Quantization of atomic vibrations

Restrictions on k-numbers because of boundary conditions; phonon density of states (DOS) as a function of k and $\omega_i n$ 3D

July 1, 2021

Boundary conditions

We can impose **periodic** boundary conditions or **finite** boundary conditions

Periodic boundary conditions

$$u_s = u_{N+s} \qquad \Rightarrow K = 0, \quad \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \pm\frac{6\pi}{L}, \dots, \frac{N\pi}{L}$$

Finite boundary conditions

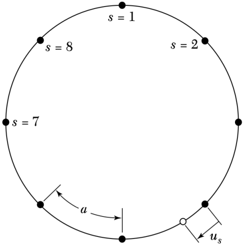
$$u_0 = u_N = 0 \qquad \Rightarrow K = \frac{\pi}{L}, \quad \frac{2\pi}{L}, \quad \frac{3\pi}{L}, \cdots, \quad \frac{(N-1)\pi}{L}$$

We have different spacing but the density of states is the same

$$N_{periodic}(k) = 2\,\frac{k}{\left(\frac{2\pi}{L}\right)} = \frac{kL}{\pi} \qquad \rightarrow \qquad DOS(k) = \frac{L}{\pi}$$

$$N_{fixed}(k) = \frac{k}{\left(\frac{\pi}{L}\right) = \frac{kL}{\pi}} \qquad \rightarrow \qquad DOS(k) = \frac{L}{\pi}$$

Figure 4 Consider N particles constrained to slide on a circular ring. The particles can oscillate if connected by elastic springs. In a normal mode the displacement u_s of atom s will be of the form $\sin sKa$ or $\cos sKa$: these are independent modes. By the geometrical periodicity of the ring the boundary condition is that $u_{N+s} = u_s$ for all s, so that NKa must be an integral multiple of 2π. For $N = 8$ the allowed independent values of K are 0, $2\pi/8a$, $4\pi/8a$, $6\pi/8a$, and $8\pi/8a$. The value $K = 0$ is meaningless for the sine form, because $\sin s0a = 0$. The value $8\pi/8a$ has a meaning only for the cosine form, because $\sin(s8\pi a/8a) = \sin s\pi = 0$. The three other values of K are allowed for both the sine and cosine modes, giving a total of eight allowed modes for the eight particles. Thus the periodic boundary condition leads to one allowed mode per particle, exactly as for the fixed-end boundary condition of Fig. 3. If we had taken the modes in the complex form $\exp(isKa)$, the periodic boundary condition would lead to the eight modes with $K = 0$, $\pm 2\pi/Na$, $\pm 4\pi/Na$, $\pm 6\pi/Na$, and $8\pi/Na$, as in Eq. (14).



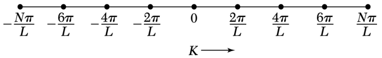


Figure 5 Allowed values of wavevector K for periodic boundary conditions applied to a linear lattice of periodicity $N = 8$ atoms on a line of length L. The $K = 0$ solution is the uniform mode. The special points $\pm N\pi/L$ represent only a single solution because $\exp(i\pi s)$ is identical to $\exp(-i\pi s)$; thus there are eight allowed modes, with displacements of the sth atom proportional to 1, $\exp(\pm i\pi s/4)$, $\exp(\pm i\pi s/2)$, $\exp(\pm i3\pi s/4)$, $\exp(i\pi s)$.

Boundary conditions

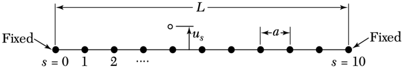


Figure 2 Elastic line of $N + 1$ atoms, with $N = 10$, for boundary conditions that the end atoms $s = 0$ and $s = 10$ are fixed. The particle displacements in the normal modes for either longitudinal or transverse displacements are of the form $u_s \propto \sin sKa$. This form is automatically zero at the atom at the end $s = 0$, and we choose K to make the displacement zero at the end $s = 10$.

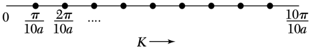


Figure 3 The boundary condition $\sin sKa = 0$ for $s = 10$ can be satisfied by choosing $K = \pi/10a$, $2\pi/10a, \ldots, 9\pi/10a$, where $10a$ is the length L of the line. The present figure is in K space. The dots are not atoms but are the allowed values of K. Of the $N + 1$ particles on the line, only $N - 1$ are allowed to move, and their most general motion can be expressed in terms of the $N - 1$ allowed values of K. This quantization of K has nothing to do with quantum mechanics but follows classically from the boundary conditions that the end atoms be fixed.

Phonons density of states in 3D

In 3D the density of states for periodic boundary conditions the number of modes is

$$N(k) = \frac{\frac{4}{3}\pi k^3}{\left(\frac{2\pi}{L}\right)^3} \qquad \longrightarrow \qquad DOS(k) = \frac{k^2 L^3}{2\pi^2}$$

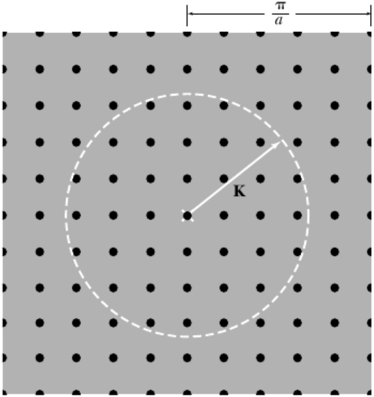


Figure 1: Reciprocal lattice points allowed for phonons in 3D with periodic boundary conditions

Quantization of phonons

By analogy with the photons, elastic waves have energies

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

where n indicates the number of quasiparticles (phonons) involved

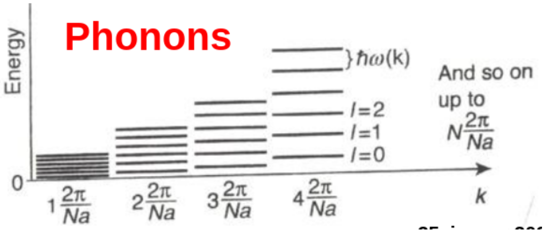


Figure 2: Phonons energy

Each phonon has energy $\hbar\omega$ but $\omega = \omega(k)$ and k is limited by boundary conditions. The total number of phonons is limited by the number of degrees of freedom in the system