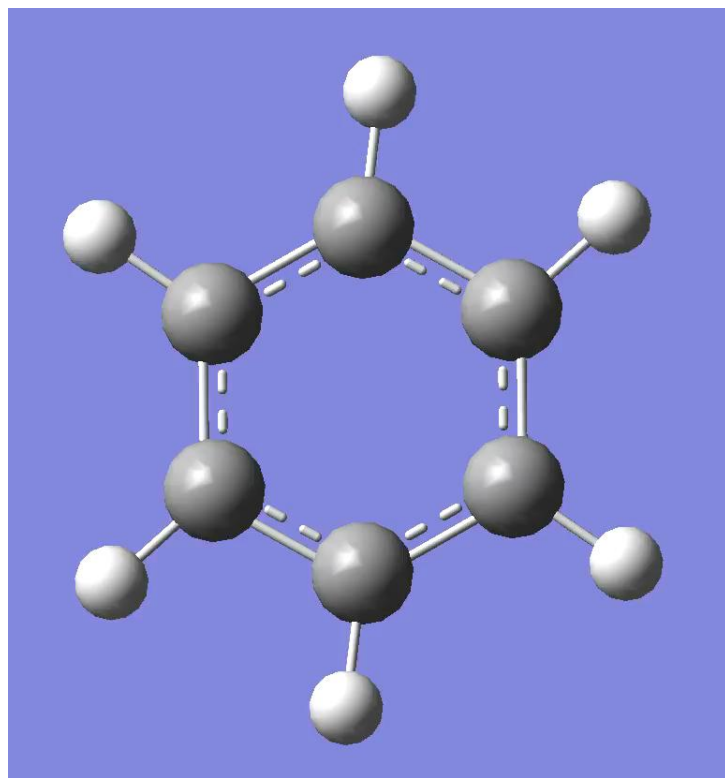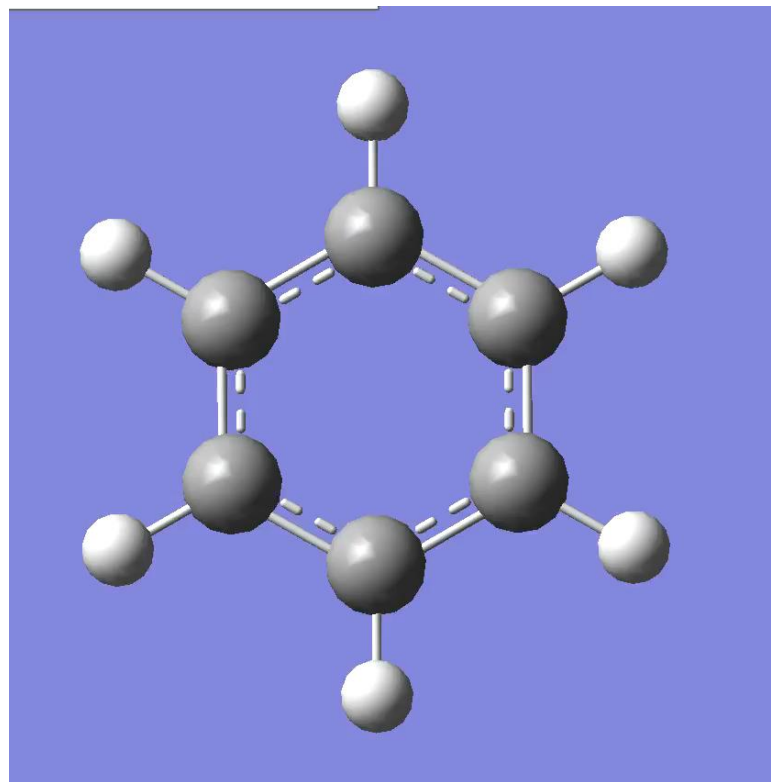# Normal modes

$$\ddot{q}_1 + \omega_0^2 q_1 = 0$$

$$\ddot{q}_2 + \left(\omega_0^2 + \frac{2k}{m} \right) q_2 = 0$$

A vibration involving only one dependent variable is called a **normal mode** of vibration and has its own **normal frequency**.
The importance of the normal modes of vibration is that they are entirely independent of each other

