Heat Capacity

DSC

Heat is not a state function, so we define a state function related to heat, $dS = dQ/T$

$dH = VdP + TdS$ $\quad dS = dQ/T$

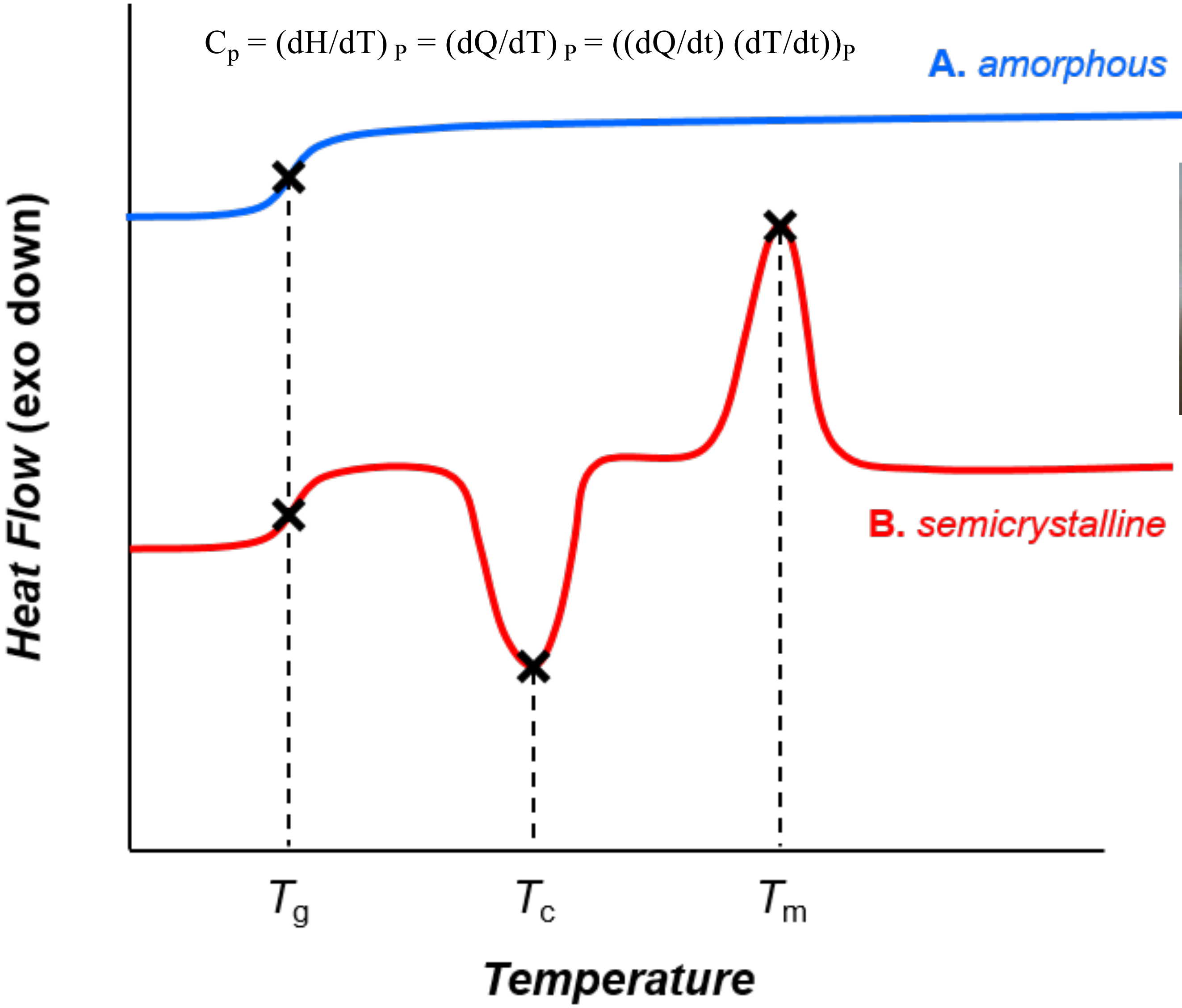
At constant P $(dH = TdS = dQ)_P$

-S U(E) V
H A(F)
-p G T

We have $C_p = (dQ/dT)_P = (dH/dT)_P$

In the DSC we measure the heat flow dQ/dt (Watts) at a constant heating rate dT/dt at constant pressure, $(dQ/dT)_P = C_p$
So, the y-axis is C_p times dT/dt the latter of which is constant

$C_p = (dH/dT)_P = (dQ/dT)_P = ((dQ/dt)\,(dT/dt))_P$



Derive the expression for $C_p – C_V$

From Chapter 1

-S	U	V
H		A
-p	G	T

$C_p - C_v = \alpha^2 VT/\kappa_T$
$\alpha = (1/V)\ (dV/dT)_p$
$\kappa_T = (1/V)\ (dV/dP)_T$

dS = dQ/T

dU = TdS – PdV
dH = TdS + VdP
dQ = TdS

$C_V = (dU/dT)_V$
From the Thermodynamic Square
dU = TdS – pdV and, $C_V = (dQ/dT)_V = T\ (dS/dT)_V - p\ (dV/dT)_V = (dU/dT)_V$
Second term is 0, dV at constant V is 0
$(dS/dT)_V = C_V/T$
Similarly
$C_p = (dH/dT)_p$
From the Thermodynamic Square
dH = TdS + Vdp so $C_p = (dH/dT)_p = T\ (dS/dT)_p - V\ (dp/dT)_p$
Second term is 0, dp at constant p is 0
$(dS/dT)_p = C_p/T$

Write a differential expression for dS as a function of T and V
$dS = (dS/dT)_V dT + (dS/dV)_T dV$ using expression for C_V above and Maxwell for $(dS/dV)_T$
$dS = C_V/T\ dT + (dp/dT)_V dV$ use chain rule: $(dp/dT)_V = -(dV/dT)_p\ (dP/dV)_T = V\alpha\ /\ (V\kappa_T)$
Take the derivative for C_p: $C_p/T = (dS/dT)_p = C_V/T\ (dT/dT)_p + (\alpha/\kappa_T)(dV/dT)_p = C_V/T + (V\alpha^2/\kappa_T)$
$C_p - C_v = \alpha^2 VT/\kappa_T$

Molecular Basis for the Heat Capacity (Gasses)

Internal Energy of a gas

$$U = \sum_{i=1}^{N} \frac{1}{2} m_i \boldsymbol{c}_i^2 + \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \ldots, \boldsymbol{r}_N)$$

For an ideal gas, the potential is 0

$$\frac{1}{2} m < \boldsymbol{c}^2 > = \frac{3k_B T}{2}$$

Monoatomic Gas: Ar
3 translational degrees of freedom each with ½ kT energy

$$U_m = L \frac{3}{2} k_B T = \frac{3}{2} RT$$

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T}\right)_V = \frac{3}{2} R$$

Linear molecule, CO_2, can rotate in two axes, $C_{V,m} = 5/2\ R$
Non-Linear, H_2O, can rotate in three axes, $C_{V,m} = 6/2\ R$
Plus, vibrational degrees of freedom

We calculate C_V since all models assume constant volume
We measure C_p since calorimetric measurements are made at atmospheric pressure

From C_V for an ideal gas, you add R to obtain C_p

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{\alpha^2 TV}{\kappa_T}$$

For an ideal gas PV = RT
α is $(dV/dT)_p/V = R/PV = 1/T$
κ is $-(dV/dP)_T/V = RT/P^2V = 1/P$
$C_p - C_v = (1/T)^2\ (TV)\ P = PV/T = R$

For other materials you need to know the thermal expansion coefficient and compressibility as a function of temperature.

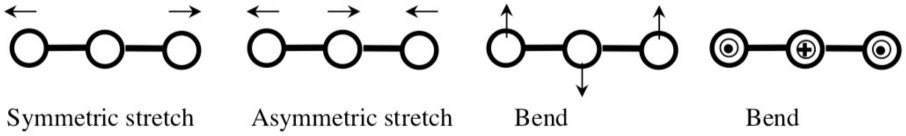
Heat Capacity, multi-atomic gasses and vibrations

$$U_{\mathrm{m}} = L\frac{3}{2}k_{\mathrm{B}}T = \frac{3}{2}RT \qquad C_{V,\mathrm{m}} = \left(\frac{\partial U_{\mathrm{m}}}{\partial T}\right)_V = \frac{3}{2}R$$

Linear molecule, CO_2, can rotate in two axes, $C_{V,m} = 5/2\ R$
Non-Linear, H_2O, can rotate in three axes, $C_{V,m} = 6/2\ R$
Plus, vibrational degrees of freedom

Potential and Kinetic degrees of vibrational freedom add 2(R/2) for each type of vibration

Generally, 3n-6 vibrational modes
(For linear 3n-5 so for CO_2 4 modes symmetric stretch, asymmetric stretch, two dimensions of bend)



For an ideal gas

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{\alpha^2 TV}{\kappa_T} = R$$

