6. Phonons

6.1 Specific heat — Debye model:

assumptions:

- solids are elastic, isotropic homogenous continua
- excitations: sound waves with linear dispersion
- Bose-Einstein distribution

internal energy:

cut-off frequency → Debye frequency

$$U(T) = \int_0^{\hbar\omega_\mathrm{D}} \hbar\omega\, \mathcal{D}(\omega)\, f(\omega, T)\, \mathrm{d}\omega$$

$\mathcal{D}(\omega) \propto \omega^2$

specific heat:

$$C_V = \frac{\partial U}{\partial T} = 9Nk_\mathrm{B}\left(\frac{T}{\Theta}\right)^3 \int_0^{x_\mathrm{D}} \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\, \mathrm{d}x$$

$x_\mathrm{D} = \hbar\omega_\mathrm{D}/k_\mathrm{B}T$

$x = \hbar\omega/k_\mathrm{B}T$

$\Theta = \hbar\omega_\mathrm{D}/k_\mathrm{B}$

6.1 Specific Heat

Limiting cases:

(i) $T \to \infty \longrightarrow x \to 0$

$$\lim_{x\to 0} \int_0^{x_D} \frac{x^4\,e^x}{(e^x-1)^2}dx \approx \int_0^{x_D} \frac{x^4 \cdot 1}{x^2}dx = \frac{x_D^3}{3} = \frac{1}{3}\left(\frac{\Theta}{T}\right)^3$$

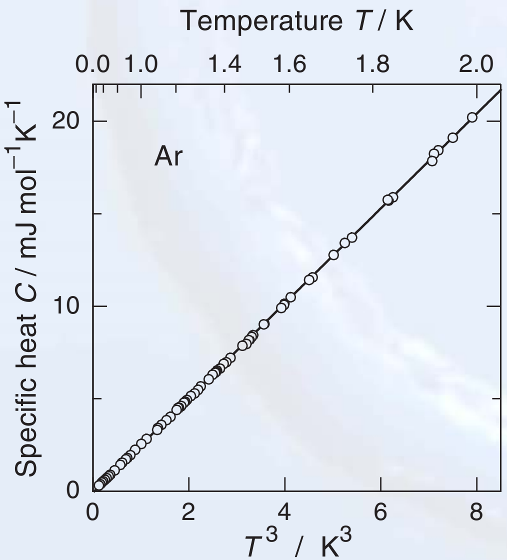
$(e^x-1)^2 \approx (1+x-1)^2$

$\longrightarrow$ $C_V = 3Nk_B$ Dulong-Petit law

(ii) $T \to 0 \longrightarrow x_D \to \infty$

$$C_V = 9Nk_B\left(\frac{T}{\Theta}\right)^3 \underbrace{\int_0^{\infty} \frac{x^4 e^x}{(e^x-1)^2}dx}_{4\pi^4/15} = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\Theta}\right)^3$$

$\longrightarrow$ $C_V = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\Theta}\right)^3$



- perfect agreement with theory
- only small temperature range
- Debye temperature $\Theta = 92\,\mathrm{K}$

6.1 Specific Heat

Element	Θ (K)	Element	Θ (K)	Element	Θ (K)	Element	Θ (K)
Ar	92	Cu	347	Mn	409	Sc	346
Ac*	100	Er	118	Mo	423	Se	152
Ag	227	Fe	477	N*	70	Si	645
Al	433	Ga	325	Na	156	Sm	169
Am	121	Gd	182	Nb	276	Sn	199
As	282	Ge	373	Nd	163	Sr	147
Au	162	H (para)	122	Ne	75	Ta	245
B	1480	H (orth)	114	Ni	477	Tb	176
Ba	111	^{3}He	19–33	Np	259	Te	152
Be	1481	Hf	252	O*	90	Th	160
Bi	120	Hg	72	Os	467	Ti	420
C (Dia.)	2250	Ho	190	Pa	185	Tl	78
C (Gra.)	413	I	109	Pb	105	Tm	200
Ca	229	In	112	Pd	271	U	248
Cd	210	Ir	420	Pr	152	V	399
Ce	179	K	91	Pt	237	W	383
Cl*	115	Kr	72	Rb	56	Xe	64
Cm	123	La	145	Re	416	Y	248
Co	460	Li	344	Rh	512	Yb	118
Cr	606	Lu	183	Ru	555	Zn	329
Cs	40	Mg	403	Sb	220	Zr	290