Normal mode: A way in which the system can move in a steady state, in which all parts of the system move with the same frequency. The parts may have different (zero or negative) amplitudes
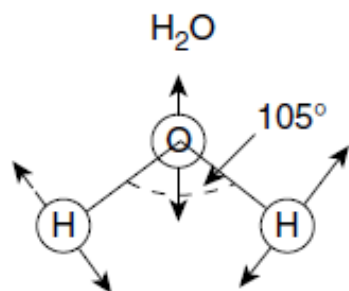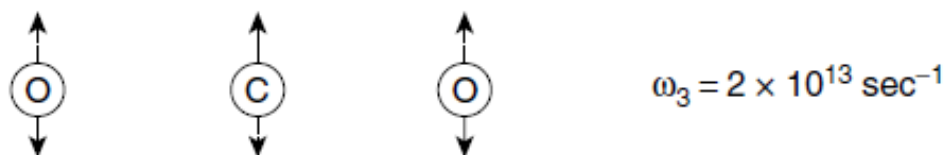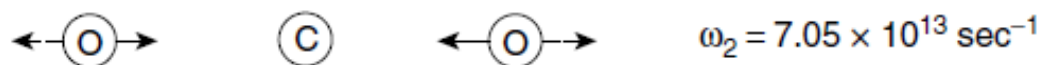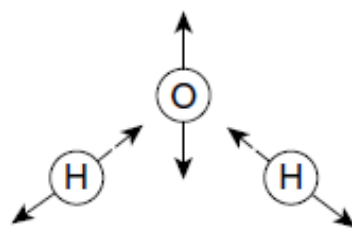
Normal modes of Benzene

Superposition of Normal Modes

In-phase mode   Out-of-phase mode
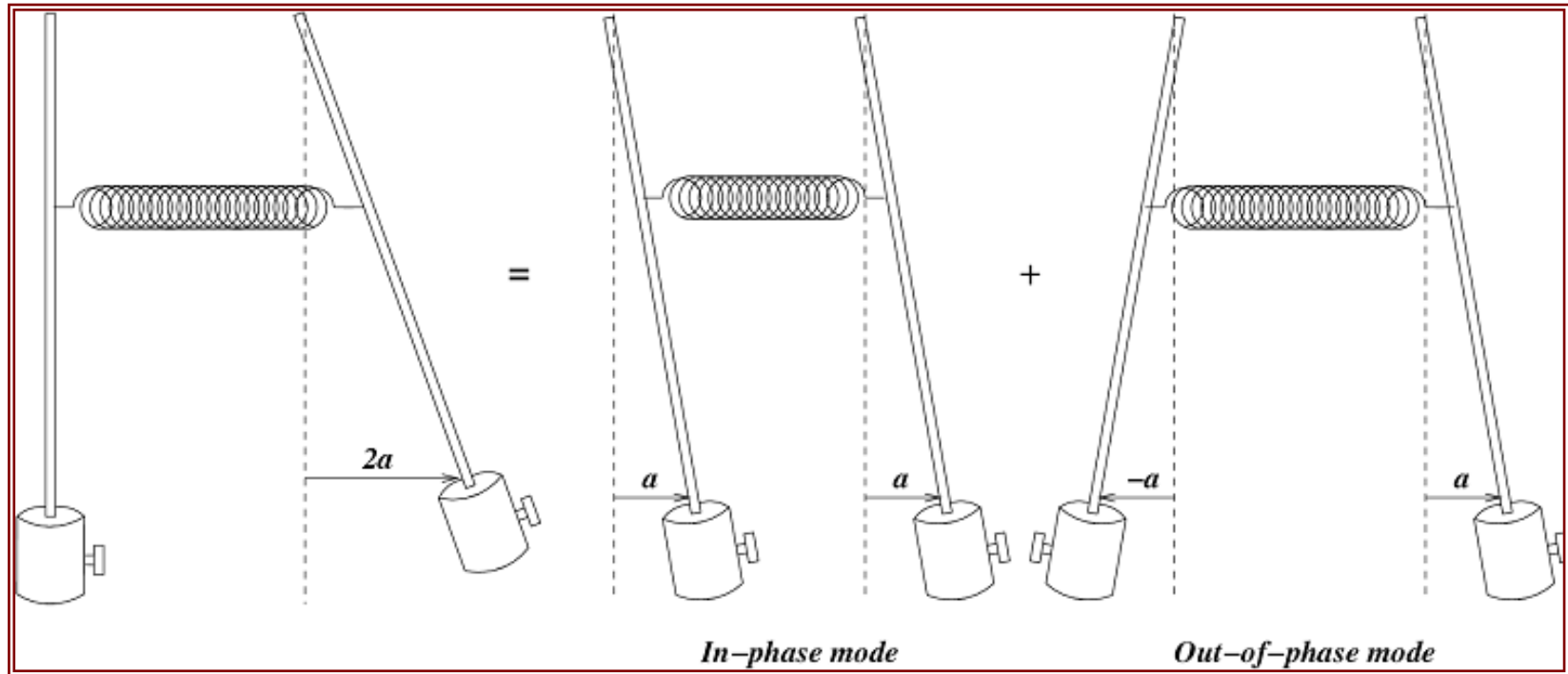
$$x_1 = \frac{1}{2}(q_1 + q_2)$$