PV = RT

dV/dT = R/P

dV/dP = -RT/P^2

α = 1/V (dV/dT) = R/PV = 1/T

κ = -1/V (dV/dP) = RT/VP^2 = 1/P

α^2TV/κ_T = VP/T = R

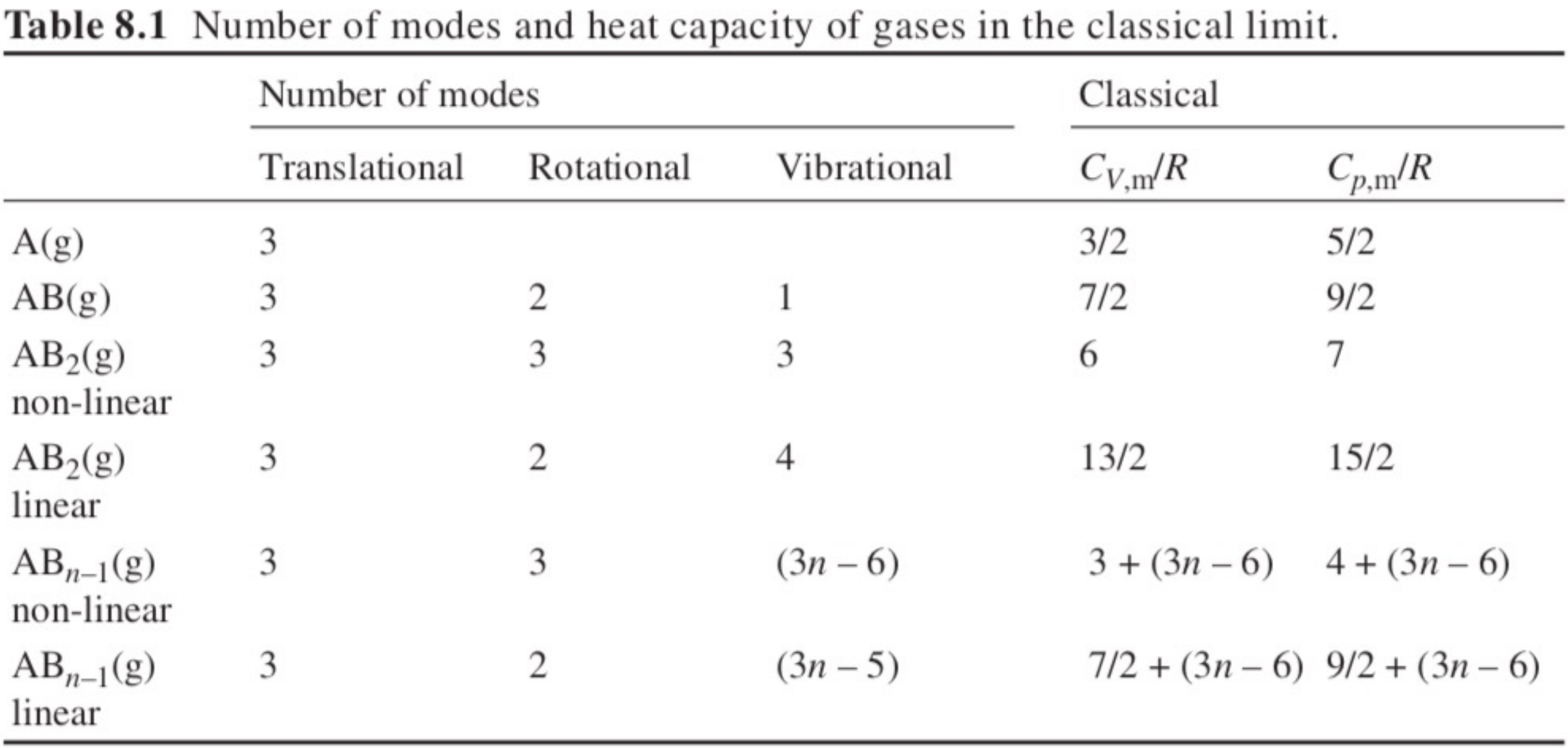


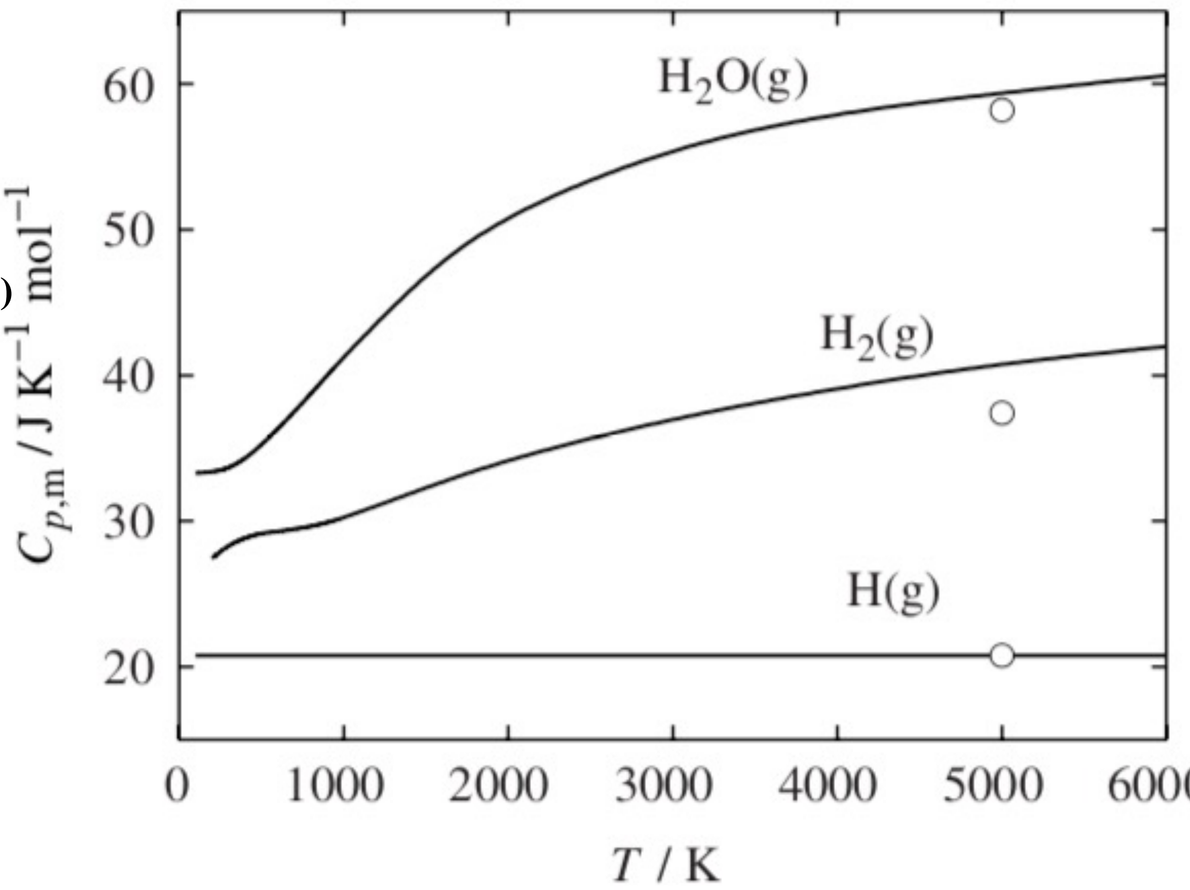
Table 8.1 Number of modes and heat capacity of gases in the classical limit.

	Number of modes			Classical	
	Translational	Rotational	Vibrational	$C_{V,\mathrm{m}}/R$	$C_{p,\mathrm{m}}/R$
A(g)	3			3/2	5/2
AB(g)	3	2	1	7/2	9/2
AB_2(g) non-linear	3	3	3	6	7
AB_2(g) linear	3	2	4	13/2	15/2
AB_{n-1}(g) non-linear	3	3	$(3n-6)$	$3+(3n-6)$	$4+(3n-6)$
AB_{n-1}(g) linear	3	2	$(3n-5)$	$7/2+(3n-6)$	$9/2+(3n-6)$

Ideal Gasses

	$C_{p,m}/R$	**J/(mol K)**
A(g)	5/2	**20.8**
AB(g)	9/2	**37.5**
AB_2(g) non-linea	7	**58.3**

3R = 25 J/(mol K)



Monoatomic H(g) with only translational degrees of freedom is already fully excited at low temperatures. The vibrational frequencies (*n*) of H2(g) and H2O(g) are much higher, in the range of 100 THz, and the associated energy levels are significantly excited only at temperatures above 1000 K. At room temperature only a few molecules will have enough energy to excite the vibrational modes, and the heat capacity is much lower than the classical value. The rotational frequencies are of the order 100 times smaller, so they are fully excited above ~10 K.

Figure 8.2 Molar heat capacity at constant pressure of H(g), H_2(g) and H_2O(g). The open symbols at 5000 K represent the limiting classical heat capacity.

