Crystal Lattice Dynamics

Classical Theory of the Harmonic Crystal

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(1884 – 1966)

An Adiabatic Theory of Lattice Vibrations

Lattice vibrations are important -

- the thermal conductivity of insulators is due to dispersive lattice vibrations, and it can be quite large.
- in scattering they reduce of the spot intensities, and also allow for inelastic scattering.
- electron-phonon interactions re-normalize the properties of electrons.
- superconductivity (conventional) comes from multiple electron-phonon scattering between time-reversed electrons.

Example: Consider the following triatomic linear molecule: The central atom of mass M is flanked by two smaller atoms of mass m. The potential between adjacent atoms is that of a spring with constant k. Assuming an equilibrium separation b the potential of the system is given by

$$V = \frac{1}{2}k\left(x_2 - x_1 - b\right)^2 + \frac{1}{2}k\left(x_3 - x_2 - b\right)^2$$

Using the generalized coordinates relative to the equilibrium position $\eta_i = x_i - x_{0i}$

$$\begin{aligned} V &= \frac{k}{2}\left[\left(\eta_2 - \eta_1\right)^2 + \left(\eta_3 - \eta_2\right)^2\right] \\ &= \frac{k}{2}\left[\eta_1^2 + 2\eta_2^2 + \eta_3^2 - 2\eta_1\eta_2 - 2\eta_2\eta_3\right] \end{aligned}$$

$$\Rightarrow \quad \mathsf{V} = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}$$

The kinetic energy of the system is $T = \frac{1}{2} t_{ij} \dot{\eta}_i \dot{\eta}_j$

or $T = \frac{1}{2} m \left(\dot{\eta}_1^2 + \dot{\eta}_3{}^2 \right) + \frac{1}{2} M \dot{\eta}_2^2$ ⇒ $\mathsf{T} = \begin{pmatrix} m & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & m \end{pmatrix}$

The secular equation becomes

$$\left| \mathsf{V} - \omega^2 \mathsf{T} \right| = \begin{vmatrix} k - \omega^2 m & -k & 0 \\ -k & 2k - \omega^2 M & -k \\ 0 & -k & k - \omega^2 m \end{vmatrix} = 0$$

$$\omega^2 \left(k - \omega^2 m \right) \left(\omega^2 m M - 2km - kM \right) = 0$$

Modes:

$\omega_1^2 = 0$ simple translational motion $\longrightarrow$

$\omega_2^2 = \frac{k}{m}$ stationary center mass withthesmaller ones oscillating $\longleftarrow\longrightarrow$

$\omega_3^2 = \frac{k}{m} \left(1 + \frac{2m}{M} \right)$ $\longleftarrow\longrightarrow\longleftarrow$

A natural expansion parameter for a daunting problem

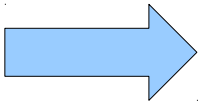
ratio of the electronic to the ionic mass: $\frac{m}{M} \ll 1$

From Newtons 3rd law:

$$F \sim e^2/a^2 \sim m\omega_{electron}^2 a \sim M\omega_{ion}^2 a$$

And therefore

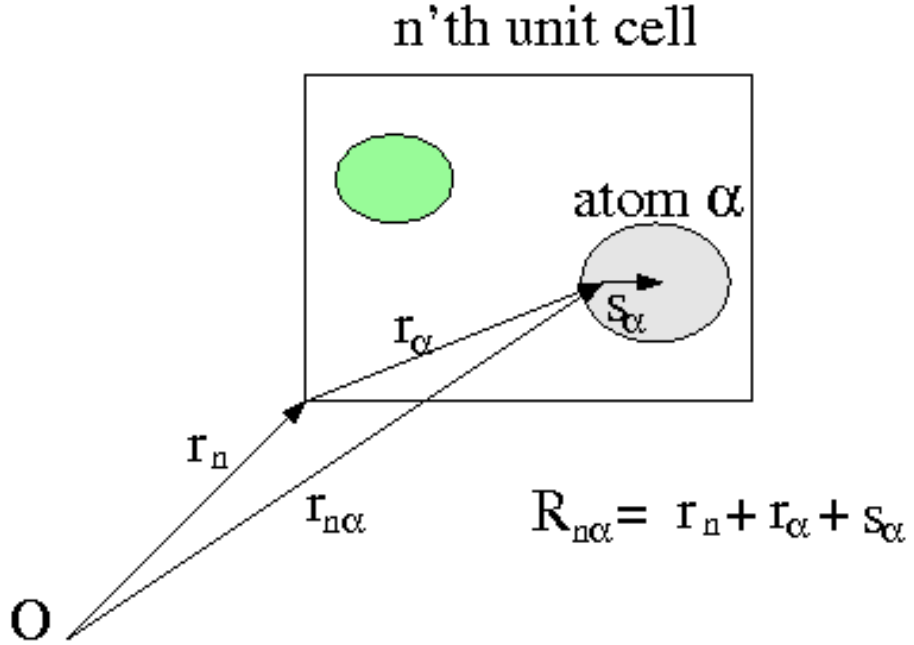
$$\frac{\omega_{ion}}{\omega_{electron}} \sim \left(\frac{m}{M}\right)^{1/2} \sim 10^{-3} \text{ to } 10^{-2}$$



Adiabatic Approximation

Adiabatic Approximation:

• we treat the ions as stationary at locations R_1 , $\cdots R_N$ and determine the electronic ground state energy, $E(R_1, \cdots R_N)$. This may be done using standard ab-initio band structure techniques.
• we then use this as a potential for the ions; i.e.. we recalculate E as a function of the ionic locations, always assuming that the electrons remain in their ground state.



Potential energy for the ions

$$\phi(\mathsf{R}_1, \cdots \mathsf{R}_N) = E(\mathsf{R}_1, \cdots \mathsf{R}_N) + \text{the ion-ion interaction}$$

We will define the zero potential such that when all $\boldsymbol{R}_n$ are at their equilibrium positions, $\phi = 0$. Then

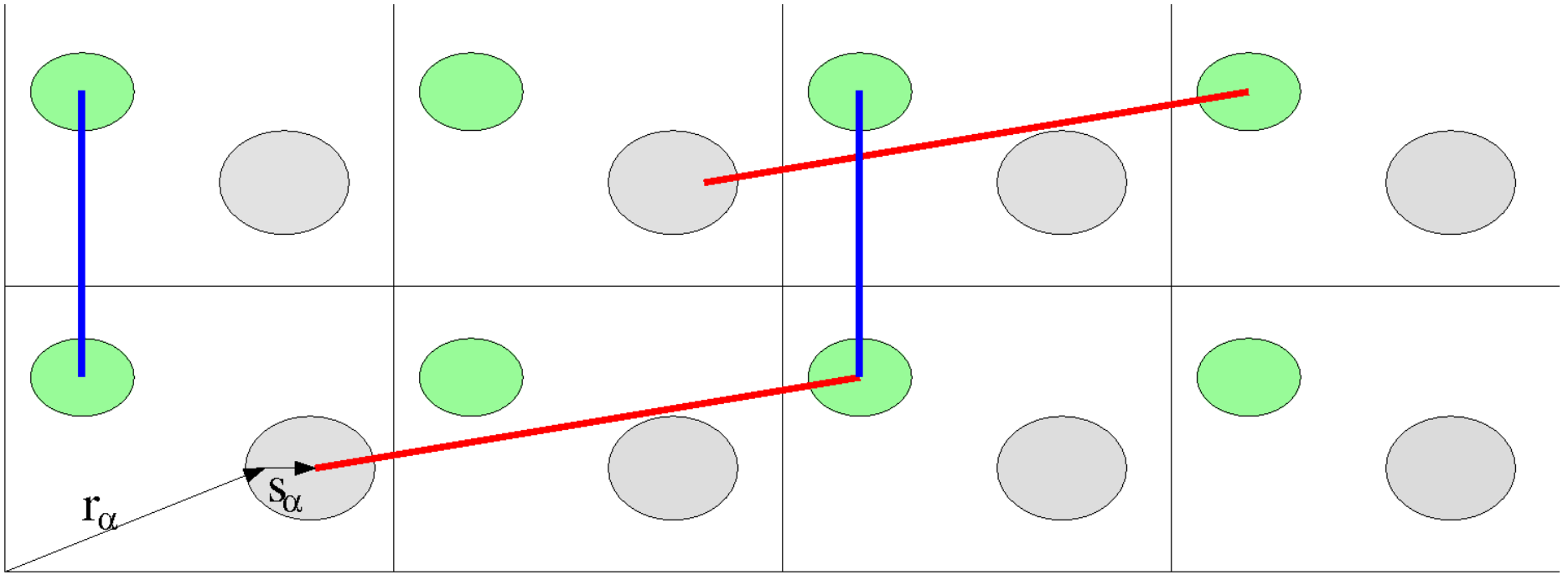
$$H = \sum_n \frac{P_n^2}{2M} + \phi(\mathsf{R}_1, \cdots \mathsf{R}_N)$$