$$x_0 = \frac{1}{2}(q_1 - q_2)$$

Normal modes of vibration of molecules

CO_2

$\omega_1 = 4.16 \times 10^{13}$ sec^{-1}

$\omega_2 = 7.05 \times 10^{13}$ sec^{-1}

$\omega_3 = 2 \times 10^{13}$ sec^{-1}

H_2O

105°

$\omega_1 = 11 \times 10^{13}$ sec^{-1} $\omega_2 = 11.27 \times 10^{13}$ sec^{-1} $\omega_3 = 4.78 \times 10^{13}$ sec^{-1}
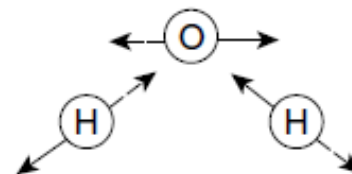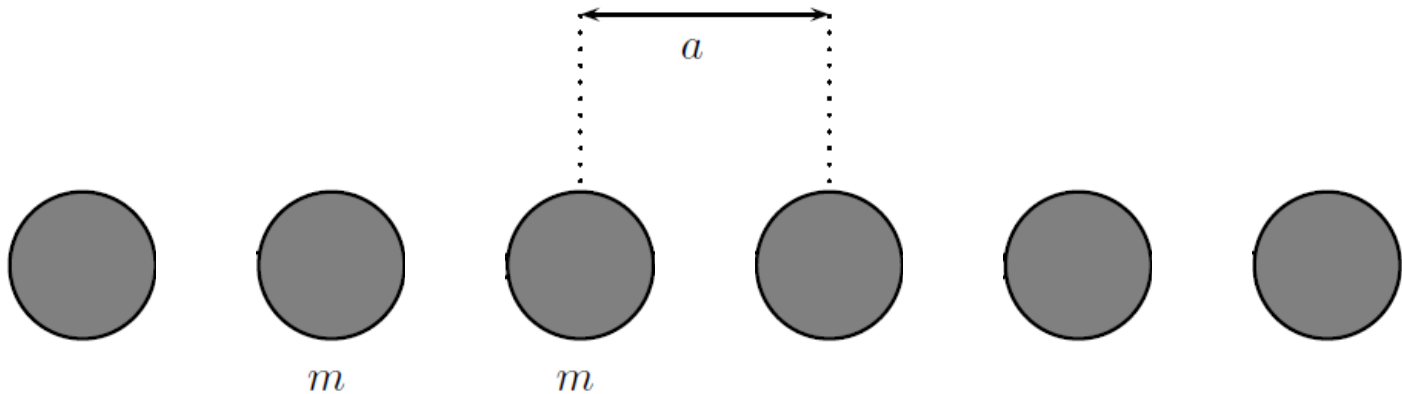
Normal modes of vibration for triatomic molecules CO_2 and H_2O