Ideal Gasses

	$C_{V,\mathrm{m}}/R$
A(g)	3/2
AB(g)	7/2
AB_2(g) non-linear	6

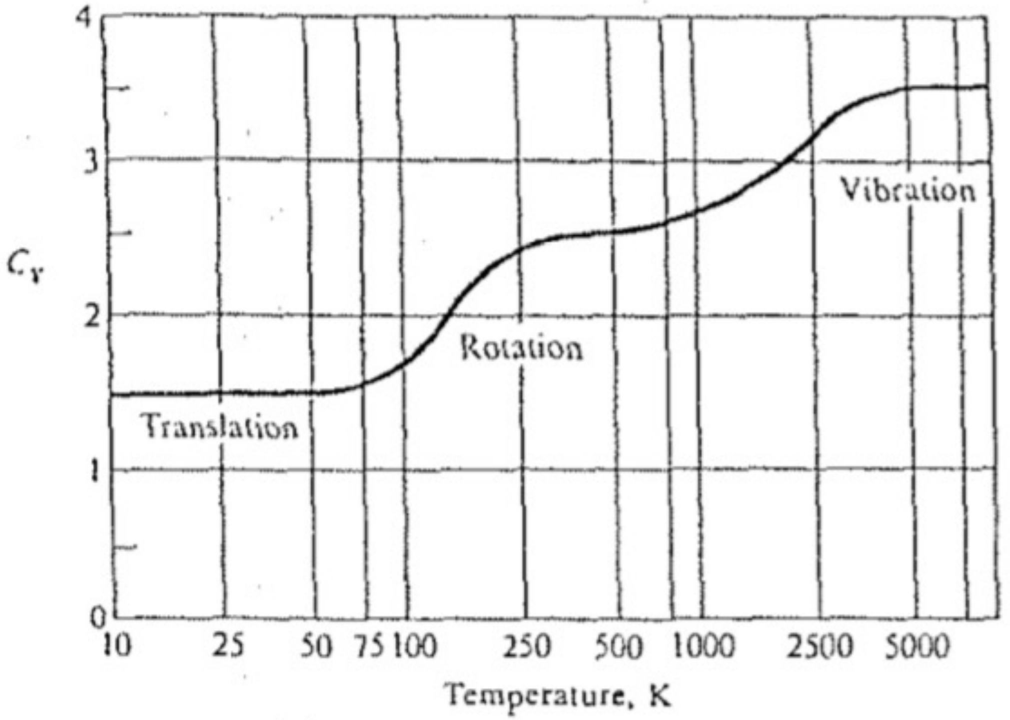


Figure 3.9 Heat capacity at constant volume of one molecule of H_2 in the gas phase. The vertical scale is in fundamental units; to obtain a value in conventional units, multiply by k_B. The contribution from the three translational degrees of freedom is $\frac{3}{2}$; the contribution at high temperatures from the two rotational degrees of freedom is 1; and the contribution from the potential and kinetic energy of the vibrational motion in the high temperature limit is 1. The classical limits are attained when $\tau \gg$ relevant energy level separations.

Monoatomic H(g) with only translational degrees of freedom is already fully excited at low temperatures. The vibrational frequencies (*n*) of H2(g) and H2O(g) are much higher, in the range of 100 THz, and the associated energy levels are significantly excited only at temperatures above 1000 K. At room temperature only a few molecules will have enough energy to excite the vibrational modes, and the heat capacity is much lower than the classical value. The rotational frequencies are of the order 100 times smaller, so they are fully excited above ~10 K.

Heat Capacity of Solids

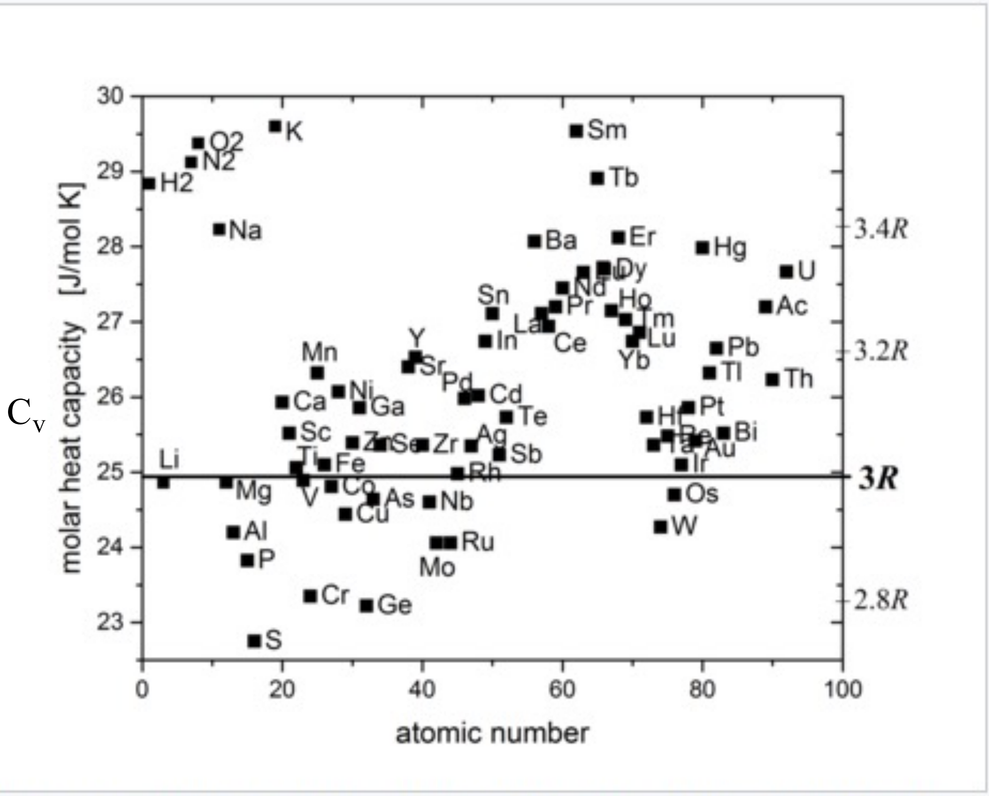
Dulong and Petit Law (Observation, heat capacity of *solids*)

$$C_V/n = 3R \quad (25\ \mathrm{J/(mol\ K)})$$

In the classical statistical theory of Ludwig Boltzmann, the heat capacity of solids approaches a maximum of $3R$ per mole of atoms because:

- full vibrational-mode degrees of freedom amount to 3 degrees of freedom per atom (x, y, z),
- each corresponding to a kinetic energy term and a potential energy term.
- By the equipartition theorem, the average of each term is $\frac{1}{2}k_BT$ per atom, or $\frac{1}{2}RT$ per mole.
- Multiplied by 3 degrees of freedom (x, y, z) and the two terms per degree of freedom (kinetic and potential), this amounts to $3R$ per mole heat capacity.

Dulong and Petit Law (Observation for Solids)

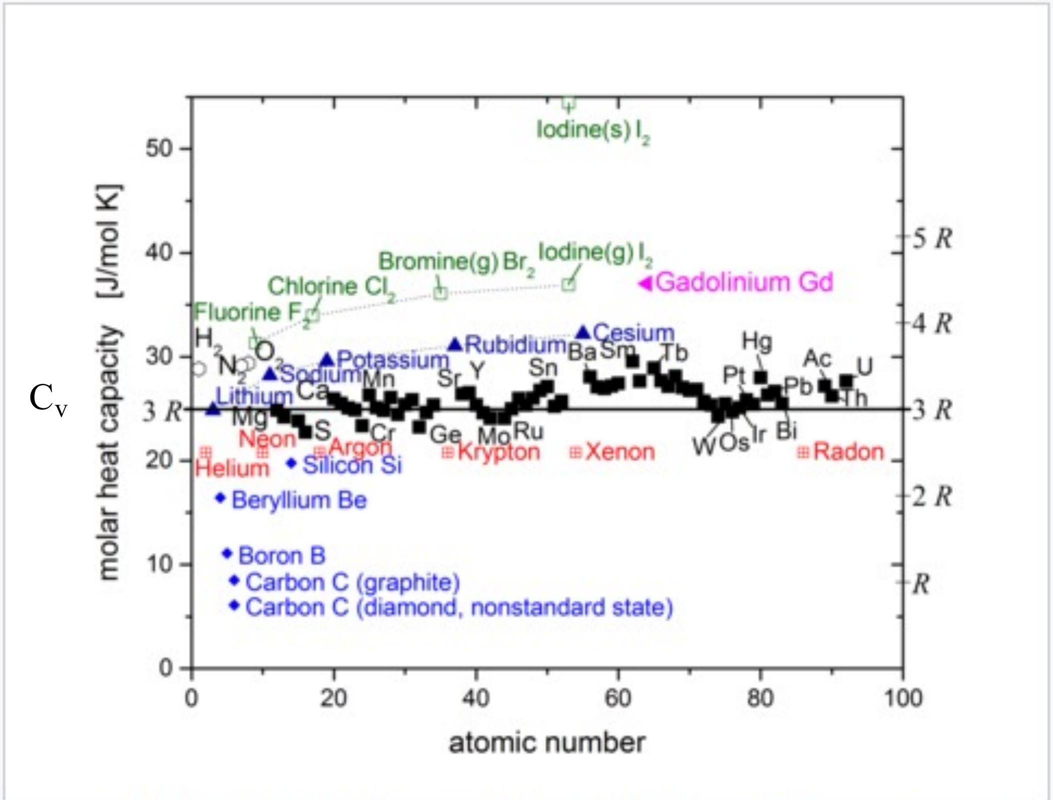


Molar heat capacity of most elements at 25 °C is in the range between 2.8 *R* and 3.4 *R*: Plot as a function of atomic number with a y range from 22.5 to 30 J/mol K.

Dulong and Petit Law (Observation for solids)

Fails for strongly bound light atoms

C_v



The molar heat capacity plotted of most elements at 25°C plotted as a function of atomic number. The value of bromine is for the gaseous state. For iodine, a value for the gas and one for the solid is shown.