6.1 Specific Heat

Compound	Θ (K)	Compound	Θ (K)	Compound	Θ (K)
$AgBr^*$	140	$Cr_2Cl_3^*$	360	MgO^*	800
$AgCl^*$	180	FeS_2^*	630	MoS_2^*	290
$As_2O_3^*$	140	KBr	173	RbBr	131
$As_2O_5^*$	240	KCl	235	RbCl	165
$AuCu_3$	285	KI	131	RbI	103
BN^*	600	InSb	206	SiO_2 (Quartz)	470
CaF_2	508	LiF	736	TiO_2^* (Rutile)	450
$CrCl_2^*$	80	LiCl	422	ZnS	315

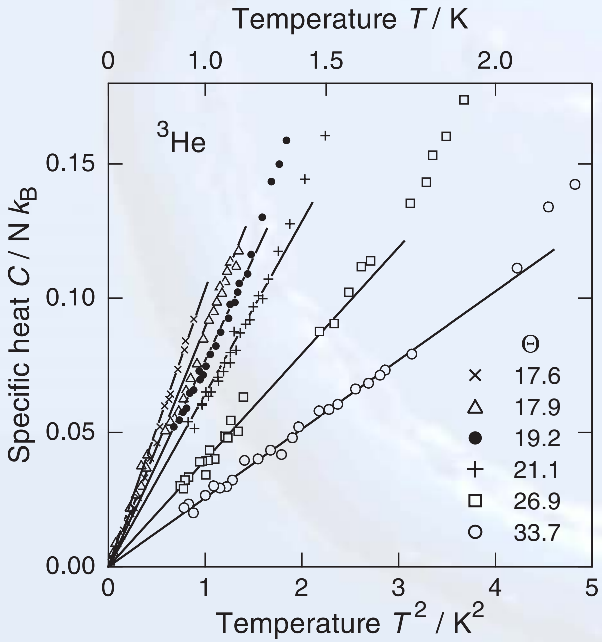
6.1 Specific Heat

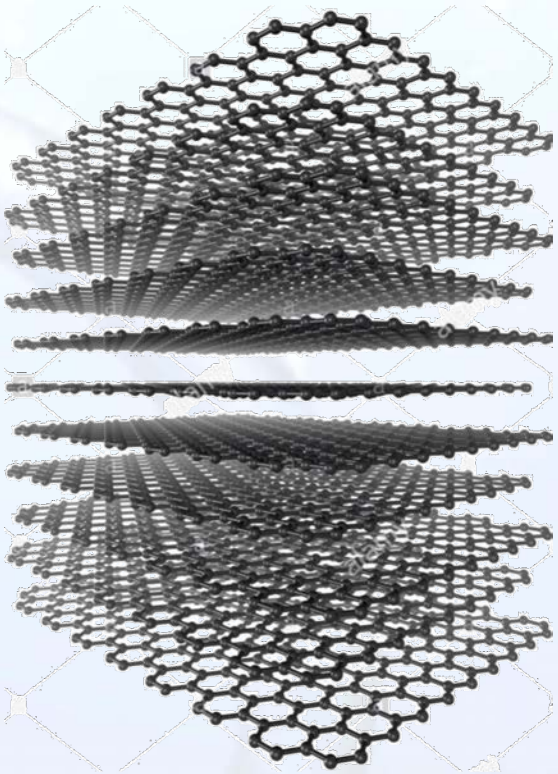
low-dimensional systems

$$D(\omega) \propto \omega^{d-1} \longrightarrow C_V \propto T^d$$

$$d = 2 \longrightarrow C_V \propto T^2.$$

example: ^{3}He atoms on graphite (sub-mono layers)





- high temperatures and low densities ⟶ gas: $C_V \approx N k_B$
- for $n > 0.078\,\text{Å}^{-2}$ ⟶ two-dimensional solid crystals
- increasing density ⟶ Θ increases
- density $0.078 \ldots 0.092\,\text{Å}^{-2}$ ⟶ $\Theta = 17.6 \ldots 37.7\,\text{K}$
- at high temperatures melting of 2d-crystals