Expanding about the equilibrium position of the ions.

$$\phi(\{r_{n\alpha i} + s_{n\alpha i}\}) = \phi(\{r_{n\alpha i}\}) + \frac{\partial \phi}{\partial r_{n\alpha i}} s_{n\alpha i} + \frac{1}{2} \frac{\partial \phi}{\partial r_{n\alpha i} \partial r_{m\beta j}} s_{n\alpha i} s_{m\beta j}$$

$$\Rightarrow \quad \Phi_{n\alpha i}^{m\beta j} = \frac{\partial^2 \phi}{\partial r_{n\alpha i} \partial r_{m\beta j}}$$

Symmetry



$$\Phi_{n\alpha i}^{m\beta j} = \Phi_{0\alpha i}^{(m-n)\beta j} = \frac{\partial^2 \phi}{\partial r_{0\alpha i} \partial r_{(n-m)\beta j}}$$

The Equation of Motion

From the derivative of the potential, we can calculate the force on each site

$$F_{n\alpha i} = -\frac{\partial \phi(\{r_{m\beta j} + s_{m\beta j}\})}{\partial s_{n\alpha i}}$$

so that the equation of motion becomes

$$-\Phi_{n\alpha i}^{m\beta j} s_{m\beta j} = M_\alpha \ddot{s}_{n\alpha i}$$

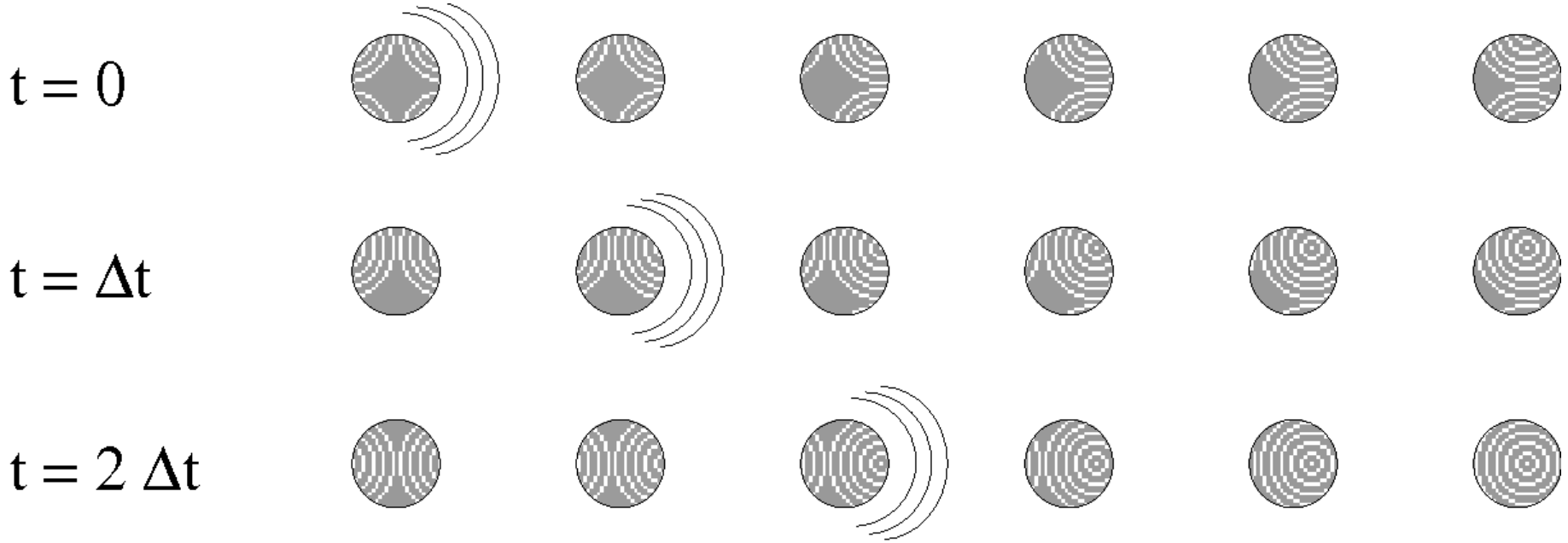
The solution to the equations of motion in Fourier space

$$s_{n\alpha i} = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\mathsf{q}) e^{i(\mathsf{q}\cdot \mathsf{r}_n - \omega t)}$$

