

PHYS 342/555

Introduction to solid state physics

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Chapter 5: Thermal properties

Lecture in pdf format will be available at:

<http://www.phys.utk.edu>

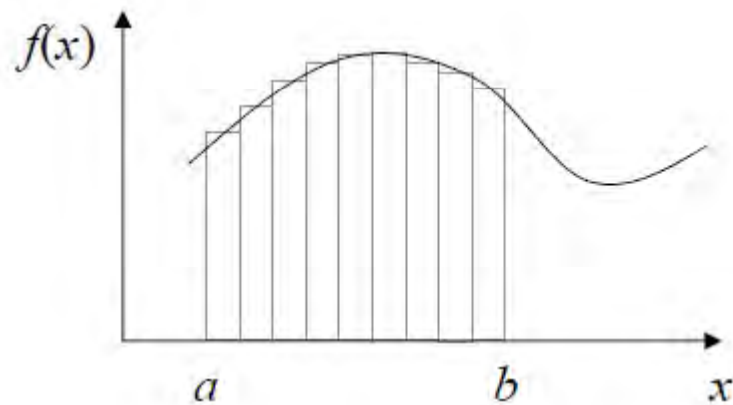
Debye temperature

Table 1 Debye temperature and thermal conductivity^a

Li	Be											B	C	N	O	F	Ne	
344	1440												2230					75
0.85	2.00											0.27	1.29					
Na	Mg											Al	Si	P	S	Cl	Ar	
158	400											428	645					92
1.41	1.56											2.37	1.48					
Low temperature limit of θ , in Kelvin																		
Thermal conductivity at 300 K, in $\text{W cm}^{-1}\text{K}^{-1}$																		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
91	230	360	420	380	630	410	470	445	450	343	327	320	374	282	90		72	
1.02		0.16	0.22	0.31	0.94	0.08	0.80	1.00	0.91	4.01	1.16	0.41	0.60	0.50	0.02			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn _w	Sb	Te	I	Xe	
56	147	280	291	275	450		600	480	274	225	209	108	200	211	153		64	
0.58		0.17	0.23	0.54	1.38	0.51	1.17	1.50	0.72	4.29	0.97	0.82	0.67	0.24	0.02			
Cs	Ba	La β	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
38	110	142	252	240	400	430	500	420	240	165	71.9	78.5	105	119				
0.36		0.14	0.23	0.58	1.74	0.48	0.88	1.47	0.72	3.17		0.46	0.35	0.08				
Fr	Ra	Ac																
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
									200		210				120	210		
			0.11	0.12	0.16		0.13		0.11	0.11	0.11	0.16	0.14	0.17	0.35	0.16		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
			163		207													
			0.54		0.28	0.06	0.07											

In general, a harder material has a higher Debye temperature

Connection between summation and integral



$$\int_a^b dx f(x) = \lim_{\Delta x \rightarrow 0} \sum_i \Delta x \cdot f(x_i), \text{ or}$$

$$\sum_i f(x_i) \cong \int_a^b \frac{dx}{\Delta x} f(x).$$

Generalization to 3-dim:

$$\sum_{\vec{x}} f(\vec{x}) \cong \int \frac{d^3x}{\Delta^3x} f(\vec{x})$$

or $\sum_{\vec{k}} f(\vec{k}) \cong \int \frac{d^3k}{\Delta^3k} f(\vec{k})$ in solid state

Chapter 5: Phonons and thermal properties

In quantum theory of specific heat, the total thermal energy of the phonons can be written as the sum of the energies over all phonon

modes:
$$U = \sum_k \sum_p \langle n_{k,p} \rangle \hbar \omega_{k,p},$$

Here $\langle n_{k,p} \rangle$ denotes the thermal equilibrium occupancy of phonons of wavevector k and polarization p . $\langle n_{k,p} \rangle$ is given by the Planck

distribution function:
$$\langle n_{k,p} \rangle = \frac{1}{\exp(\hbar \omega / \tau) - 1}.$$

The heat capacity is then defined as
$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V.$$

Planck distribution function:

Consider a set of identical harmonic oscillators in thermal equilibrium.

The harmonic oscillator has an energy of $(n + \frac{1}{2})\hbar\omega$.

$N_{n+1} / N_n = \exp(-\hbar\omega / \tau)$, $\tau = k_B T$. Thus the fraction of the total number of oscillators in the n th quantum state is

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{\exp(-n\hbar\omega / \tau)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega / \tau)}$$

The average excitation quantum # of an oscillator is:

$$\langle n \rangle = \frac{\sum s \exp(-s\hbar\omega / \tau)}{\sum \exp(-s\hbar\omega / \tau)} = \frac{1}{\exp(\hbar\omega / \tau) - 1}$$

Normal mode enumeration

The energy of a collection of oscillators in thermal equilibrium

$$U = \sum_k \sum_p \frac{\hbar \omega_{k,p}}{\exp(\hbar \omega / \tau) - 1}, \text{ If crystal had } D_p(\omega) d\omega \text{ modes of}$$

a given polarization p between ω and $\omega + d\omega$.