6.2 Heat transport

Fourier equation $\boldsymbol{j} = -\Lambda \nabla T$

$$\Lambda = \frac{1}{3} C\, v\, \ell$$

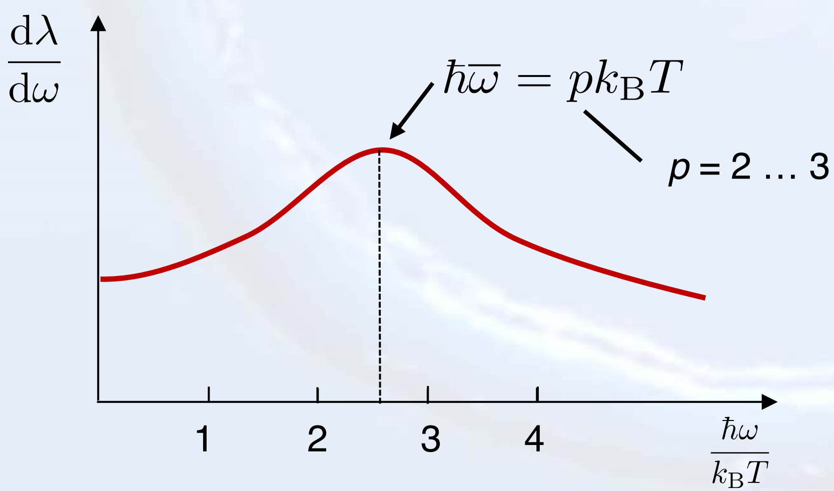
in general

$$\Lambda = \frac{1}{3} \sum_i \int c_i(\omega)\, v_i(\omega)\, \ell_i(\omega)\, \mathrm{d}\omega$$

spectral specific heat

different “particles” ⟶ phonon branches

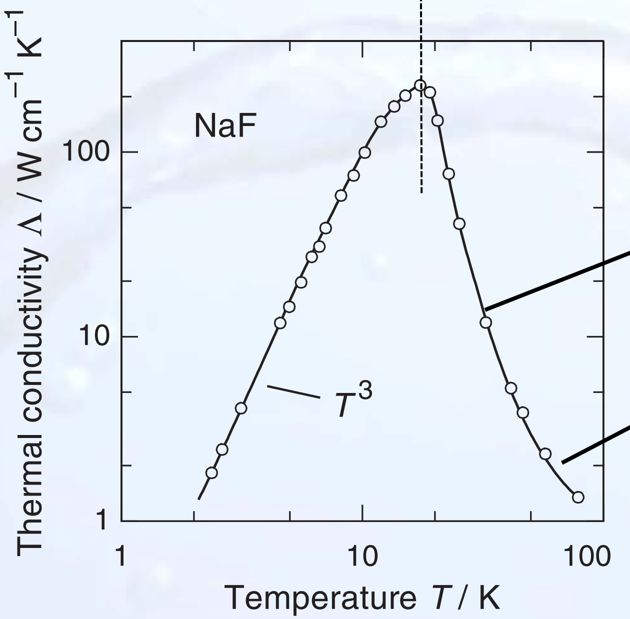
dominate phonon approximation (Debye)