Vibrations of a 1D mono-atomic chain

Considering a chain of identical atoms of mass m

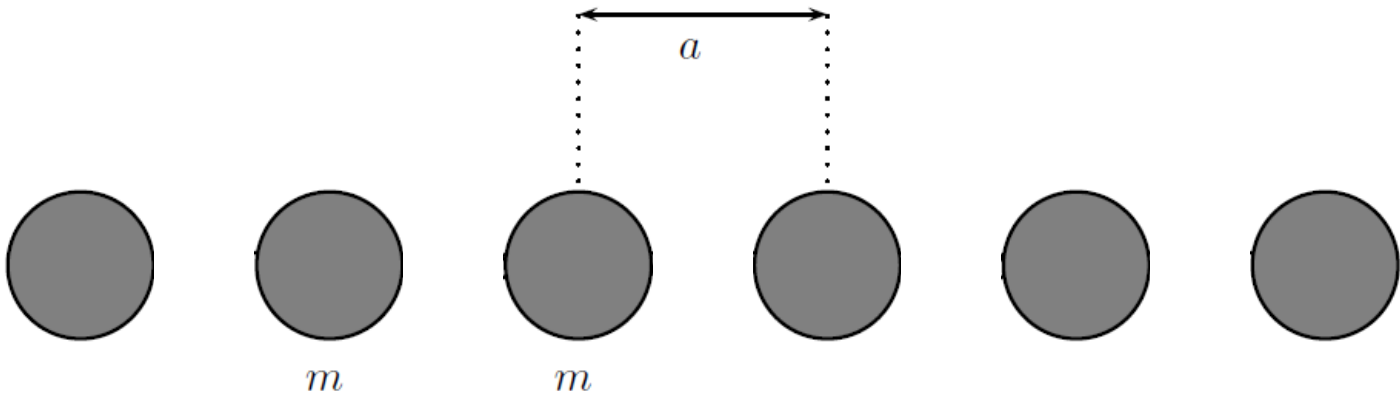Equilibrium spacing between the atoms is a

Vibrations of a 1D mono-atomic chain

Considering a chain of identical atoms of mass m

Equilibrium spacing between the atoms is a

Position of the nth atom is x_n

The potential V(x) between the neighboring atoms has a minimum at the equilibrium position

Equilibrium position of the nth atom is $x_n^{eq} = na$
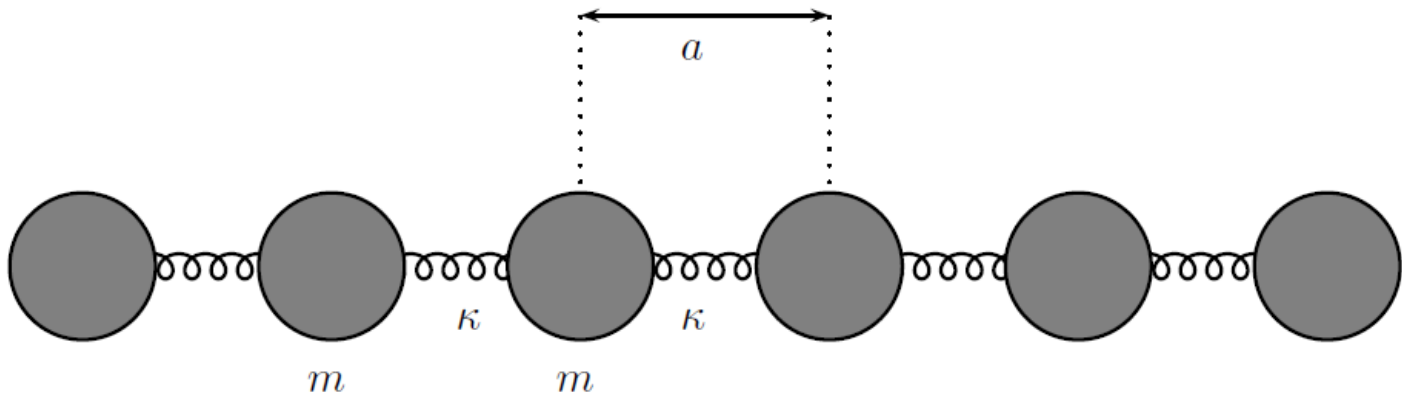
Vibrations of a 1D mono-atomic chain

Taylor expanding the potential around the minimum position -

$$V(x) \approx V(x_{eq}) + \frac{\kappa}{2}(x - x_{eq})^2 + \frac{\kappa_3}{3!}(x - x_{eq})^3 + \dots$$

For small deviations from the equilibrium position the leading quadratic term will dominate