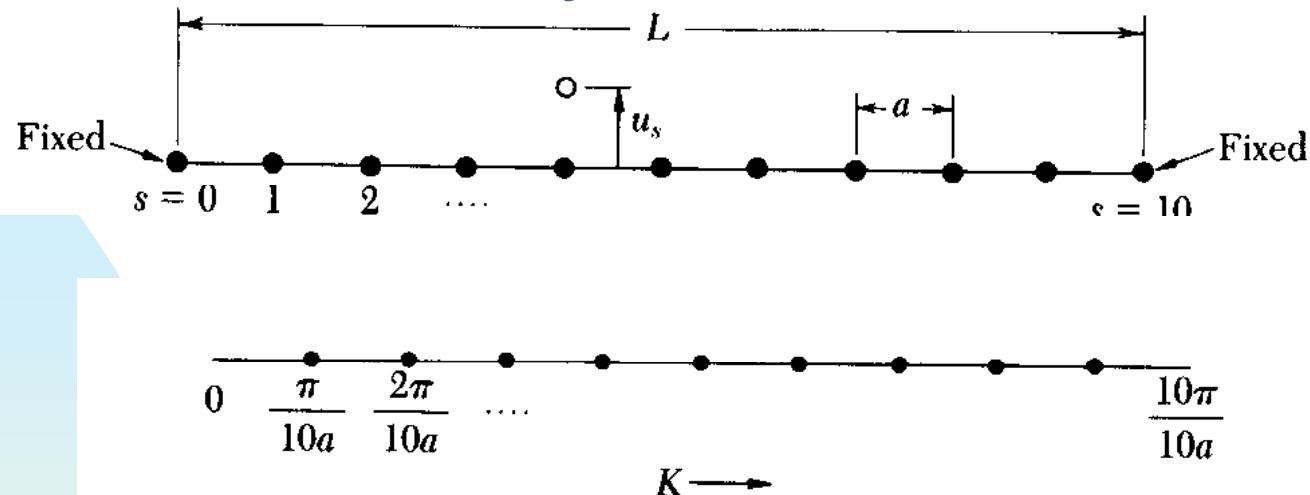
$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{\exp(\hbar \omega / \tau) - 1}, \text{ where } D_p(\omega) \text{ is the number}$$

of modes per unit frequency, called the density of modes or density of states.

Assume $x = \hbar \omega / k_B T$. Then $\partial U / \partial T$

$$C_{lat} = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 \exp(x)}{[\exp(x) - 1]^2}.$$

Density of states in 1D



If each normal vibrational mode of polarization p has the form of a standing wave, where

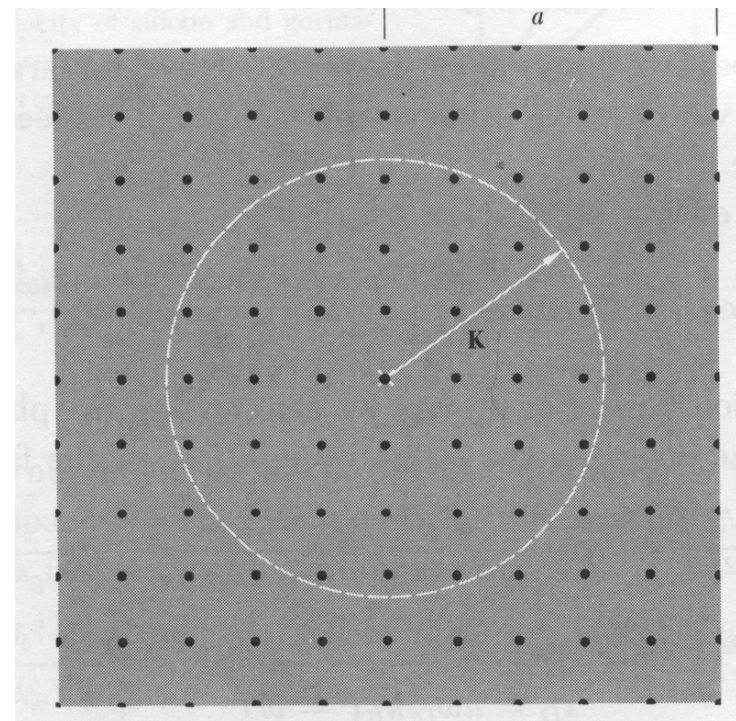
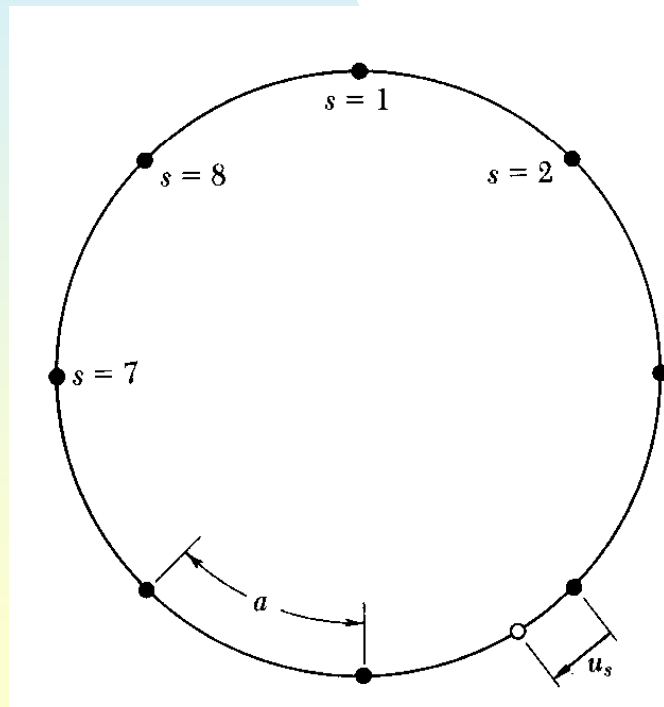
$$u_s = u(0) \exp(-i\omega_{k,p}t) \sin ska$$