- summation and integration can be avoided
- in addition: linear dispersion

6.2 Heat Transport

phonon-defect scattering ← → phonon-phonon scattering

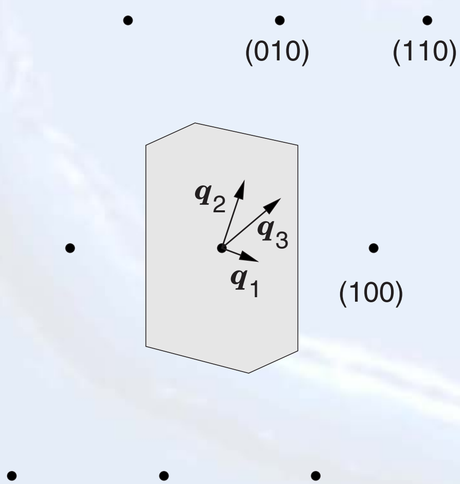


$\Lambda \propto \ell_U \propto e^{\Theta/2T}$

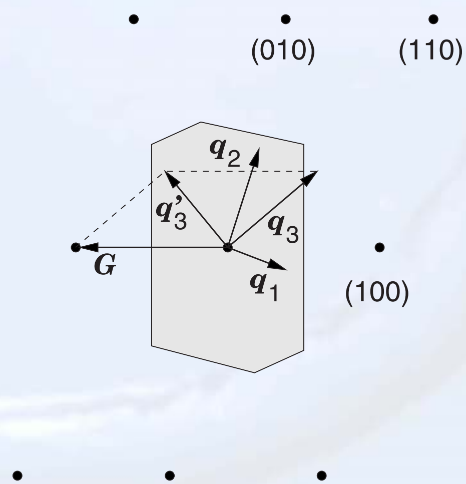
$\Lambda \propto T^{-1}$

number of umklapp processes increases with temperature

normal process



umklapp process



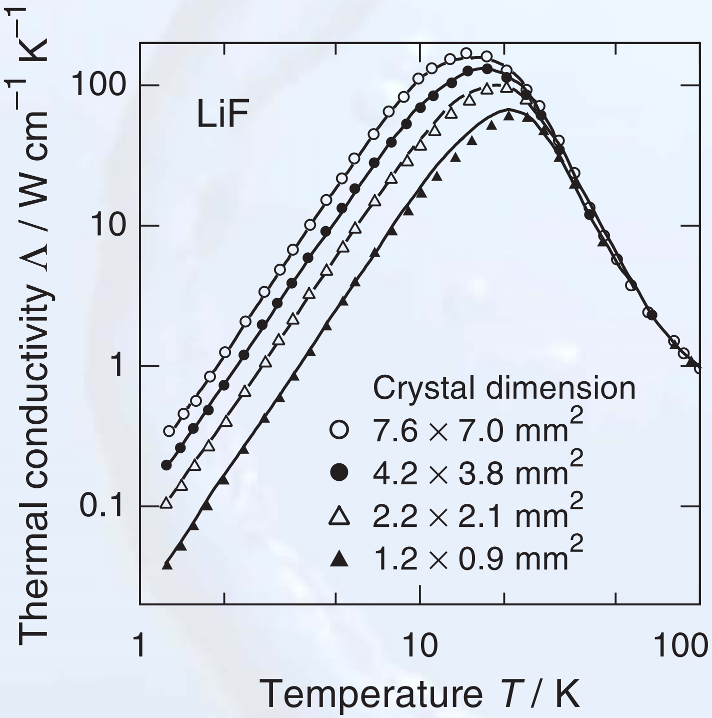
6.2 Heat Transport

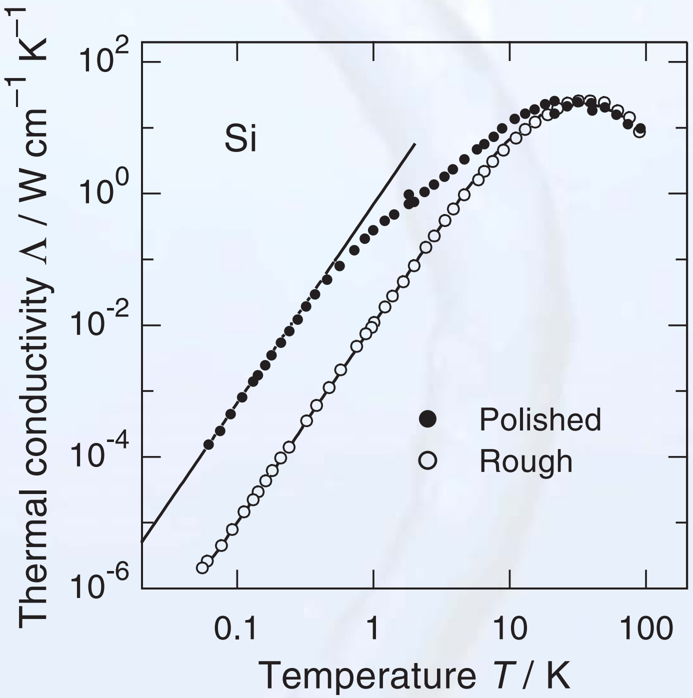
phonon-defect scattering

a) surfaces

$$\Lambda = \frac{1}{3} C\, v\, \ell \quad \xrightarrow{\ell \approx d} \quad \Lambda \approx \tfrac{1}{3} C_V v d \;\propto T^3$$