Atoms in a crystal (Dulong and Petit Law)

Works at high temperature

Boltzman 1877 Explains
Each atom in a solid has 6 springs
Each spring with ½ kT energy
So, 6/2R = 3R = C_v

Three Harmonic oscillators, x, y, z
Spring (Potential Energy)
$dU/dx = F = -Kx$ where x is 0 at the rest position
$U = -1/2\ Kx^2$
Kinetic Energy
$U = ½\ mc^2$
c is the velocity of the atom so dx/dt

Force Balance
$-K\ x = m\ d^2x/dt^2$
Plug in a sine wave solution,
$x = A \sin(\omega t)$
Yields $\omega = \sqrt{(K/m)}$
So, there is a fixed frequency for a fixed spring constant and mass, since $E = h\omega/2\pi$, there is a fixed or ***quantized*** energy

$$U = \frac{1}{2}mc^2 + \frac{1}{2}Kx^2 = \frac{1}{2}mA^2\omega^2\cos^2\omega t + \frac{1}{2}KA^2\sin^2\omega t$$

$$x = A\sin\omega t \qquad \omega = 2\pi\nu = \sqrt{\frac{K}{m}}$$

Potential and Kinetic Energies balance in an oscillatory spring so U = 0

Three degree of freedom oscillators per atom so $U_m = 3RT$

$$C_{V,m} = 3R = 24.94\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$dU = -pdV + TdS$
$(dU/dT)_V = T(dS/dT)_V = C_V$

-SUV
H A
-pGT

Einstein Model

Atoms in a crystal (Dulong and Petit Law)

Works at high temperature

Force Balance
$-K x = m\, d^2x/dt^2$
Plug in a sine wave solution,
$x = A \sin(\omega t)$
Yields $\omega = \sqrt{(K/m)}$
So, there is a **fixed frequency** for a fixed spring constant and mass, since $E = h\omega/2\pi$, there is a fixed or ***quantized*** energy

For something like a guitar string, we have quantized energy and frequency, it has one tone, but also overtones so, $\mathbf{E = nE_1}$ where n is the mode of vibration or quantized state, and **n has integer values starting with 1**. E_1 is the energy of the primary mode, $E = nh\nu$ or $nh\omega/2\pi$ for the vibration.

For quantum mechanics (very small particles like atoms) there is a problem with $E = nh\nu$ or $nh\omega/2\pi$

1) At absolute 0 there is a ”zero-point energy” that keeps everything from collapsing for instance, we don’t observe collapse as we approach absolute 0. Schrodinger equation finds this zero-point energy is ½ hν
2) If energy were 0 at absolute 0 then we would know both the position of an atom and its momentum = 0 This would disagree with the Heisenberg uncertainty principle. So, you need a “zero-point energy”
3) A “zero-point energy” can be measured experimentally

$\mathbf{E = h\nu\,(1/2 + n)}$ and n has integer values starting at 0 for the ground state energy.

Einstein Derivation of Dulong Petit

-S	U(E)	V
H		A(F)
-p	G	T

U = A + TS
dA = -SdT – pdV
$(dA/dT)_V = -S$

$U = A - T\,(dA/dT)_V$

$A = NE_0 + NkT \sum_i \; log\left(\frac{h\omega_i}{kT}\right)$
$(dA/dT)_V = Nk \sum_i \; \left(log\left(\frac{h\omega_i}{kT}\right)\right) - NkT\left(\frac{-1}{T}\right)$

dlnx = dx/x

$$\log \bar{\omega} = \frac{1}{g}\sum_{\alpha} \log \omega_{\alpha},$$

$U = NE_0 + NkT \sum_i \; log\left(\frac{h\omega_i}{kT}\right)$
$\quad - NkT \sum_i \; log\left(\frac{h\omega_i}{kT}\right) - \sum_i \; NkT$
$\quad = NE_0 + gNkT$

g is number of DOF or 3

$C_V = (dU/dT)_V = gNk = 3Nk$

Einstein Model

Consider **the crystal is made up of free atoms confined into boxes as harmonic oscillators in 3D**, x, y, z. All the atoms have the **same Einstein frequency, ν_E**. There are then, **3N** "independent" harmonic oscillators, where N is the number of moles of atoms in the crystal. First consider one harmonic oscillator using k then multiply by 3N to get 3R.

The **energy of one harmonic oscillator** for quantum state (mode) "n" is $\boldsymbol{\varepsilon_n = h\nu_E (1/2 + n)}$ where n is 0, 1, 2, 3,…,∞
The harmonic oscillators are at equilibrium at temperature T so **the partition function** (Zustandssumme, sum of states),

$$Z = \sum_{n=0}^{\infty} exp(-\beta\varepsilon_n) = \sum_{n=0}^{\infty} exp\left(-\beta h\nu_E\left(n+\tfrac{1}{2}\right)\right) = e^{-x/2}\sum_{n=0}^{\infty} e^{-xn} \qquad where\ x = \beta h\nu_E \text{ and } \beta = 1/kT$$

Sum of geometric progress series $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$

$$\boxed{Z = \frac{e^{-x/2}}{1-e^{-x}}} \quad \boldsymbol{x = \beta h\nu_E}$$

Note that this explicitly includes the ground state energy, if you start with just an energy you get Z = 1/(1-e^{-x})

Equipartition theorem: Energy is partitioned according to the probability of states

The average energy = <U> =$\sum_{n=0}^{\infty} \frac{\varepsilon_n exp(-nx)}{Z} = -\frac{1}{Z}\frac{dZ}{d\beta} = -\frac{dlnZ}{d\beta} = h\nu_E \frac{e^{-\beta h\nu_e}}{1-e^{-\beta h\nu_e}} = h\nu_E \frac{e^{-h\nu_e/kT}}{1-e^{-h\nu_e/kT}} = \boxed{\frac{h\nu_E}{e^{h\nu_e/kT}-1}}$

because $Z = \sum_{n=0}^{\infty} exp(-\beta\varepsilon_n)$ $\quad \boxed{Z = \frac{e^{-x/2}}{1-e^{-x}}}$

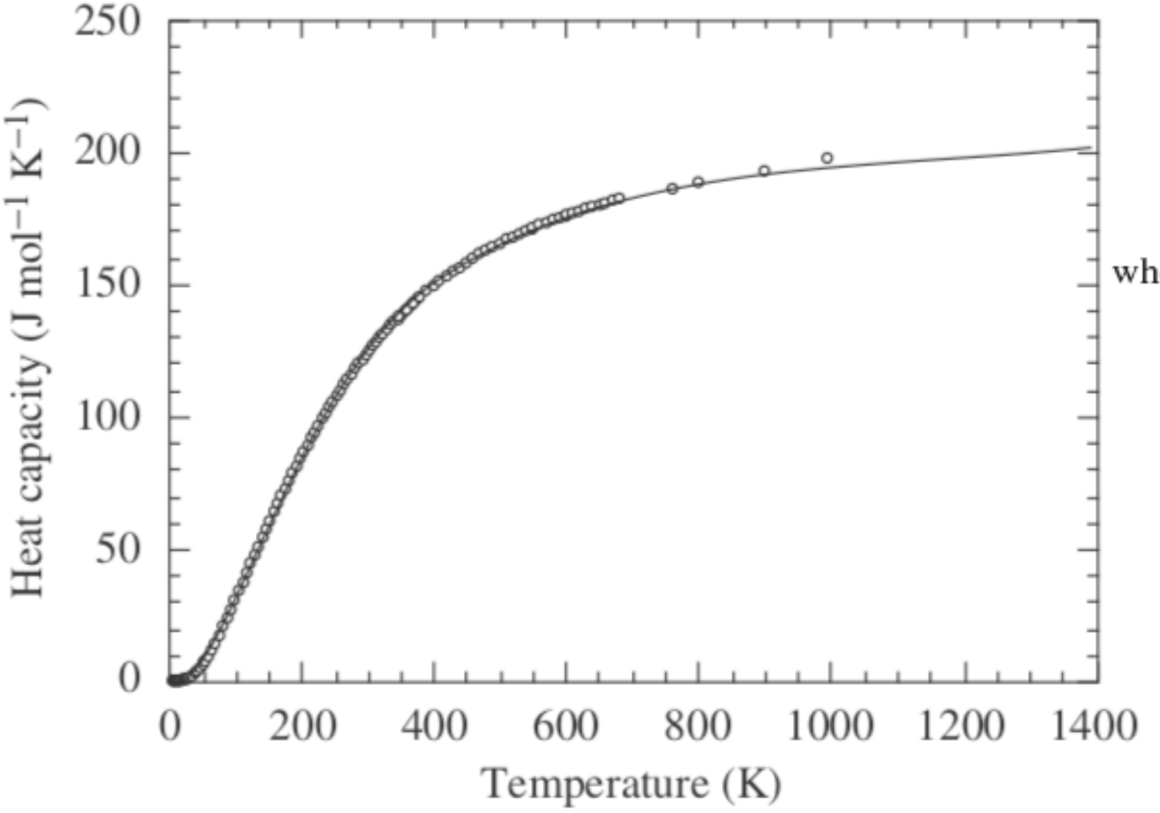
$$C_V = \left(\frac{dU}{dT}\right)_V = k\left(\frac{h\nu_e}{kT}\right)^2 \frac{e^{\frac{h\nu_e}{kT}}}{\left(e^{\frac{h\nu_e}{kT}}-1\right)^2} = k\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}}-1\right)^2}$$

For 3N, $C_V\ per\ mole = \boxed{3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}}-1\right)^2} \quad \theta_E = \frac{h\upsilon_E}{k}}$

Einstein Model

Phonons From Dove

Almost perfect fit, very high value for C_V
(see homework paper Caplin Grüner Dunlap)



$$C_{V,\mathrm{m}} = \left(\frac{\mathrm{d}\overline{U}}{\mathrm{d}T}\right)_V = 3R\left(\frac{\Theta_\mathrm{E}}{T}\right)^2 \frac{\exp(\Theta_\mathrm{E}/T)}{[\exp(\Theta_\mathrm{E}/T)-1]^2}$$

where Θ_E, the **Einstein temperature**, is defined by

$$\Theta_\mathrm{E} = \frac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}}$$

Fig. 9.2 Comparison of calculated (line) and experimental (points) heat capacity of the mineral andalusite, Al_2SiO_5.