The equation of motion now becomes

$$\omega^2 u_{\alpha i}(\mathbf{q}) = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{n\alpha i}^{m\beta j} e^{i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n)} u_{\beta j}(\mathbf{q}) \quad \text{sum repeated indices}$$

Where $u_{\alpha i}$ ($\boldsymbol{q}$) is independent of n so that a lattice vibration can propagate and respect the translational invariance of the lattice.



Recalling that $\Phi_{n\alpha i}^{m\beta j} = \Phi_{0\alpha i}^{(m-n)\beta j}$

$$D_{\alpha i}^{\beta j} = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{n\alpha i}^{m\beta j} e^{i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n)} = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0\alpha i}^{p\beta j} e^{i\mathbf{q}\cdot(\mathbf{r}_p)}$$

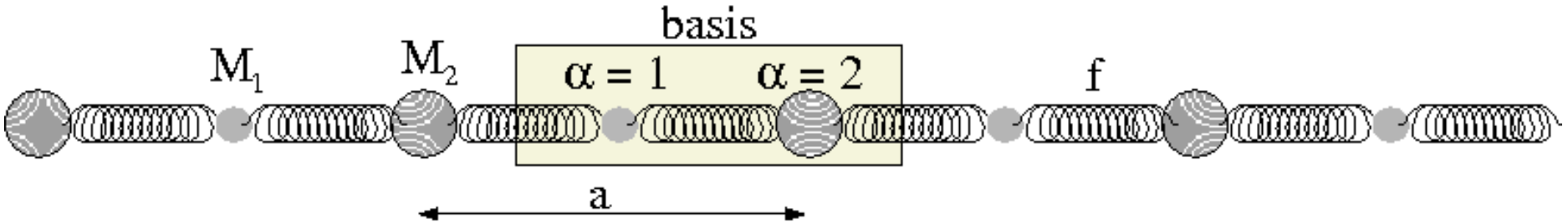
where $\boldsymbol{r}_p = \boldsymbol{r}_m - \boldsymbol{r}_n$, then the equation of motion becomes

$$\omega^2 u_{\alpha i}(\mathbf{q}) = D_{\alpha i}^{\beta j} u_{\beta j}(\mathbf{q})$$

or

$$\left(D_{\alpha i}^{\beta j} - \omega^2 \delta_{\alpha i}^{\beta j} \right) u_{\beta j}(\mathbf{q}) = 0$$