The wavevector k is restricted by the fixed-end boundary conditions to the values

$$k = \frac{\pi}{L}, \frac{2\pi}{L}, \dots, \frac{(N-1)\pi}{L}$$

For 1D line there is one mode for each interval $\Delta k = \pi / L$, so that the number of modes per unit range of k is L / π for $k \leq \pi / a$ and 0 for $k > \pi / a$. The number of modes $D(\omega)d\omega$ in $d\omega$ at ω

$$D(\omega)d\omega = \frac{L}{\pi} \frac{dk}{d\omega} d\omega, \quad d\omega / dk \text{ is the group velocity.}$$



Density of states in three dimensions

In three dimensional lattice with N^3 primitive cells side L , periodic condition requires

$$\exp[i(k_x x + k_y y + k_z z)] \equiv \exp[i(k_x (x + L) + k_y (y + L) + k_z (z + L))]$$

$$\text{Therefore } k_x, k_y, k_z = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; \dots; \pm \frac{N\pi}{L}$$

There is one allowed value of k per volume $(2\pi / L)^3$ in k space or the total # of modes with wavevector less than k

$N = (L / 2\pi)^3 (4\pi k^3 / 3)$. The density of states for each polarization is $D(\omega) = dN / d\omega = (Vk^2 / 2\pi^2)(dk / d\omega)$

Density of states $D(\omega)$ (DOS, 態密度)

- $D(\omega)d\omega$ is the number of states within the surfaces of constant ω and $\omega+d\omega$

$$D(\omega)d\omega = \frac{\int_{shell} d^3k}{\Delta^3k}, \quad \Delta^3k = \left(\frac{2\pi}{L}\right)^3$$

Alternative definition:

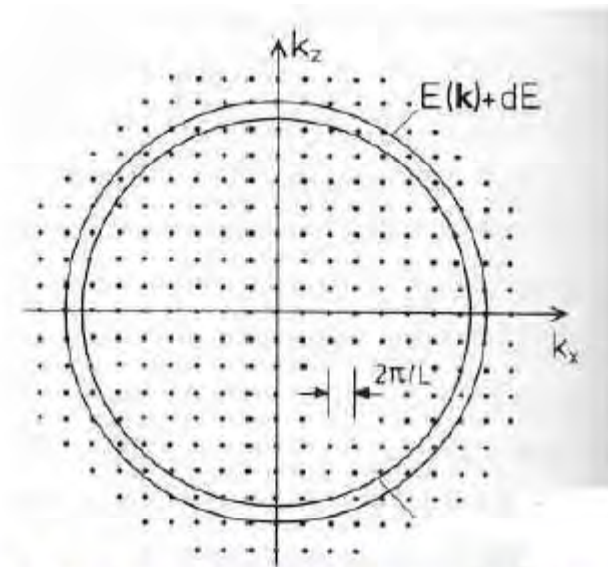
$$D(\omega) = \int \frac{d^3k}{\Delta^3k} \delta(\omega_{\vec{k}} - \omega)$$

$$\sum_{\vec{k}} f(\omega_{\vec{k}}) \cong \int \frac{d^3k}{\Delta^3k} f(\omega_{\vec{k}})$$

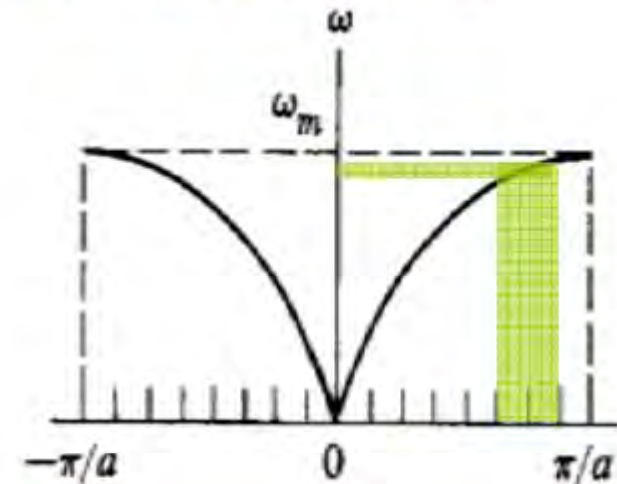
$$= \int d\omega D(\omega) f(\omega)$$

does not
work for $f(k)$

- Once we know the DOS, we can reduce the 3-dim \mathbf{k} -integral to a 1-dim ω integral.



- For example, assume $N=16$, then there are $2 \times 2 = 4$ states within the interval $d\omega$



- Flatter $\omega(k)$ curve, higher DOS.

DOS: 1-dim

$$D(\omega)d\omega = 2 \frac{dk}{\Delta k} = 2 \frac{dk/d\omega}{\Delta k} d\omega$$

$$\therefore D(\omega) = \begin{cases} \frac{L}{\pi} \frac{1}{d\omega/dk} & \text{for } \omega \leq \omega_M \\ 0 & \text{otherwise} \end{cases}$$

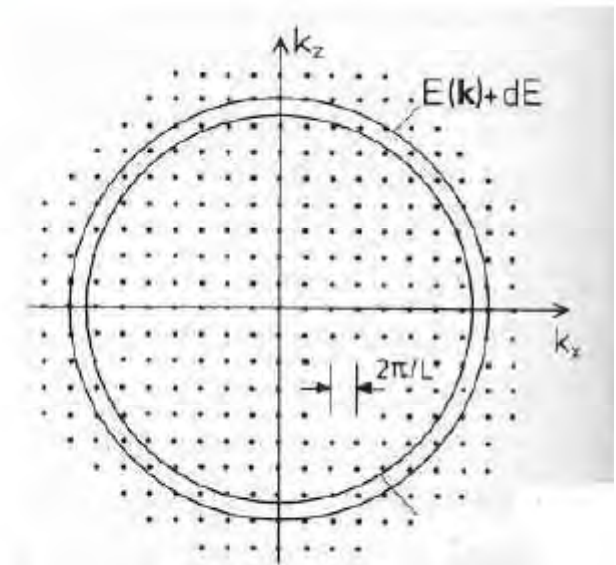
Ex: Calculate $D(\omega)$ for the 1-dim string with $\omega(k) = \omega_M |\sin(ka/2)|$

DOS: 3-dim (assume $\omega(\mathbf{k}) = \omega(k)$ is isotropic)

$$D(\omega)d\omega = \int_{Shell} \frac{d^3k}{\Delta^3k} = \frac{4\pi}{\Delta^3k} k^2 dk = \frac{L^3}{2\pi^2} \frac{k^2}{d\omega/dk} d\omega$$

for example, if $\omega = vk$, then $D(\omega) = V \omega^2 / 2\pi^2 v^3$

There is no use to memorize the result,
just remember the way to derive it.