Einstein Model

Works at low and high temperature (3R)

Error in dependence near 0K

$$C_{V,\mathrm{m}} = 3R = 24.94\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$C_{V,\mathrm{m}} = \left(\frac{\mathrm{d}\overline{U}}{\mathrm{d}T}\right)_V = 3R\left(\frac{\Theta_\mathrm{E}}{T}\right)^2 \frac{\exp(\Theta_\mathrm{E}/T)}{[\exp(\Theta_\mathrm{E}/T)-1]^2}$$

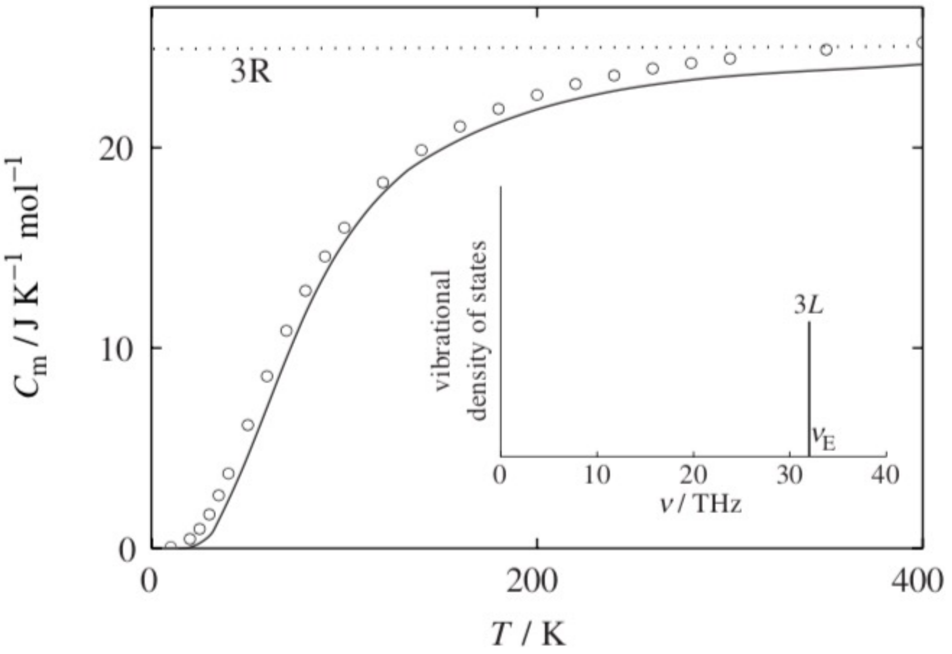


Figure 8.3 Experimental heat capacity of Cu at constant pressure compared with $C_{V,\mathrm{m}}$ calculated by the Einstein model using $\Theta_\mathrm{E} = 244$ K. The vibrational frequency used in the Einstein model is shown in the insert.

Einstein Model

Works at low and high temperature (3R)

Error in dependence near 0K

$$C_{V,\mathrm{m}} = 3R = 24.94\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$C_{V,\mathrm{m}} = \left(\frac{\mathrm{d}\bar{U}}{\mathrm{d}T}\right)_V = 3R\left(\frac{\Theta_\mathrm{E}}{T}\right)^2 \frac{\exp(\Theta_\mathrm{E}/T)}{[\exp(\Theta_\mathrm{E}/T)-1]^2}$$

Single vibrational mode for all three DOF
Low T behavior $\exp(\Theta_\mathrm{E}/T)$ doesn't work
C_v follows T^3
The deviation is because Einstein ignored that lattice vibrations are coupled to each other, not independent
"*Collective Lattice Vibrations*"

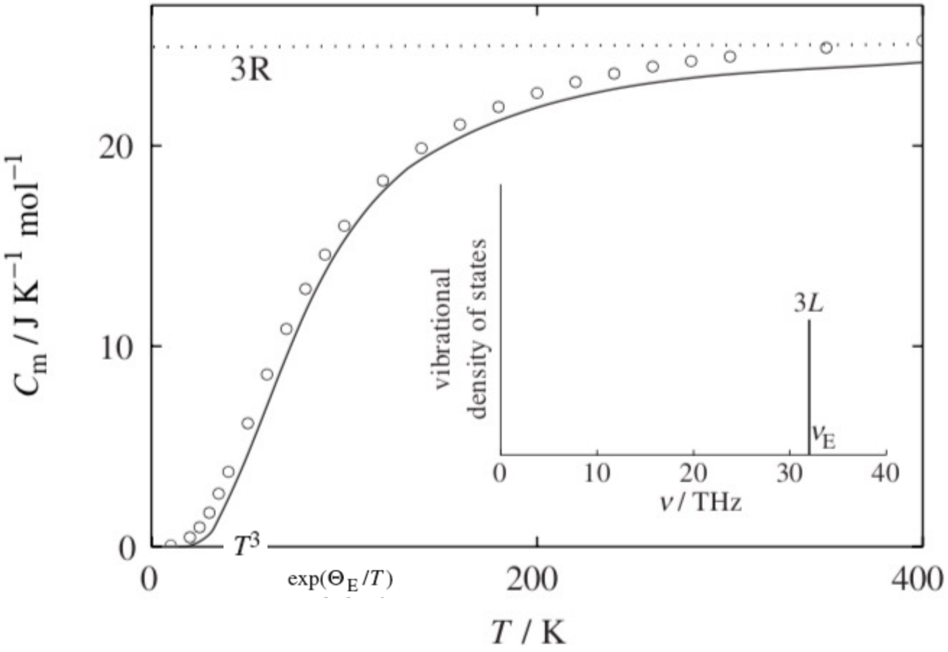


Figure 8.3 Experimental heat capacity of Cu at constant pressure compared with $C_{V,\mathrm{m}}$ calculated by the Einstein model using $\Theta_\mathrm{E} = 244$ K. The vibrational frequency used in the Einstein model is shown in the insert.

Debye Model
Works

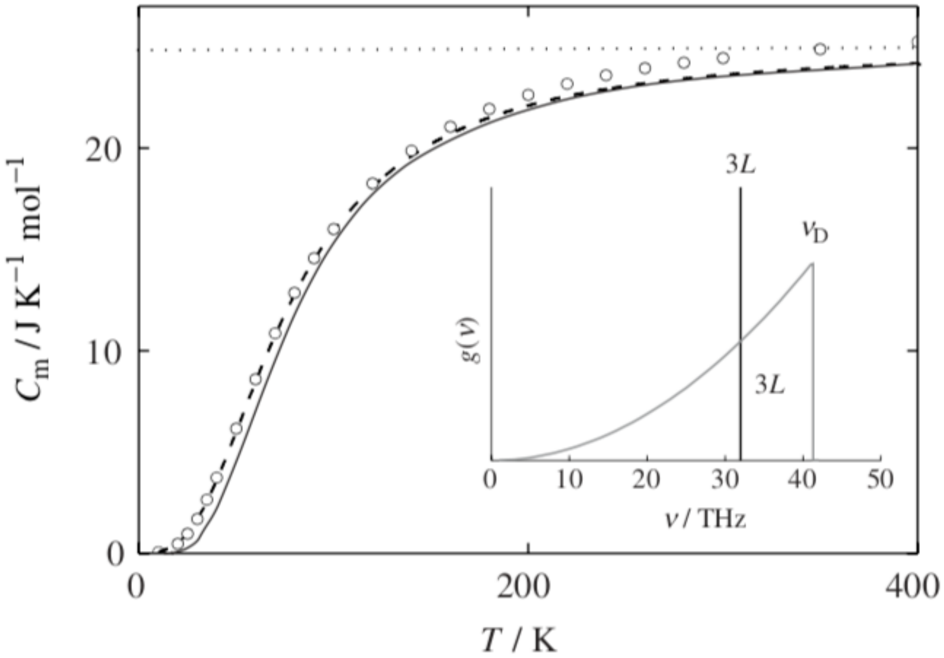


Figure 8.12 Experimental heat capacity of Cu at constant pressure compared with the Debye and Einstein $C_{V,m}$ calculated by using $\Theta_E = 244$ K and $\Theta_D = 314$ K. The vibrational density of states according to the two models is shown in the insert.

Electronic Contribution to Heat Capacity (Briefly)

Hence, only a very small fraction of electrons, those lying within ~kΔT of the Fermi level, are able to absorb the energy and contribute to the heat capacity.