Casimir regime





- depends on sample cross-section
- temperature dependence as expected

- roughed: mean free path factor 50 shorter
- polished: mean free path 7 cm, sample length

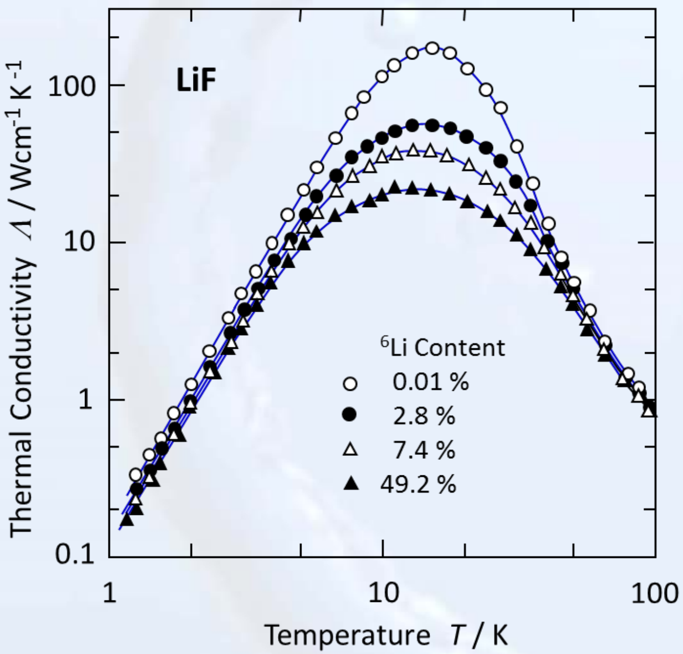
6.2 Heat Transport

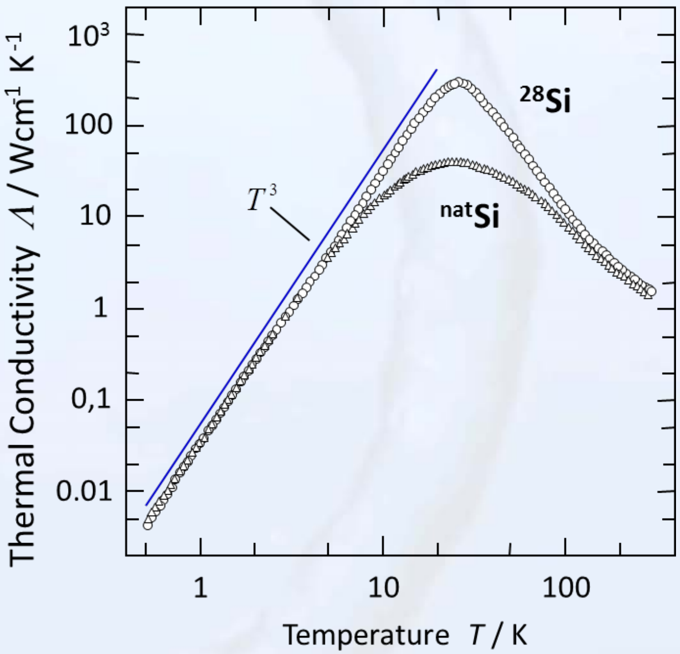
b) influence of point defects (elastic scattering)

⟶ Rayleigh scattering, since $\lambda_{\text{phonon}} \gg d_{\text{defect}}$

$$\ell^{-1} = \frac{n_{\text{p}} V_{\text{A}}^2}{4\pi} \left(\frac{\Delta M}{M}\right)^2 q^4 \propto \omega^4$$

is important at intermediate temperatures, since at low temperature q is too small and at high temperatures phonon-phonon scattering dominates





- adding ^{6}Li reduces heat transport
- maximum becomes rounded

- ^{nat}Si: 10% of all Si atoms have mass difference
- ^{28}Si: sharp peak ⟶ little scattering on point defects