Debye Model for density of states

In the Debye approximation, $\omega = vk$, v is sound velocity.

$$D(\omega) = dN / d\omega = (Vk^2 / 2\pi^2)(dk / d\omega) = \frac{V\omega^2}{2\pi^2v^3}.$$

If there are N primitive cells, the total # of acoustic modes is N . The cutoff frequency ω_D is $\omega_D^3 = 6\pi^2v^3N/V$.

The cutoff wavevector in k space: $k_D = \omega_D / v = (6\pi^2N/V)^{1/3}$

The thermal energy is

$$U = \int d\omega D(\omega) \langle n(\omega) \rangle \hbar\omega = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2v^3} \left(\frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} \right)$$

If the phonon velocity is independent of the polarization

$$U = \int_0^{\omega_D} d\omega \frac{3V\omega^2}{2\pi^2 v^3} \left(\frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} \right) = \frac{3Vk_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} dx \left(\frac{x^3}{e^x - 1} \right),$$

where $x \equiv \hbar\omega/\tau \equiv \theta/T$

the Debye temperature θ is $\theta = \frac{\hbar v}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3}$

the total phonon energy $U = 9Nk_B T \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \left(\frac{x^3}{e^x - 1} \right),$

the heat capacity $C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \left(\frac{\omega^4 e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2} \right)$

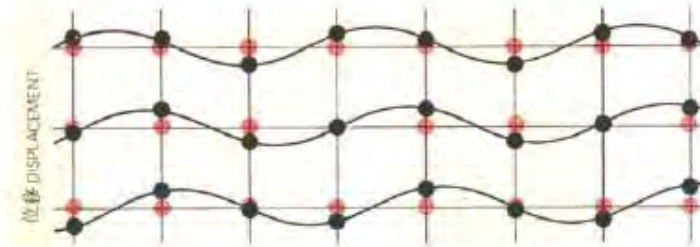
$$= 9Nk_B T \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \left(\frac{x^4 e^x}{(e^x - 1)^2} \right).$$

Debye model (1912)

Atoms vibrate collectively in a wave-like fashion.

$$U(T) = \sum_{k,s} \langle n_{k,s} \rangle \hbar \omega_{k,s} \quad (\hbar \omega_{k,s} / 2 \text{ neglected})$$

$$= \sum_{s=1}^3 \int d\omega D_s(\omega) \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1}$$



- Debye assumed a simple dispersion relation:
 $\omega = v_s k$. Therefore, $D_s(\omega) = V \omega^2 / 2\pi^2 v_s^3$ (quadratic)
- Also, the 1st BZ is approximated by a sphere with the same total number of states.

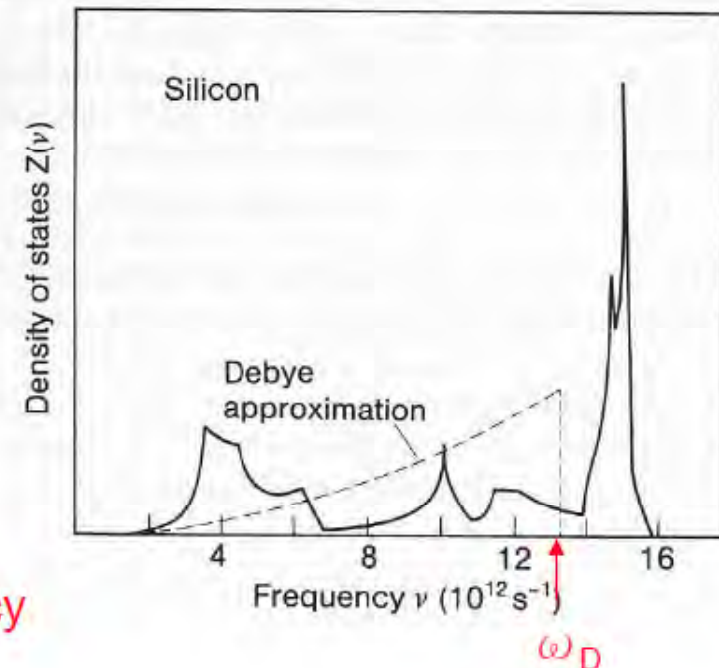
Cut-off frequency:

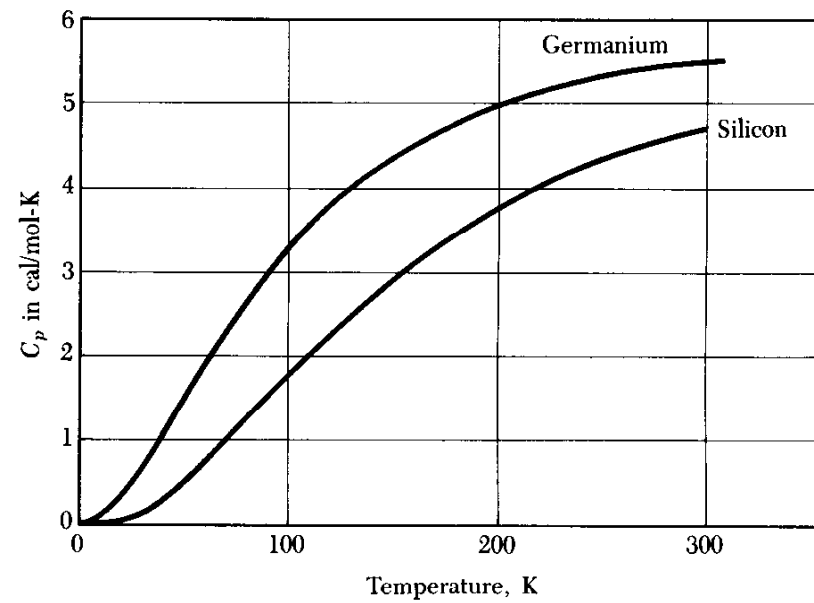
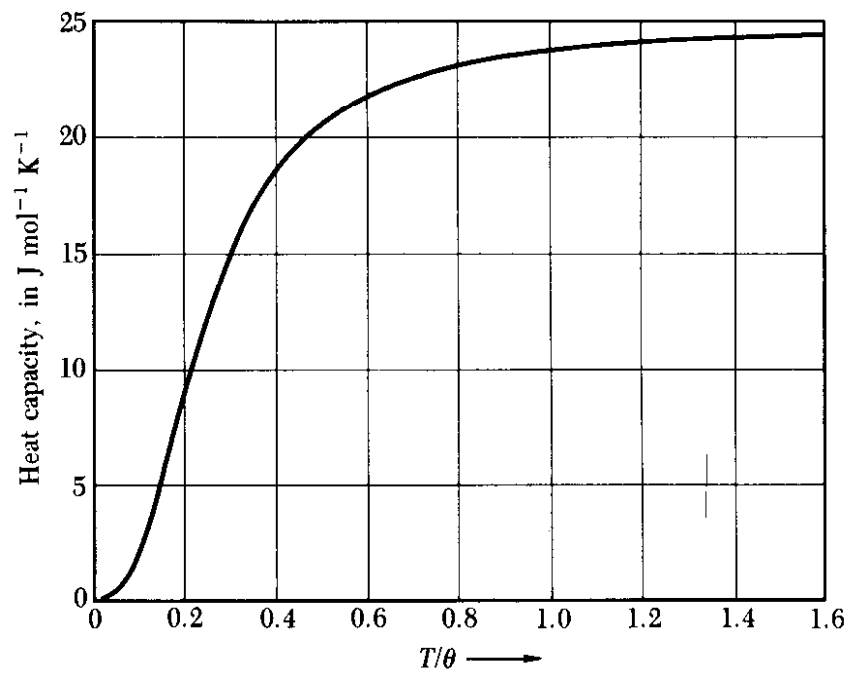
$$\sum_{s=1}^3 \int d\omega D_s(\omega) = 3N$$

$$\rightarrow \sum_{s=1}^3 \frac{V \omega_D^3}{6\pi^2 v_s^3} = 3N$$

$$\frac{3}{v^3} = \sum_{s=1}^3 \frac{1}{v_s^3}$$

$$\rightarrow \omega_D = v(6\pi^2 n)^{1/3}, \quad n = N/V \quad \text{Debye frequency}$$



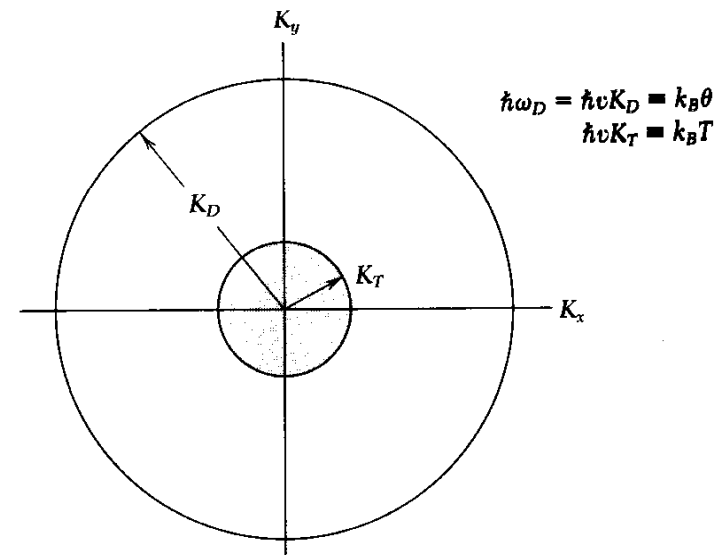
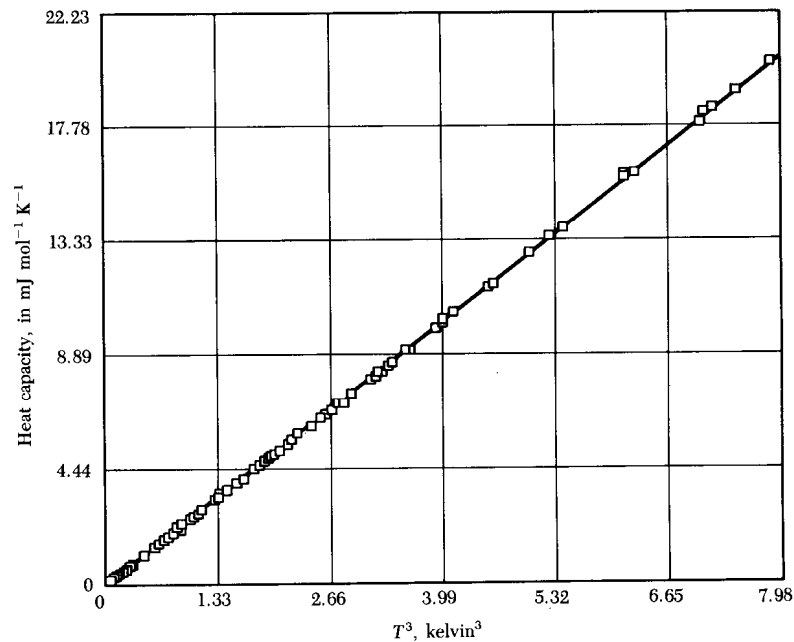