The heat capacity per electron turns out to be

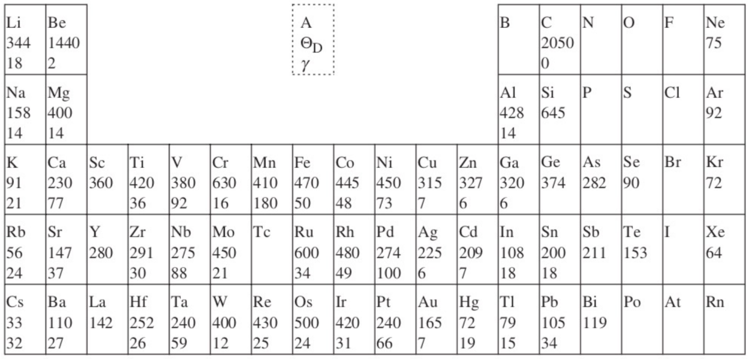
$$C_V = \frac{\pi^2}{2} k \frac{T}{T_F}$$

At room temperature this is a very small contribution to the overall heat capacity (on the order of a few percent). However, at very low temperatures the electronic heat capacity dominates, since it is linear in temperature while the lattice heat capacity is proportional to T^3.

<u>Einstein Temp.</u>
Copper 236K
Aluminum 294K
Lead 72.8 K
Iron 355K

http://vallance.chem.ox.ac.uk/pdfs/EinsteinDebye.pdf

Table 8.2. Debye temperature (Θ_D in K) and electronic heat capacity coefficient (see Section 8.4) (γ in mJ K^{-1} mol^{-1}) of the elements.



Li 344 18	Be 1440 2						A Θ_D γ					B	C 2050 0	N	O	F	Ne 75
Na 158 14	Mg 400 14											Al 428 14	Si 645	P	S	Cl	Ar 92
K 91 21	Ca 230 77	Sc 360	Ti 420 36	V 380 92	Cr 630 16	Mn 410 180	Fe 470 50	Co 445 48	Ni 450 73	Cu 315 7	Zn 327 6	Ga 320 6	Ge 374	As 282	Se 90	Br	Kr 72
Rb 56 24	Sr 147 37	Y 280	Zr 291 30	Nb 275 88	Mo 450 21	Tc	Ru 600 34	Rh 480 49	Pd 274 100	Ag 225 6	Cd 209 7	In 108 18	Sn 200 18	Sb 211	Te 153	I	Xe 64
Cs 33 32	Ba 110 27	La 142	Hf 252 26	Ta 240 59	W 400 12	Re 430 25	Os 500 24	Ir 420 31	Pt 240 66	Au 165 7	Hg 72 19	Tl 79 15	Pb 105 34	Bi 119	Po	At	Rn

For T < 10K

$$C_V = \beta T^3 + \gamma T$$

Grüner Constant

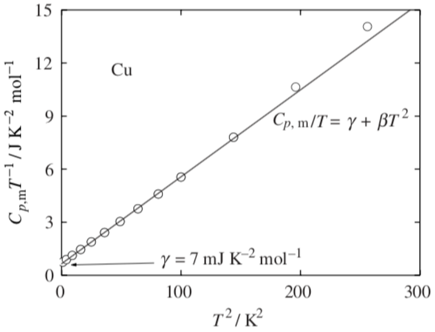
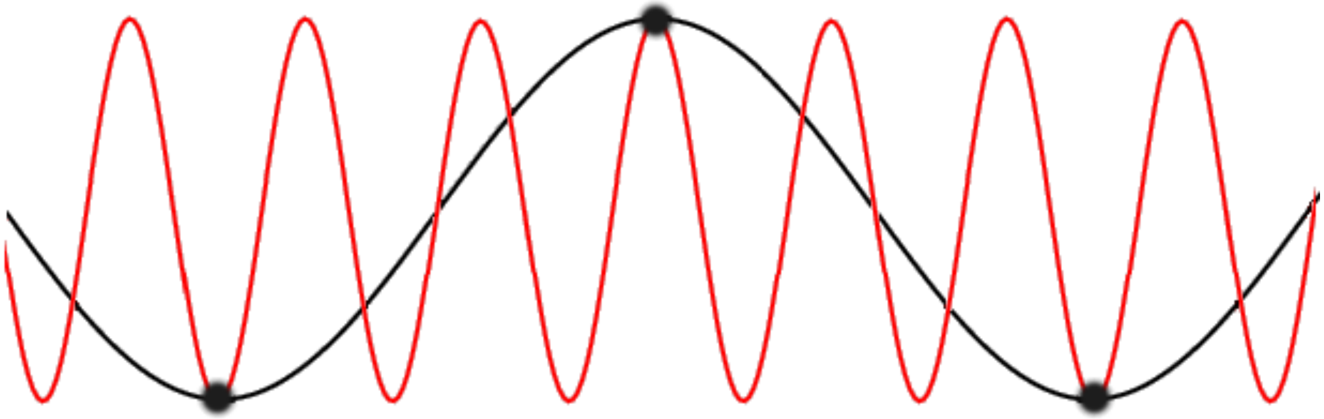


Figure 8.21 Heat capacity of Cu plotted as $C_{p,m} \cdot T^{-1}$ versus T^2.

Crystal of lattice spacing a; Sound waves of wavelength λ or k vector 2π/λ

Phonons

Two size scales, a and λ
If λ ≥ a you are within a Brillouin Zone
Wavevector k = 2π/λ



k-vectors exceeding the first Brillouin zone (red) do not carry any more information than their counterparts (black) in the first Brillouin zone.

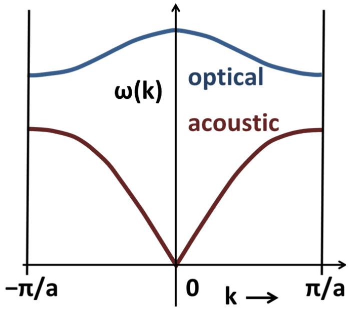
Black are atoms subject to a high frequency transverse (wave) vibration (red)

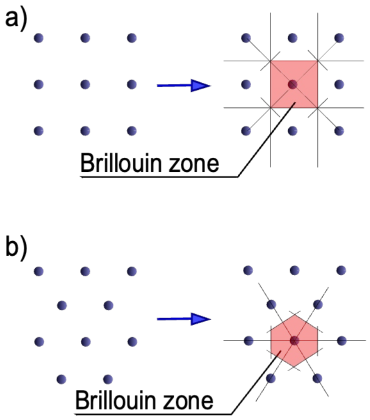
Phonons

Two size scales, a and λ
If λ ≥ a you are within a Brillouin Zone
Wavevector $k = 2\pi/\lambda$

k-vector is like the inverse-space vectors for the lattice (or the Miller indices)
It is seen to repeat in inverse space making an inverse lattice

A phonon with wavenumber k is thus equivalent to an infinite family of phonons with wavenumbers $k \pm 2\pi/a$, $k \pm 4\pi/a$, and so forth.





Brillouin zones, (a) in a square lattice, and (b) in a hexagonal lattice

those whose bands become zero at the center of the Brillouin zone are called acoustic phonons, since they correspond to classical sound in the limit of long wavelengths. The others are optical phonons, since they can be excited by electromagnetic radiation.

Phonons

Two size scales, a and λ
If λ ≥ a you are within a Brillouin Zone
Wavevector k = 2π/λ

The partition function (Z) can be defined in terms of energy (E), $E = -NkT\ lnZ$,
or in terms of the wavevector k=2π/λ = 2πE/hc = -2π$NkT\ lnZ$/hc
E and k are related by the **dispersion relationship** (dispersion of energy in k)
which differs for different systems
(longitudinal, transverse, acoustic, optical phonons)

The density of states is defined by $$D(E) = \frac{1}{V} \cdot \frac{\mathrm{d}Z_m(E)}{\mathrm{d}E}$$ $$\mathcal{Z} = \sum_{N=0}^{\infty} \exp(N(\mu - \varepsilon)/k_B T)$$

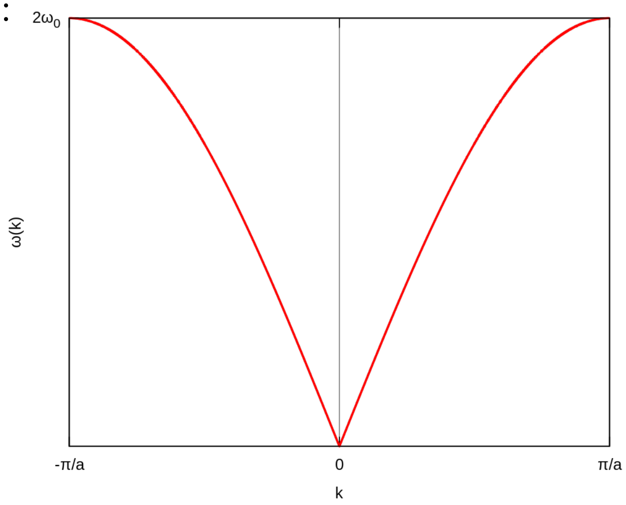
For a Longitudinal Phonon in a string of atoms the dispersion relation is:

Transverse is like an ocean wave or a guitar string, longitudinal is a compressive wave like sound

$$E = 2\hbar\omega_0 \left|\sin\left(\frac{ka}{2}\right)\right|$$

sin x = x – x^3/3! + x^5/5! - …
For small x; sin x = x

where $\omega_0 = \sqrt{k_F/m}$ is the oscillator frequency, m the mass of the atoms, k_F the inter-atomic force constant and a inter-atomic spacing.