We can then deal with a simple Hooke's law quadratic potential around the minimum

Vibrations of a 1D mono-atomic chain

Deviation from the equilibrium position

$$\delta x_n = x_n - x_n^{eq}$$

With the quadratic interatomic potential, the total potential energy of the chain -

$$
\begin{aligned}
V_{tot} &= \sum_i V(x_i - x_{i+1}) \\
&= V_{eq} + \sum_i \frac{\kappa}{2}(\delta x_i - \delta x_{i+1})^2
\end{aligned}
$$

The force on the nth mass on the chain is -

$$F_n = -\frac{\partial V_{tot}}{\partial x_n} = \kappa(\delta x_{n+1} - \delta x_n) + \kappa(\delta x_{n-1} - \delta x_n)$$

Vibrations of a 1D mono-atomic chain

Thus, the Newton's equation of motion is -

$$m(\delta\ddot{x}_n) = F_n = \kappa(\delta x_{n+1} + \delta x_{n-1} - 2\delta x_n)$$

Continuum Limit – The Wave Equation
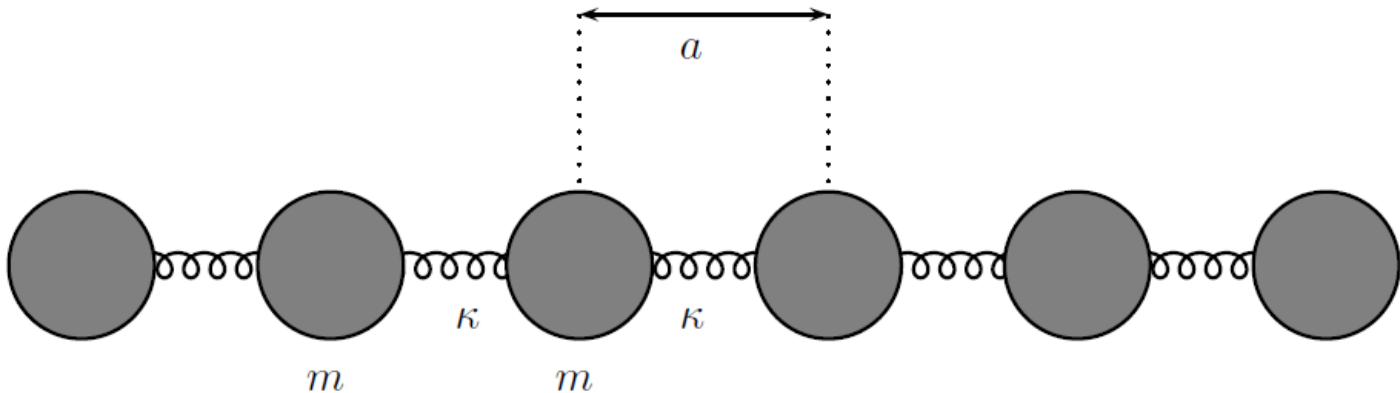
$$x = x_r$$

$$a = \delta x \rightarrow 0$$

$$x_r = x, x_{r+1} = x + \delta x$$

$$x_{r-1} = x - \delta x$$

Continuum Limit – The Wave Equation
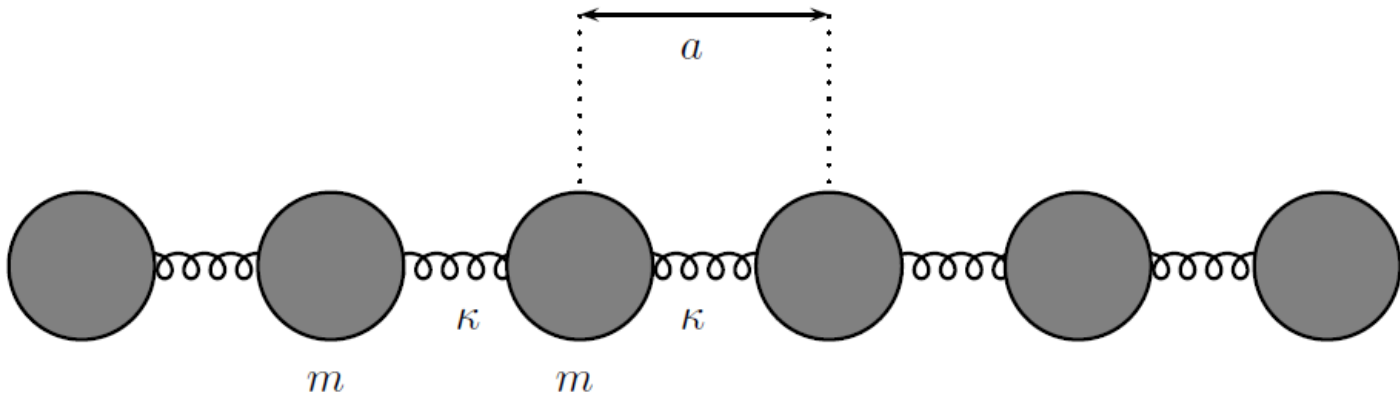
$$\frac{\mathrm{d}^2 y_r}{\mathrm{d}t^2} = \frac{T}{ma}(y_{r+1} - 2y_r + y_{r-1})$$