Debye T^3 law

At low temperatures,

$$\int_0^{\infty} dx \left(\frac{x}{e^x - 1} \right) = \sum_{n=1}^{\infty} \int_0^{\infty} x^3 e^{-nx} dx = 6 \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{15},$$

the heat capacity $C_V \cong \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta} \right)^3$.

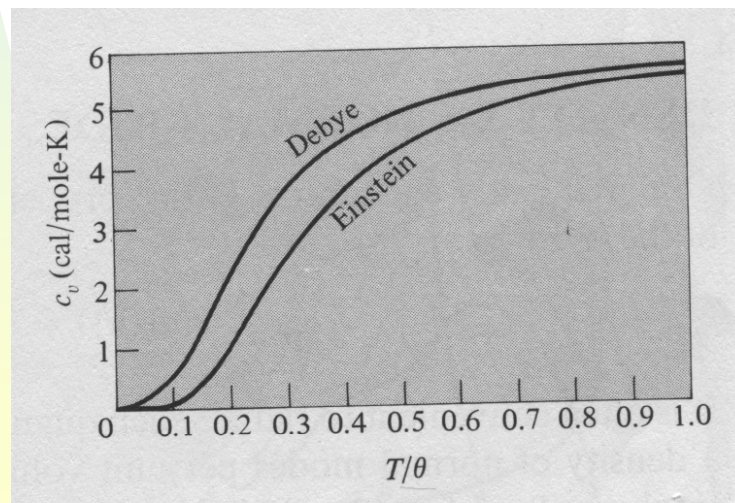


Einstein models of the density of states

In the case of N oscillators of the same frequency ω_0 in 1D, the Einstein density of states is $D(\omega) = N\delta(\omega - \omega_0)$

$$U = N \langle n \rangle \hbar \omega = \left(\frac{N \hbar \omega}{e^{\hbar \omega / \tau} - 1} \right).$$

$$\text{The heat capacity } C_V = N \left(\frac{\partial U}{\partial T} \right)_V = N k_B \left(\frac{\hbar \omega}{\tau} \right)^2 \frac{e^{\hbar \omega / \tau}}{(e^{\hbar \omega / \tau} - 1)^2}$$



Anharmonic crystal interactions

Two lattice waves do not interact;
No thermal expansion;
The elastic constants are independent of pressure and temperature;
The heat capacity becomes constant at high temperatures.

Thermal expansion

The potential energy of the atoms displaced x from their equilibrium,

$$U(x) = cx^2 - gx^3 - fx^4$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x \exp[-\beta U(x)] dx}{\int_{-\infty}^{\infty} \exp[-\beta U(x)] dx} = \frac{3g}{4c^2} k_B T.$$

Thermal conductivity

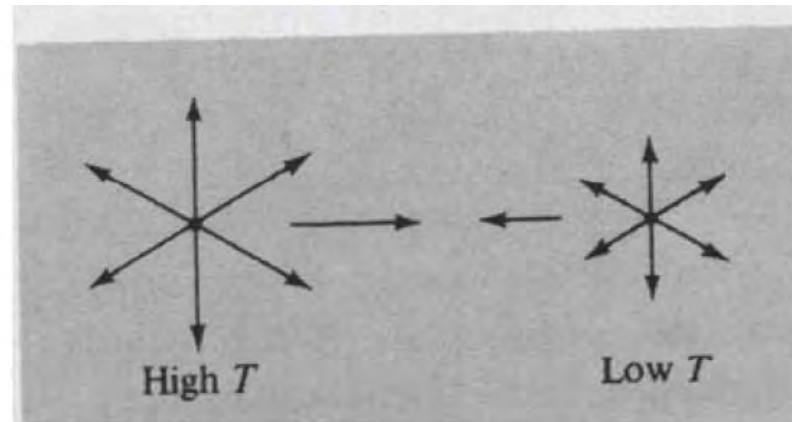
The thermal conductivity coefficient K of a solid is defined as,

$j_U = -K \frac{dT}{dx}$, where j_U is the flux of thermal energy, and

x is distance. From the kinetic theory of gases we find

$K = \frac{1}{3} C v l = \frac{1}{3} C v^2 \tau$, where C is the heat capacity per volume,

v is the average particle velocity, and l is the mean free path of a particle between collisions, τ^{-1} is the phonon collision rate.