This relates modulus to frequency

Phonons

Dispersion Relationship is value of energy or frequency of vibrations at a size-scale or wavelengths or what happens to vibrational energy in the crystal, i.e., modulus.

$$E = 2\hbar\omega_0 \left|\sin\left(\frac{ka}{2}\right)\right|$$

Density of States is how the total energy is distributed to different frequencies of vibration. This is related to what happens at different wavenumbers to different wavelength phonons.

$$D(E) = \frac{1}{V} \cdot \frac{\mathrm{d}Z_m(E)}{\mathrm{d}E}$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} \exp(N(\mu - \varepsilon)/k_\mathrm{B}T)$$

N is an integer related to the vibrational state k

Frequency of a Harmonic Oscillator

Do a Force Balance
$F = mx'' = Kx$ where K is the spring constant, m is the mass
Then $mx'' - Kx = 0$ is a second order differential equation or
$x'' - (K/m)x = 0$
If you know that the derivative of exponential is the exponential
Then you can guess one answer (this helps)
$x = \exp(\pm\sqrt{(K/m)}\; t)$; $x' = \pm\sqrt{(K/m)}\exp(\pm\sqrt{(K/m)}\; t)$; $x'' = K/m \exp(\pm\sqrt{(K/m)}\; t)$
$\sqrt{(K/m)}$ and t have to have inverse units so $\sqrt{(K/m)} = \omega$
This is the native frequency of the oscillator

Phonons

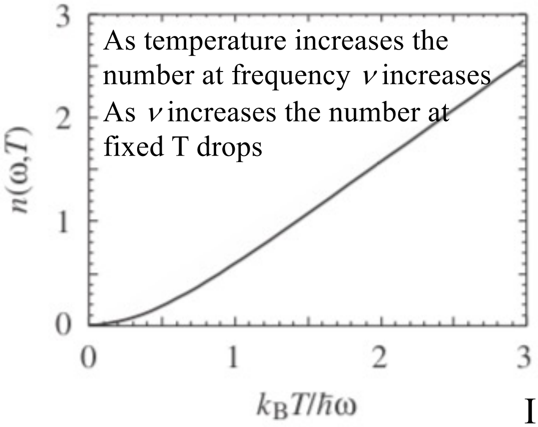
$$\mathcal{Z} = \sum_{N=0}^{\infty} \exp(N(\mu - \varepsilon)/k_{\mathrm{B}}T) = \sum_{N=0}^{\infty} [\exp((\mu - \varepsilon)/k_{\mathrm{B}}T)]^N$$
$$= \frac{1}{1 - \exp((\mu - \varepsilon)/k_{\mathrm{B}}T)}.$$

μ is the ground state energy and ε is the energy of a state

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$$

which is valid for $|x| < 1$

Bose-Einstein statistics gives the probability of finding a phonon in a given state:



As temperature increases the number at frequency ν increases
As ν increases the number at fixed T drops

Fig. 9.1 The Bose–Einstein distribution $n(\omega, T)$ as a function of $k_{\mathrm{B}}T/\hbar\omega$.

$$n\left(\omega_{k,s}\right) = \frac{1}{\exp\left(\dfrac{\hbar\omega_{k,s}}{k_{\mathrm{B}}T}\right) - 1}$$

If n = exp(($\mu-\varepsilon$)/kT)/Z and A/(1-A) = 1/((1/A)-1) and 1/e(x) = e(-x)

Phonons

Atoms or ions of mass m_1, m_2
Separated by a distance a
With spring constant K

2 modes of vibration result for a crystal with two atoms in a primitive cell

+ is optical (atoms move against each other, picture Na^+ Cl^- subject to an oscillating electric field, i.e. IR light) finite value at $k = 0$ reflects the polarization of the material i.e. the dielectric constant

- is acoustic (atoms move with each other) move at speed of sound. 0 energy at $k = 0$ or infinite λ means motion of the whole object

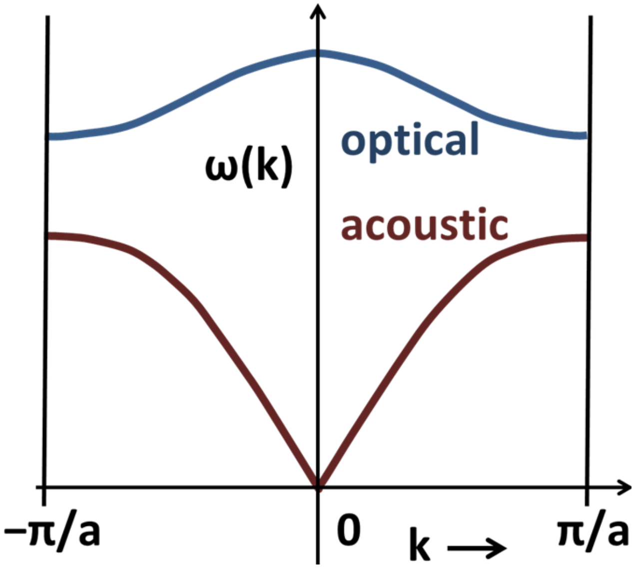
For three or more atoms in a primitive cell there are Three *acoustic* modes: One longitudinal (sound) and Two transverse (ocean)

Number of *optical* models is 3N-3

Fluids can't support shear stress so, they only have longitudinal (sound) acoustic modes

Dispersion relation (relating E to **k**) for phonons (much math to get this expression)

$$\omega_\pm^2 = K\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \pm K\sqrt{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)^2 - \frac{4\sin^2\frac{ka}{2}}{m_1 m_2}}$$



Plus optical

Minus Acoustic

Phonons From Dove

Phonons have energy $h\omega/2\pi$
The energy at 0K is not 0 it is ½ $h\omega/2\pi$
This is a consequence of energy quantization (lattice calculations are done at 0K)
(Uncertainty principle)

$$E = \hbar\omega\left[\frac{1}{2} + n(\omega, T)\right]$$

n is the number of phonons at wavelength
ω and temperature T

Bose-Einstein Relationship

$$\langle q \rangle = \frac{\sum_q q \exp(-\beta E(q))}{\sum_q \exp(-\beta E(q))}$$

Average of some parameter ”q”

Dulong Petit result for the Bose-Einstein Relationship at high T

Phonons From Dove

At high T

Bose-Einstein Relationship

$$
\begin{aligned}
\frac{1}{2} + n(\omega, T) = \frac{1}{2} + \frac{1}{\exp(\beta\epsilon) - 1} &= \frac{\exp(\beta\epsilon) + 1}{2[\exp(\beta\epsilon) - 1]} \\
&= \frac{(1 + \beta\epsilon + \cdots) + 1}{2[(1 + \beta\epsilon + \beta^2\epsilon^2/2 \cdots) - 1]} \\
&= \frac{2 + \beta\epsilon + \cdots}{\beta\epsilon(2 + \beta\epsilon + \cdots)} \\
&\approx \frac{1}{\beta\epsilon} = \frac{k_B T}{\hbar\omega} \qquad (9.10)
\end{aligned}
$$

$$E = \hbar\omega \left[\frac{1}{2} + n\right] = k_B T$$

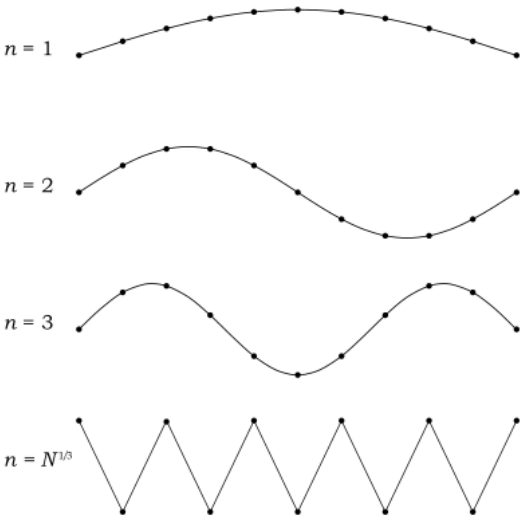
3 vibrations for each atom

E = 3RT

Debye Model (Wikipedia) *Why the cutoff in $g(\nu)$ at ν_D?*

For a cube of size L vibrations are limited to certain modes like a string of length L

Modes of vibration, n



(Transverse Wave)

$$\lambda_n = \frac{2L}{n}$$

$$E_n = h\nu_n = \frac{hc_s}{\lambda_n} = \frac{hc_s n}{2L}$$

c_s is the speed of sound in the solid

$$E_n^2 = p_n^2 c_s^2 = \left(\frac{hc_s}{2L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)$$

For 3d

p_n is the momentum of a phonon

$$E = \sum_n E_n \, \bar{N}(E_n) \qquad U = \sum_{n_x} \sum_{n_y} \sum_{n_z} E_n \, \bar{N}(E_n)$$

$$\lambda_{\min} = \frac{2L}{\sqrt[3]{N}},$$

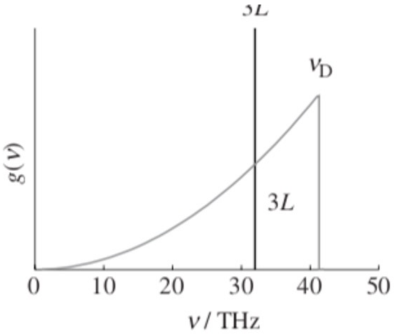
For N atoms in the box

making the maximum mode number n (infinite for photons)

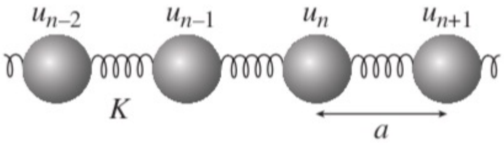
$$n_{\max} = \sqrt[3]{N}.$$

This is the highest energy vibration

At high temperature all of the vibrations are excited



Debye Model *(This is "borrowed" by Rouse for polymer dynamics)*



(Longitudinal Wave)

Figure 8.4 One-dimensional chain of atoms with interatomic distance *a* and force constant *K*.

