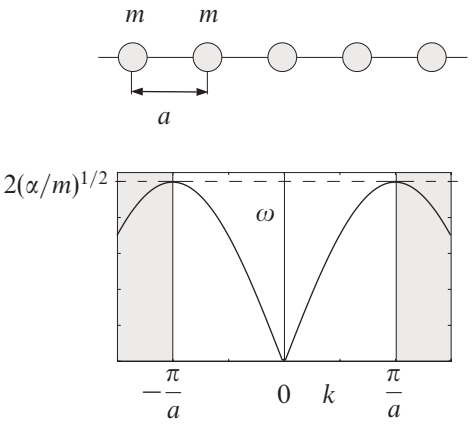
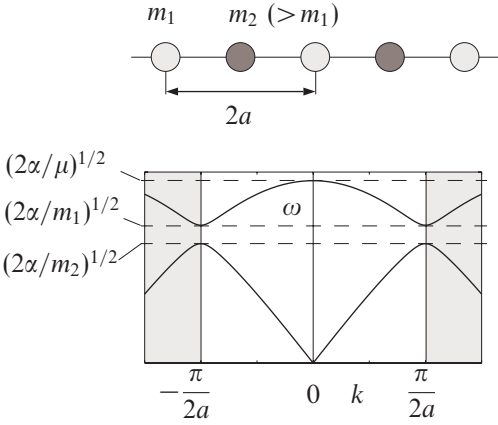
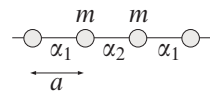


6.4 Lattice dynamics

Phonon dispersion relations^a

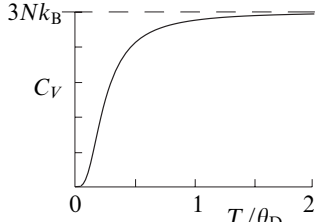
 monatomic chain  diatomic chain	
Monatomic linear chain	$\omega^2 = 4 \frac{\alpha}{m} \sin^2 \left(\frac{ka}{2} \right) \quad (6.34)$ $v_p = \frac{\omega}{k} = a \left(\frac{\alpha}{m} \right)^{1/2} \text{sinc} \left(\frac{a}{\lambda} \right) \quad (6.35)$ $v_g = \frac{\partial \omega}{\partial k} = a \left(\frac{\alpha}{m} \right)^{1/2} \cos \left(\frac{ka}{2} \right) \quad (6.36)$
Diatomic linear chain ^c	$\omega^2 = \frac{\alpha}{\mu} \pm \alpha \left[\frac{1}{\mu^2} - \frac{4}{m_1 m_2} \sin^2(ka) \right]^{1/2} \quad (6.37)$
Identical masses, alternating spring constants	$\omega^2 = \frac{\alpha_1 + \alpha_2}{m} \pm \frac{1}{m} (\alpha_1^2 + \alpha_2^2 + 2\alpha_1 \alpha_2 \cos ka)^{1/2} \quad (6.38)$ $= \begin{cases} 0, & 2(\alpha_1 + \alpha_2)/m & \text{if } k=0 \\ 2\alpha_1/m, & 2\alpha_2/m & \text{if } k=\pi/a \end{cases} \quad (6.39)$ 

^aAlong infinite linear atomic chains, considering simple harmonic nearest-neighbour interactions only. The shaded region of the dispersion relation is outside the first Brillouin zone of the reciprocal lattice.

^bIn the sense α = restoring force/relative displacement.

^cNote that the repeat distance for this chain is $2a$, so that the first Brillouin zone extends to $|k| < \pi/(2a)$. The optic and acoustic branches are the + and – solutions respectively.