C is the heat capacity, then in moving from $T + \Delta T$ to T a particle will give up energy $C\Delta T$, the temperature gradient is given by

$$\Delta T = \frac{dT}{dx} l_x = \frac{dT}{dx} v_x \tau, \text{ where } \tau \text{ is the average time between collision.}$$

In 3D case, we have $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} v^2$

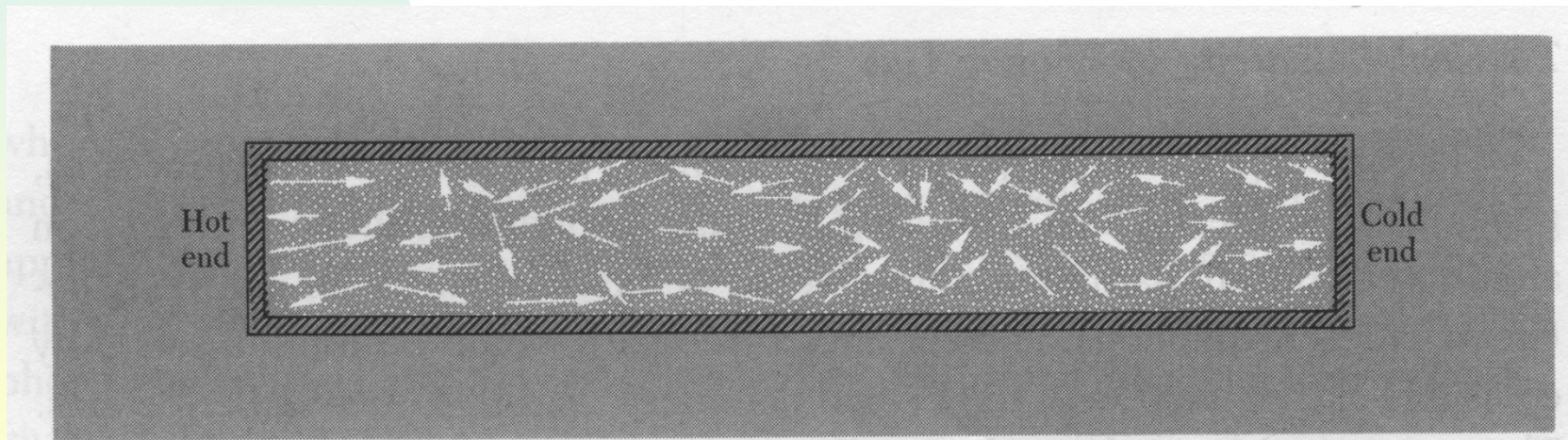
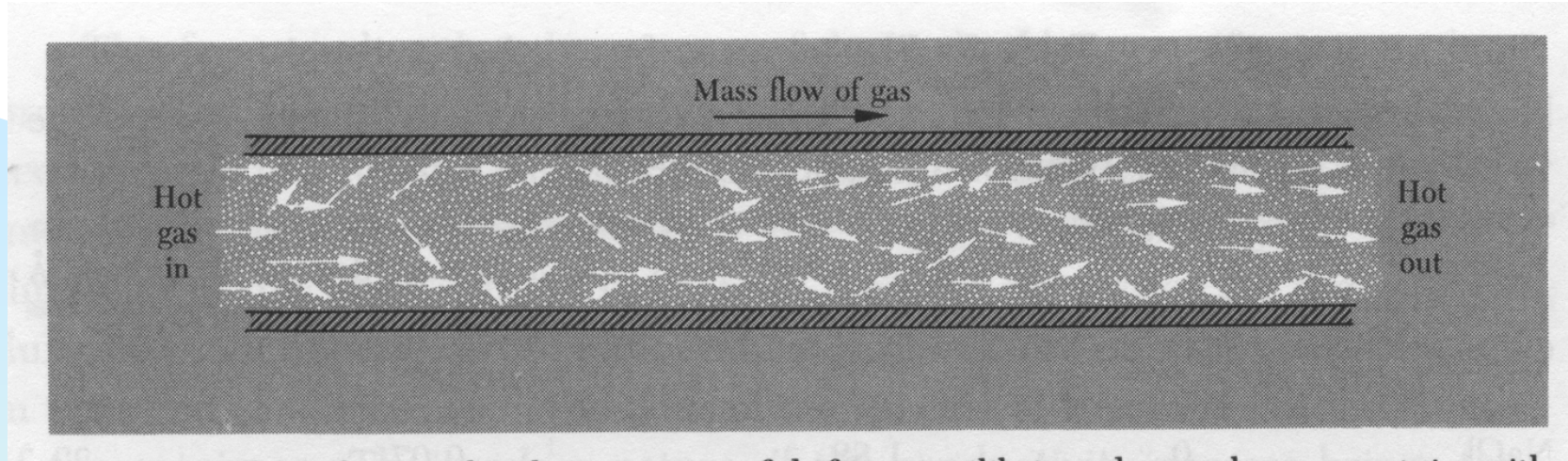
$$j_U = -n \langle v_x^2 \rangle c \tau \frac{dT}{dx} = -\frac{1}{3} n \langle v^2 \rangle c \tau \frac{dT}{dx} = -K \frac{dT}{dx}$$