$$\frac{\partial^2 y_r}{\partial t^2} \longrightarrow \frac{\partial^2 y}{\partial t^2}$$

$$y_r(t) \longrightarrow y(x,t), \, y_{r+1}(t) \longrightarrow y(x + \delta x, t)$$

$$y_{r-1}(t) \longrightarrow y(x - \delta x, t)$$

Continuum Limit – The Wave Equation

$$y(x \pm \delta x, t) = y(x) \pm \delta x \frac{\partial y}{\partial x} + \frac{1}{2}(\pm \delta x)^2 \frac{\partial^2 y}{\partial x^2}$$

$$\frac{\partial^2 y}{\partial t^2} = \frac{T}{m}\left(\frac{y_{r+1} - y_r}{a} - \frac{y_r - y_{r-1}}{a}\right)$$

$$= \frac{T}{m}\left(\frac{\delta x \frac{\partial y}{\partial x} + \frac{1}{2}(\delta x)^2 \frac{\partial^2 y}{\partial x^2}}{\delta x} - \frac{\delta x \frac{\partial y}{\partial x} - \frac{1}{2}(\delta x)^2 \frac{\partial^2 y}{\partial x^2}}{\delta x}\right)$$

Continuum Limit – The Wave Equation

$$\frac{\partial^2 y}{\partial t^2} = \frac{T}{m} \frac{(\delta x)^2}{\delta x} \frac{\partial^2 y}{\partial x^2} = \frac{T}{m} \delta x \frac{\partial^2 y}{\partial x^2}$$

$$\frac{\partial^2 y}{\partial t^2} = \frac{T}{m} \frac{(\delta x)^2}{\delta x} \frac{\partial^2 y}{\partial x^2} = \frac{T}{m} \delta x \frac{\partial^2 y}{\partial x^2}$$

$$m = \rho \, \delta x$$

$$\frac{\partial^2 y}{\partial t^2} = \frac{T}{\rho} \frac{\partial^2 y}{\partial x^2}$$

Continuum Limit – The Wave Equation

$$\frac{\partial^2 y}{\partial t^2} = \frac{T}{\rho} \frac{\partial^2 y}{\partial x^2}$$

$$y = e^{i(\omega t + kx)}$$

$$\frac{\partial y}{\partial t} = i\omega\, e^{i(\omega t + kx)} = i\omega y \quad \text{and} \quad \frac{\partial^2 y}{\partial t^2} = -\omega^2 y$$

$$\frac{\partial y}{\partial x} = ik\, e^{i(\omega t + kx)} = iky \quad \text{and} \quad \frac{\partial^2 y}{\partial x^2} = -k^2 y$$

Vibrations of a 1D mono-atomic chain

Thus, the Newton's equation of motion is -

$$m(\delta\ddot{x}_n) = F_n = \kappa(\delta x_{n+1} + \delta x_{n-1} - 2\delta x_n)$$

For any coupled system –
A normal mode is a collective oscillation where all particles move with the same frequency

Normal modes are assumed to be waves with amplitude A

$$\delta x_n = Ae^{i\omega t - ikx_n^{eq}} = Ae^{i\omega t - ikna}$$

Complex representation of δx_n is for calculational convenience
We implicitly mean to take the real part