Debye theory

Mean energy per phonon mode ^a	$\langle E \rangle = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\exp[\hbar \omega / (k_B T)] - 1}$ (6.40)	$\langle E \rangle$ mean energy in a mode at ω $\hbar$ (Planck constant)/(2 π) ω phonon angular frequency k_B Boltzmann constant T temperature
Debye frequency	$\omega_D = v_s (6\pi^2 N/V)^{1/3}$ (6.41) where $\frac{3}{v_s^3} = \frac{1}{v_l^3} + \frac{2}{v_t^3}$ (6.42)	ω_D Debye (angular) frequency v_s effective sound speed v_l longitudinal phase speed v_t transverse phase speed
Debye temperature	$\theta_D = \hbar \omega_D / k_B$ (6.43)	N number of atoms in crystal V crystal volume θ_D Debye temperature
Phonon density of states	$g(\omega) d\omega = \frac{3V\omega^2}{2\pi^2 v_s^3} d\omega$ (6.44) (for $0 < \omega < \omega_D$, $g = 0$ otherwise)	$g(\omega)$ density of states at ω C_V heat capacity, V constant U thermal phonon energy within crystal $D(x)$ Debye function
Debye heat capacity	$C_V = 9Nk_B \frac{T^3}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$ (6.45)	
Dulong and Petit's law	$\simeq 3Nk_B \quad (T \gg \theta_D)$ (6.46)	
Debye T^3 law	$\simeq \frac{12\pi^4}{5} Nk_B \frac{T^3}{\theta_D^3} \quad (T \ll \theta_D)$ (6.47)	
Internal thermal energy ^b	$U(T) = \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar \omega^3}{\exp[\hbar \omega / (k_B T)] - 1} d\omega \equiv 3Nk_B T D(\theta_D/T)$ (6.48) where $D(x) = \frac{3}{x^3} \int_0^x \frac{y^3}{e^y - 1} dy$ (6.49)	

^aOr any simple harmonic oscillator in thermal equilibrium at temperature T .

^bNeglecting zero-point energy.

Lattice forces (simple)

Van der Waals interaction ^a	$\phi(r) = -\frac{3}{4} \frac{\alpha_p^2 \hbar \omega}{(4\pi\epsilon_0)^2 r^6} \quad (6.50)$	$\phi(r)$ two-particle potential energy r particle separation α_p particle polarisability
Lennard–Jones 6-12 potential (molecular crystals)	$\phi(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \quad (6.51)$	$\hbar$ (Planck constant)/(2 π)
	$= 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (6.52)$	ϵ_0 permittivity of free space ω angular frequency of polarised orbital
	$\sigma = (B/A)^{1/6}; \quad \epsilon = A^2/(4B)$ $\phi_{\min} \quad \text{at} \quad r = \frac{2^{1/6}}{\sigma} \quad (6.53)$	A, B constants ϵ, σ Lennard–Jones parameters
De Boer parameter	$\Lambda = \frac{h}{\sigma(m\epsilon)^{1/2}} \quad (6.54)$	Λ de Boer parameter h Planck constant m particle mass
Coulomb interaction (ionic crystals)	$U_C = -\alpha_M \frac{e^2}{4\pi\epsilon_0 r_0} \quad (6.55)$	U_C lattice Coulomb energy per ion pair α_M Madelung constant $-e$ electronic charge r_0 nearest neighbour separation

^aLondon’s formula for fluctuating dipole interactions, neglecting the propagation time between particles.

Lattice thermal expansion and conduction

Grüneisen parameter ^a	$\gamma = -\frac{\partial \ln \omega}{\partial \ln V} \quad (6.56)$	γ Grüneisen parameter ω normal mode frequency V volume
Linear expansivity ^b	$\alpha = \frac{1}{3K_T} \left. \frac{\partial p}{\partial T} \right _V = \frac{\gamma C_V}{3K_T V} \quad (6.57)$	α linear expansivity K_T isothermal bulk modulus p pressure T temperature C_V lattice heat capacity, constant V
Thermal conductivity of a phonon gas	$\lambda = \frac{1}{3} \frac{C_V}{V} v_s l \quad (6.58)$	λ thermal conductivity v_s effective sound speed l phonon mean free path
Umklapp mean free path ^c	$l_u \propto \exp(\theta_u/T) \quad (6.59)$	l_u umklapp mean free path θ_u umklapp temperature ($\sim \theta_D/2$)

^aStrictly, the Grüneisen parameter is the mean of γ over all normal modes, weighted by the mode’s contribution to C_V .

^bOr “coefficient of thermal expansion,” for an isotropically expanding crystal.

^cMean free path determined solely by “umklapp processes” – the scattering of phonons outside the first Brillouin zone.