Example, a Linear Chain



Consider a linear chain of oscillators composed of a two-element basis with different masses, M_1 and M_2 and equal strength springs with spring constant f . It has the potential energy

$$\phi = \frac{1}{2} f \sum_n \left(s_{n,1} - s_{n,2}\right)^2 + \left(s_{n,2} - s_{n+1,1}\right)^2$$

Suppress the indices i and j, the solution to the differential equation

$$\omega^2 u_\alpha(\mathsf{q}) = D_\alpha^\beta u_\beta(\mathsf{q}) \;\text{ where }\; D_\alpha^\beta = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0\alpha}^{p,\beta} e^{i\mathsf{q}\cdot(\mathsf{r}_p)}$$

will have the form

$$s_{n\alpha} = \frac{1}{\sqrt{M_\alpha}} u_\alpha(\mathsf{q}) e^{i(\mathsf{q}\cdot\mathsf{r}_n - \omega t)}$$

The potential matrix has the form

$$\Phi_{n,1}^{n,1} = \Phi_{n,2}^{n,2} = 2f$$

$$\Phi_{n,1}^{n,2} = \Phi_{n,2}^{n,1} = \Phi_{n,1}^{n-1,2} = \Phi_{n,2}^{n+1,1} = -f\,.$$

Which yields

$$D_\alpha^\beta = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0\alpha}^{p\beta} e^{i\mathbf{q}\cdot(\mathbf{r}_p)}$$

$$= \begin{pmatrix} \frac{2f}{M_1} & -\frac{f}{\sqrt{M_1 M_2}}\left(1+e^{-iqa}\right) \\ -\frac{f}{\sqrt{M_1 M_2}}\left(1+e^{+iqa}\right) & \frac{2f}{M_2} \end{pmatrix}$$

The secular equation $\det(\mathbf{D}(\mathbf{q}) - \omega^2\mathbf{I}) = 0$ becomes

$$\omega^4 - \omega^2 2f\left(\frac{1}{M_1}+\frac{1}{M_2}\right) + \frac{4f^2}{M_1 M_2}\sin^2(qa/2) = 0$$

