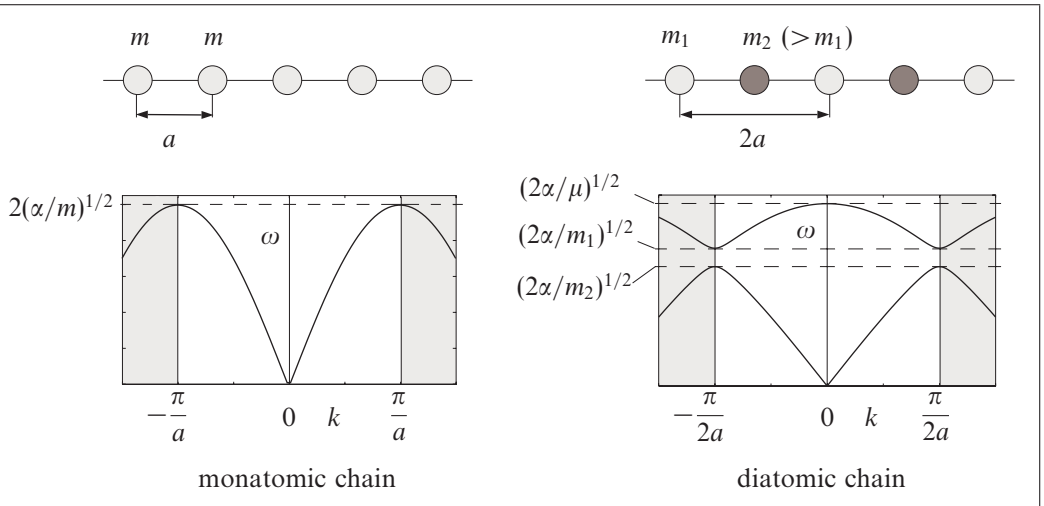
6.4 Lattice dynamics

Phonon dispersion relations[a]



Monatomic linear chain

$$\omega^2 = 4\frac{\alpha}{m}\sin^2\left(\frac{ka}{2}\right) \tag{6.34}$$

$$v_p = \frac{\omega}{k} = a\left(\frac{\alpha}{m}\right)^{1/2}\operatorname{sinc}\left(\frac{a}{\lambda}\right) \tag{6.35}$$

$$v_g = \frac{\partial\omega}{\partial k} = a\left(\frac{\alpha}{m}\right)^{1/2}\cos\left(\frac{ka}{2}\right) \tag{6.36}$$

Diatomic linear chain[c]

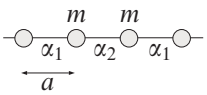
$$\omega^2 = \frac{\alpha}{\mu} \pm \alpha\left[\frac{1}{\mu^2} - \frac{4}{m_1 m_2}\sin^2(ka)\right]^{1/2} \tag{6.37}$$

Identical masses, alternating spring constants

$$\omega^2 = \frac{\alpha_1+\alpha_2}{m} \pm \frac{1}{m}(\alpha_1^2+\alpha_2^2+2\alpha_1\alpha_2\cos ka)^{1/2} \tag{6.38}$$

$$= \begin{cases} 0, & 2(\alpha_1+\alpha_2)/m \quad \text{if } k=0 \\ 2\alpha_1/m, & 2\alpha_2/m \quad \text{if } k=\pi/a \end{cases} \tag{6.39}$$

ω	phonon angular frequency
α	spring constant[b]
m	atomic mass
v_p	phase speed ($\operatorname{sinc}x \equiv \frac{\sin\pi x}{\pi x}$)
v_g	group speed
λ	phonon wavelength
k	wavenumber ($=2\pi/\lambda$)
a	atomic separation
m_i	atomic masses ($m_2 > m_1$)
μ	reduced mass $[=m_1m_2/(m_1+m_2)]$
α_i	alternating spring constants

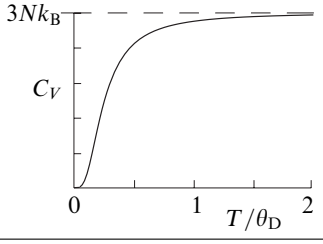


[a] Along infinite linear atomic chains, considering simple harmonic nearest-neighbour interactions only. The shaded region of the dispersion relation is outside the first Brillouin zone of the reciprocal lattice.
[b] In the sense α = restoring force/relative displacement.
[c] Note that the repeat distance 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)
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)
Debye temperature	$\theta_D = \hbar\omega_D/k_B$	(6.43)
Phonon density of states	$g(\omega)\,d\omega = \frac{3V\omega^2}{2\pi^2 v_s^3}\,d\omega$ (for $0<\omega<\omega_D$, $g=0$ otherwise)	(6.44)
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)

$\langle E\rangle$ mean energy in a mode at ω
$\hbar$ (Planck constant)/(2π)
ω phonon angular frequency
k_B Boltzmann constant
T temperature
ω_D Debye (angular) frequency
v_s effective sound speed
v_l longitudinal phase speed
v_t transverse phase speed
N number of atoms in crystal
V crystal volume
θ_D Debye temperature
$g(\omega)$ density of states at ω
C_V heat capacity, V constant
U thermal phonon energy within crystal
$D(x)$ Debye function



[a] Or any simple harmonic oscillator in thermal equilibrium at temperature T.
[b] Neglecting zero-point energy.

Lattice forces (simple)

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

[a]London's formula for fluctuating dipole interactions, neglecting the propagation time between particles.

Lattice thermal expansion and conduction

Grüneisen parameter[a]	$\gamma = -\frac{\partial \ln \omega}{\partial \ln V}$	(6.56)	γ Grüneisen parameter ω normal mode frequency V volume
Linear expansivity[b]	$\alpha = \frac{1}{3K_T}\frac{\partial p}{\partial T}\Big\vert_V = \frac{\gamma C_V}{3K_T V}$	(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	$\lambda = \frac{1}{3}\frac{C_V}{V} v_s l$	(6.58)	λ thermal conductivity v_s effective sound speed l phonon mean free path
Umklapp mean free path[c]	$l_u \propto \exp(\theta_u/T)$	(6.59)	l_u umklapp mean free path θ_u umklapp temperature ($\sim\theta_D/2$)

[a]Strictly, the Grüneisen parameter is the mean of γ over all normal modes, weighted by the mode's contribution to C_V.
[b]Or "coefficient of thermal expansion," for an isotropically expanding crystal.
[c]Mean free path determined solely by "umklapp processes" – the scattering of phonons outside the first Brillouin zone.