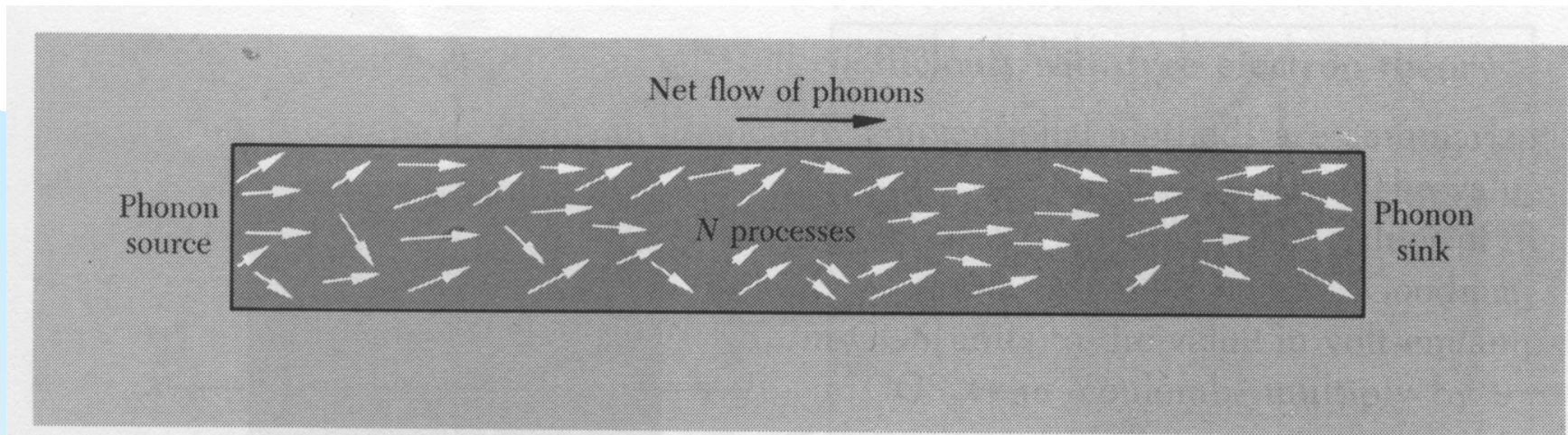
Case 1 ($T \gg \Theta_D$) At high temperatures the total # of photons present in the crystal is proportional to T because the thermal equilibrium phonon occupation # reduced to:

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1} \approx \frac{k_B T}{\hbar\omega}.$$

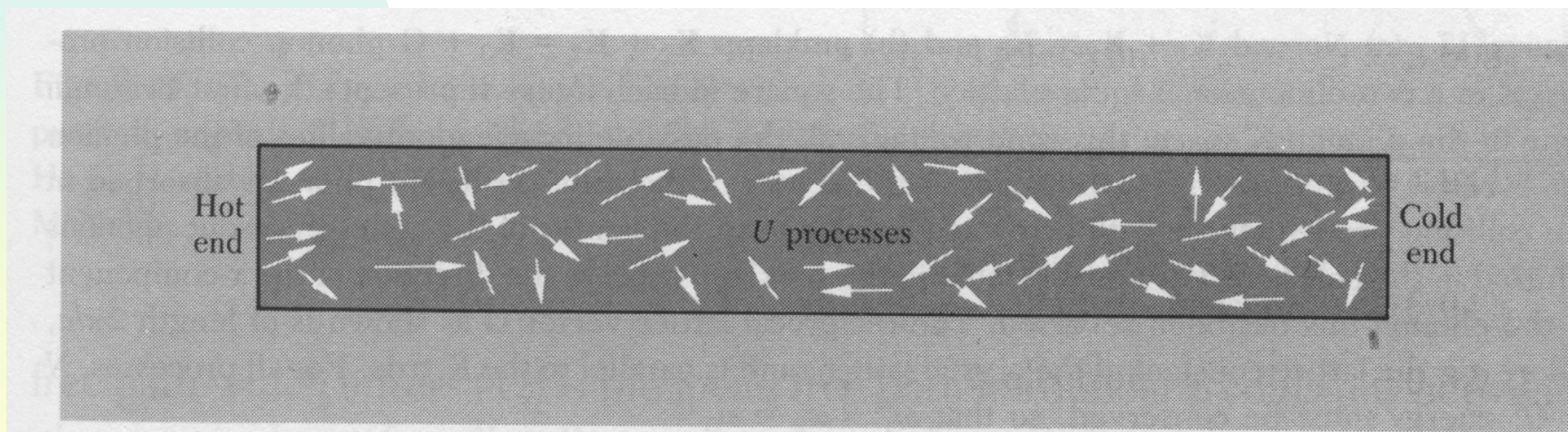
Since a given phonon that contributes to the thermal current is more likely to be scattered the more other phonons there are present to do the scattering, we should expect the relaxation time to decline with increasing temperature. Since at high temperatures C_V is temperature-independent, we should expect the thermal conductivity to decline with increasing temperature, $K \sim 1/T^x$, where x is between 1 and 2.

Case 2 ($T \ll \Theta_D$) At T , only phonons with energy comparable or less than $k_B T$ will have appreciable #. The only collisions occurring with appreciable probability are those that conserve the total crystal momentum exactly. Normal and Umklapp process: A normal process is a phonon collision in which the total initial and final crystal momenta are strictly equal; in an umklapp process they differ by a nonzero reciprocal lattice vector.

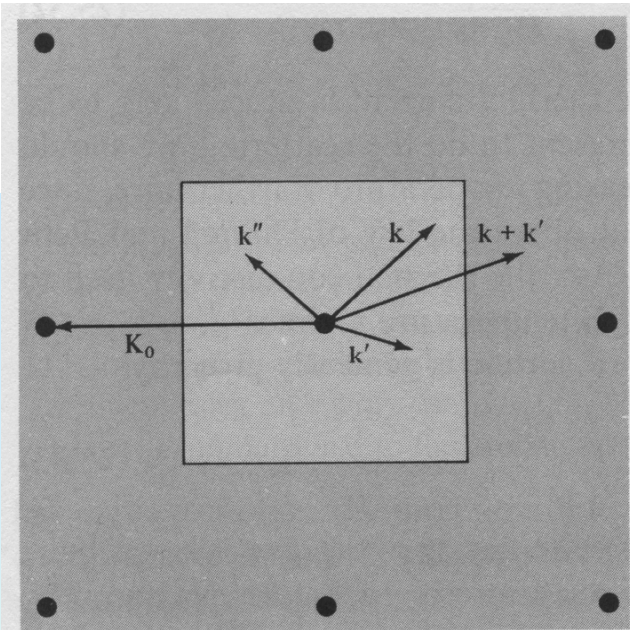




$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3$$



$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{K}$$



(a)