which has solutions

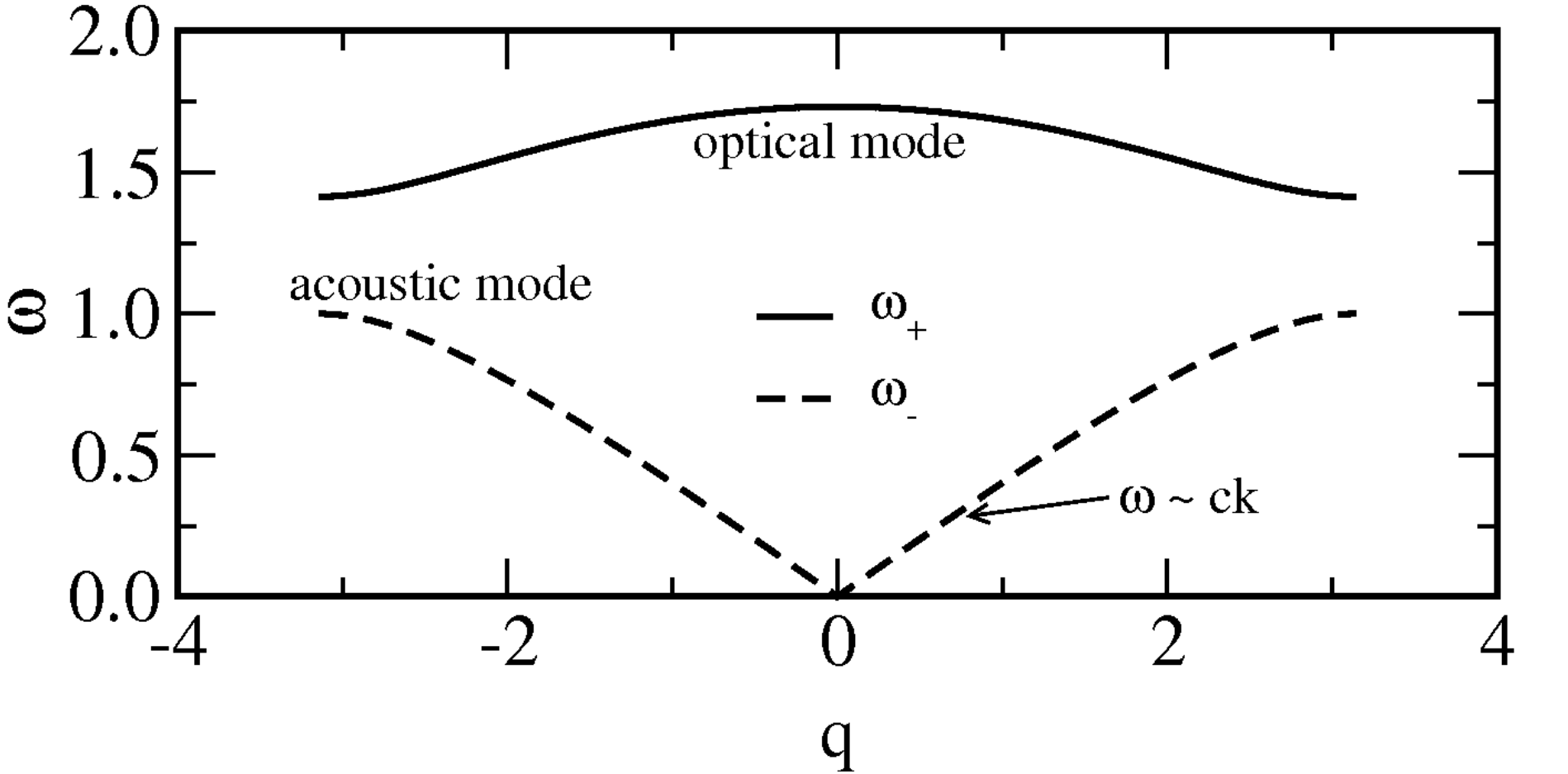
$$\omega^2 = f\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm f\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4}{M_1 M_2}\sin^2(qa/2)}$$

This equation simplifies significantly in the $q \to 0$ and $q/a \to \pi$ limits.

$$\lim_{q\to 0} \omega_-(q) = qa\sqrt{\frac{f\mu}{2M_1M_2}} \qquad \lim_{q\to 0} \omega_+(q) = \sqrt{\frac{2f}{\mu}}$$