Vibrations of a 1D mono-atomic chain

We thus obtain -

$$-m\omega^2 A e^{i\omega t - ikna} = \kappa A e^{i\omega t} \left[e^{-ika(n+1)} + e^{-ika(n-1)} - 2e^{-ikan} \right]$$

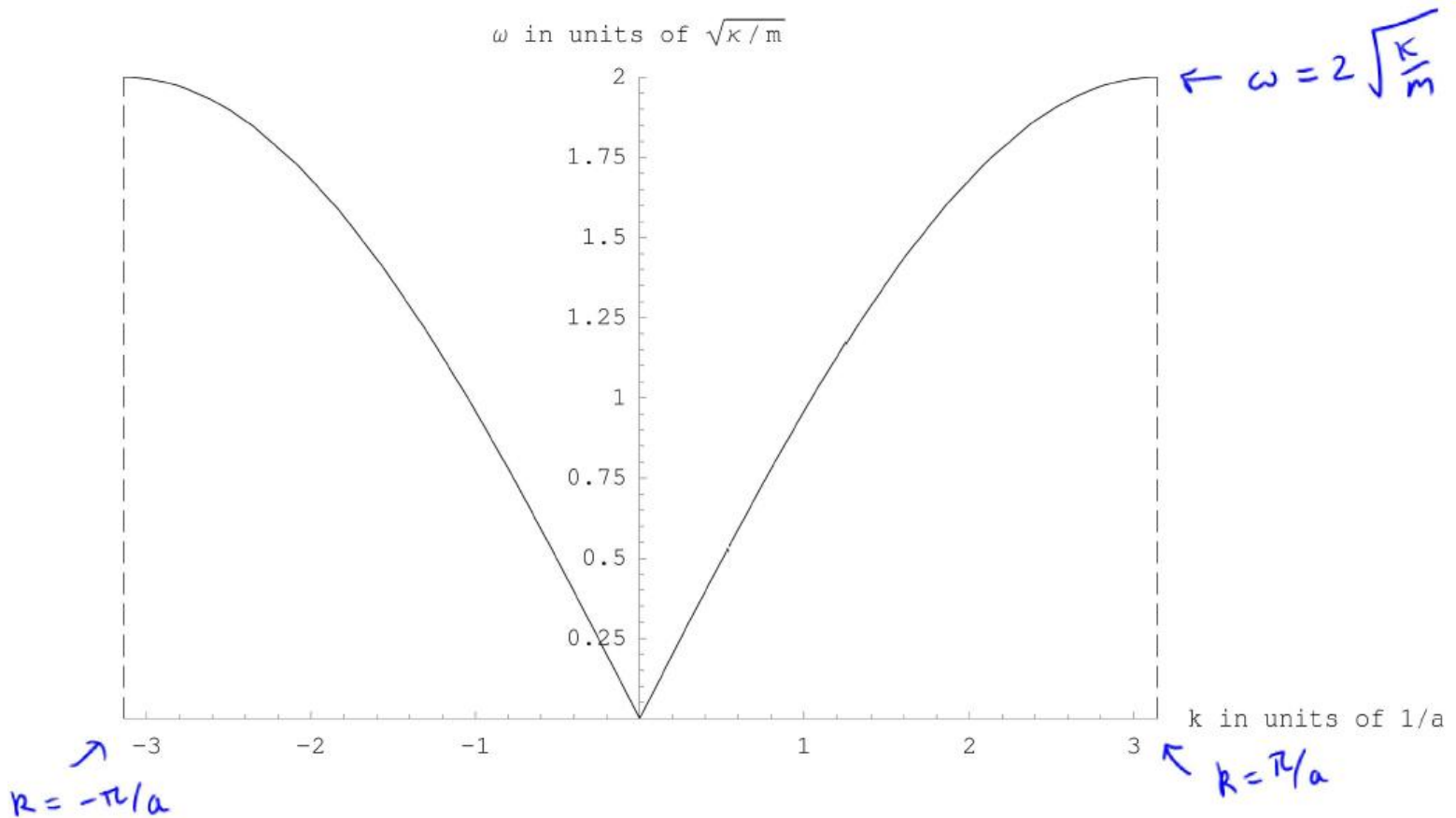$$m\omega^2 = 2\kappa[1 - \cos(ka)] = 4\kappa \sin^2(ka/2)$$