and

$$\omega_-(q=\pi/a) = \sqrt{2f/M_2} \qquad \omega_+(q=\pi/a) = \sqrt{2f/M_1}$$



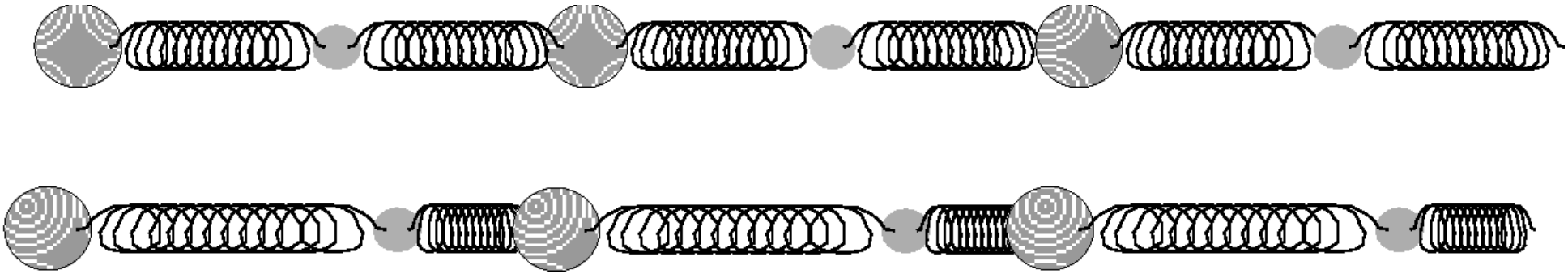
Looking at the optical mode at $q = 0$, $\omega_+(0) = 2f/\mu$

$$\mathbf{D} = \begin{pmatrix} 2f/M_1 & -2f/\sqrt{M_1 M_2} \\ -2f/\sqrt{M_1 M_2} & 2f/M_2 \end{pmatrix}$$

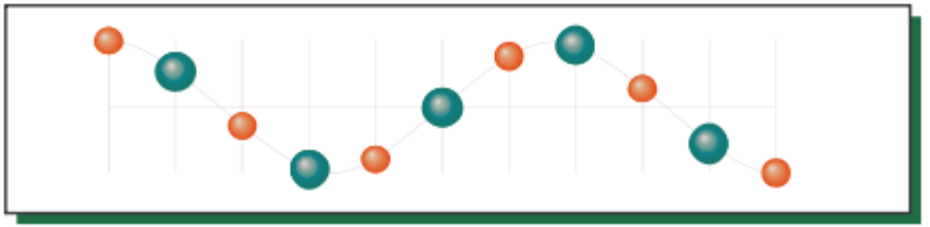
We find the Eigenvectors which are non-trivial solutions to $(\omega^2 \boldsymbol{I} - \boldsymbol{D})\boldsymbol{u} = 0$

$$0 = \begin{pmatrix} 2f/\mu - 2f/M_1 & 2f/\sqrt{M_1 M_2} \\ 2f/\sqrt{M_1 M_2} & 2f/\mu - 2f/M_2 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$$

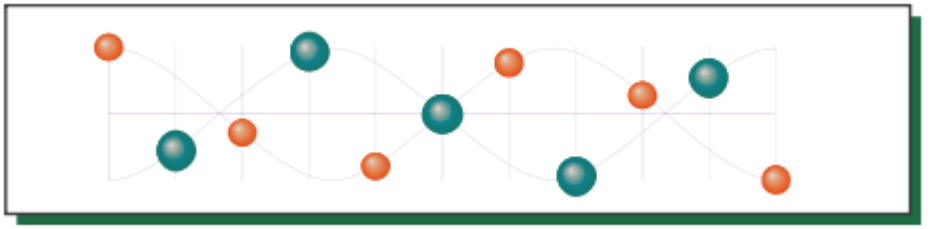
To be $u_1 = -M_2/M_1\, u_2$



Acoustic modes:

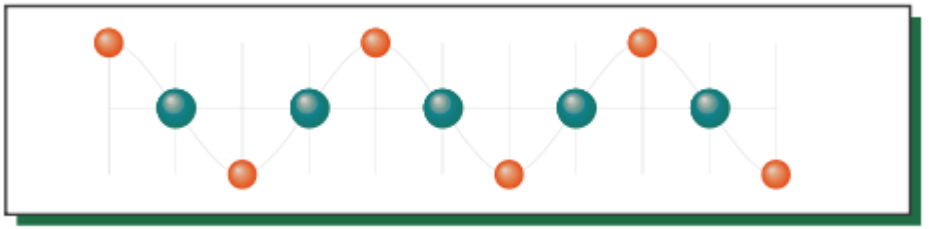


Optical modes:



Zone-boundary modes:

High energy mode



Low energy mode