The dispersion relation -

$$\omega = 2\sqrt{\frac{\kappa}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

In general, a relationship between frequency (or energy) and wavevector (or momentum) is known as dispersion relation

Vibrations of a 1D mono-atomic chain

Plot of the dispersion relation -

$$\omega = 2\sqrt{\frac{\kappa}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

ω in units of $\sqrt{\kappa/m}$

$\leftarrow \omega = 2\sqrt{\frac{\kappa}{m}}$

k in units of 1/a

$k = -\pi/a$

$k = \pi/a$

Vibrations of a 1D mono-atomic chain

Sound wave is a vibration that has a long wavelength (compared to the inter-atomic spacing)

Human can hear sound wavelengths roughly between 1 cm and 10 m

Dispersion relation close to k = 0

$$\omega = 2\sqrt{\frac{\kappa}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

For small x, we can retain the leading term - $\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} -$

In the long-wavelength limit, the dispersion relation is linear in k

Since $\omega = v_{sound} k$ we get $v_{sound} = a\sqrt{\frac{\kappa}{m}}$

Vibrations of a 1D mono-atomic chain

At larger k the dispersion is no longer linear, which is in disagreement with what Debye predicted in his calculation

This is clearly a short-coming of Debye theory

<u>Counting Normal Modes</u> –

If we put periodic boundary conditions -

$$x_{n+N} = x_n$$

We must therefore have

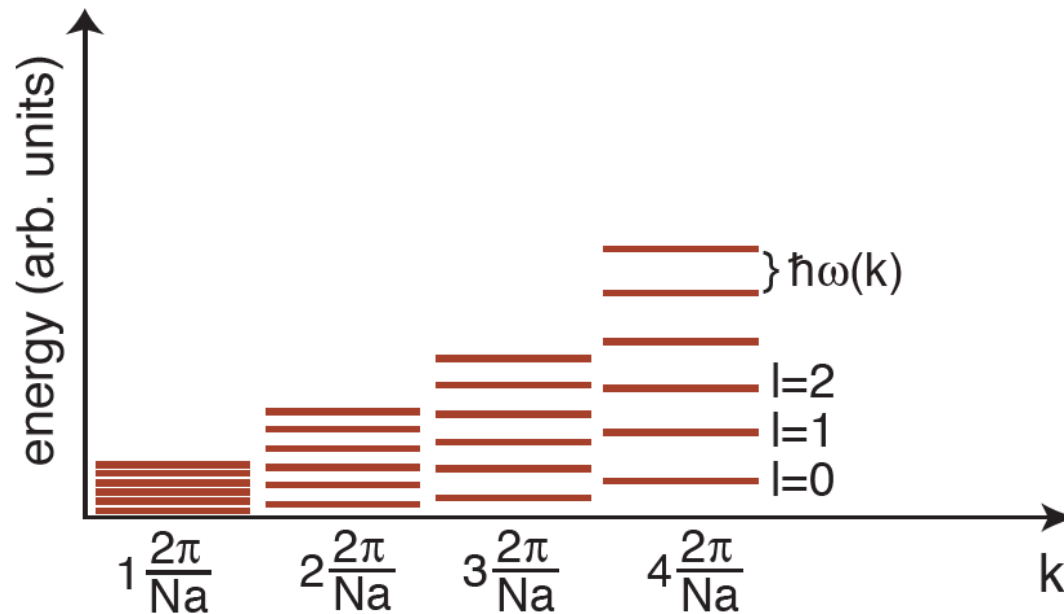$$e^{i\omega t - ikna} = e^{i\omega t - ik(N+n)a}$$

$$e^{ikNa} = 1$$

So the allowed values of k are $\quad k = \dfrac{2\pi p}{Na} = \dfrac{2\pi p}{L}$

Quantum correspondence - Phonons

The corresponding quantum system has eigenstates with energies

$$E_n = \hbar\omega(n + \frac{1}{2})$$

The harmonic oscillator here is a collective normal mode and not just motion of a single particle

Normal modes can thus be excited in discrete energy quanta

This quantized excitation is known as a "phonon"

Considering a phonon as a particle, we can put many phonons (*n* can be any number) in the same state