Collective modes of vibration

If atom n vibrates and atoms n+1 and n-1 vibrate, the potential energy of n isn't independent of the motion of the neighboring atoms.

u is POSITION (*x*) and *F* is FORCE here

Before we had F = -Ku for uncoupled pairs

Force

$$F = -K(u_n - u_{n+1} + u_n - u_{n-1})$$

For coupled units

Force Balance

$$m\frac{\partial^2 u_n}{\partial t^2} = -\frac{\partial U}{\partial u_n} = F = -K(2u_n - u_{n+1} - u_{n-1})$$

F is *ma* also *Kx* also
d*U* = *F* d*x*

Propose a solution:

$$u_n = u_0 \cos(\omega t - qna)$$

wave vector $q = 2\pi/\lambda$

Phase angle δ

Atomic spacing is “a”
”n” is the atom index

Use in the equation of motion and solve for frequency

Force

$$m\frac{\partial^2 u_n}{\partial t^2} = -\frac{\partial U}{\partial u_n} = F = -K(2u_n - u_{n+1} - u_{n-1})$$

$$\omega(q) = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

Angular frequency of vibrations as a function of wavevector, q
This is a dispersion relation relating energy to q or wavelength

Debye Dispersion Relation

$$\omega(q) = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

Angular frequency of vibrations as a function of wavevector, q
This is a dispersion relation relating energy to q or wavelength

Einstein Dispersion Relation

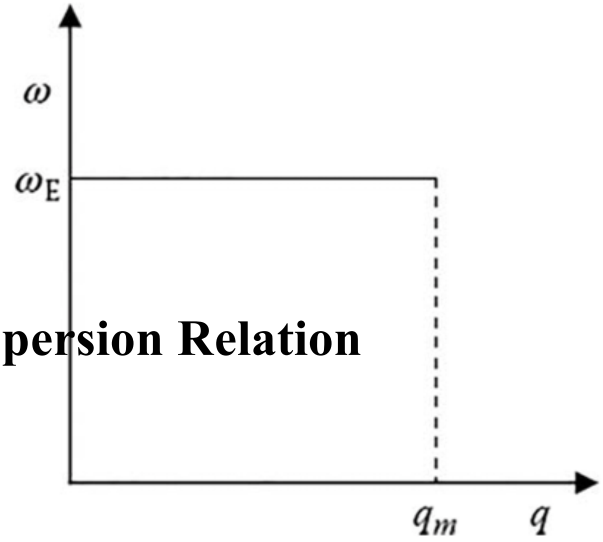
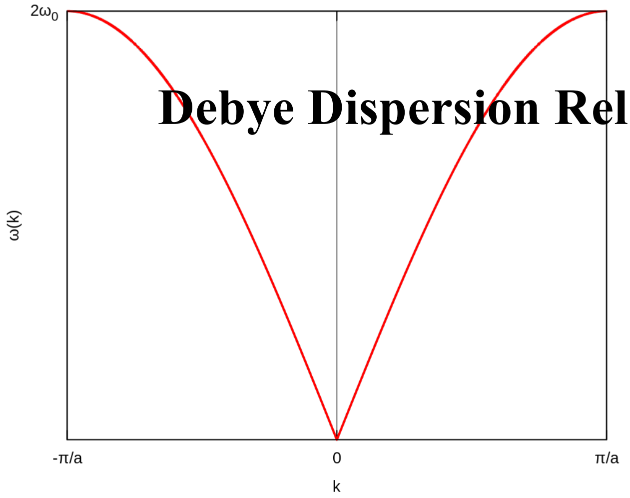


FIGURE 15.4 Dispersion curve w versus q for the Einstein solid. All 3N oscillators have the same Einstein frequency for wave vectors in the accessible range 0 to q,,,.

Debye Dispersion Relation



https://ebrary.net/196904/mathematics/einstein_model_specific_heat_solids

Phonons

Two size scales, a and λ
If $\lambda \geq a$ you are within a Brillouin Zone
Wavevector $k = 2\pi/\lambda$

The partition function (Z) can be defined in terms of E or in terms of the wavevector $k=2\pi/\lambda= 2\pi E/hc$
E and k are related by the dispersion relationship which differs for different systems
(longitudinal, transverse, acoustic, optical phonons)

The **density of states** is defined by

$$D(E) = \frac{1}{V} \cdot \frac{\mathrm{d}Z_m(E)}{\mathrm{d}E}$$

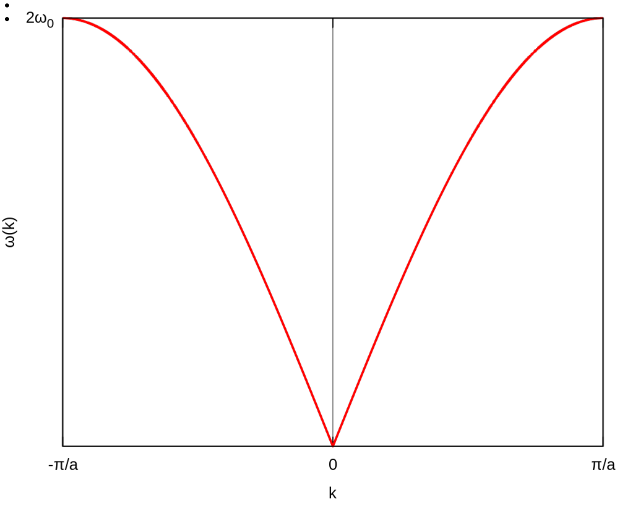
$$\mathcal{Z} = \sum_{N=0}^{\infty} \exp(N(\mu - \varepsilon)/k_B T)$$

For a longitudinal Phonon in a string of atoms the **dispersion relation** is:

Transverse is like an ocean wave or a guitar string, longitudinal is a compressive wave like sound

$$E = 2\hbar\omega_0 \left|\sin\left(\frac{ka}{2}\right)\right|$$

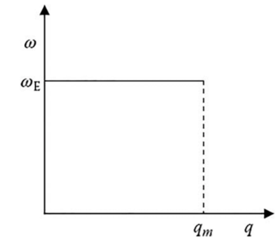
where $\omega_0 = \sqrt{k_F/m}$ is the oscillator frequency, m the mass of the atoms, k_F the inter-atomic force constant and a inter-atomic spacing.



Debye Dispersion Relation

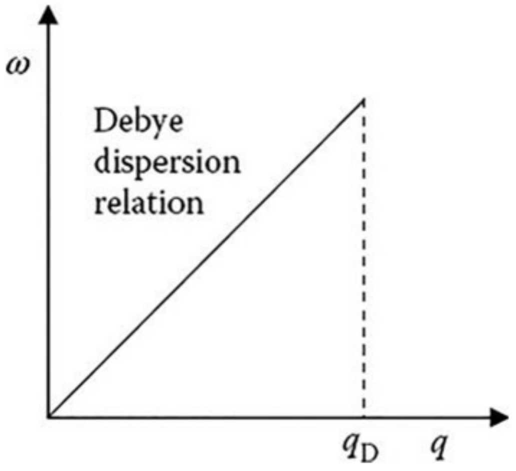
$$\omega(q) = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

Angular frequency of vibrations as a function of wavevector, q
This is a dispersion relation relating energy to q or wavelength



Einstein Dispersion Relation

FIGURE 15.4 Dispersion curve w versus q for the Einstein solid. All 3N oscillators have the same Einstein frequency for wave vectors in the accessible range 0 to q,,,.



Debye Dispersion Relation
For small qa, sin(qa/2) = qa/2
(to q_D related to n_{max})

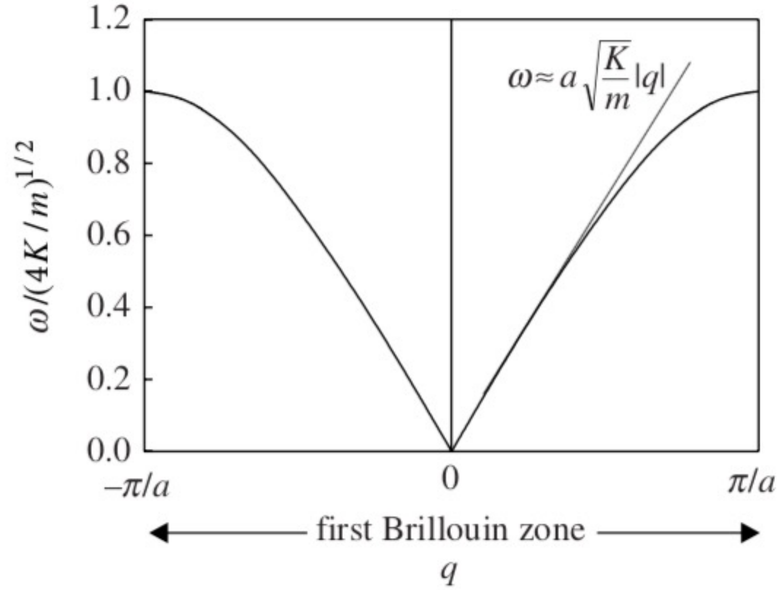
FIGURE 15.6 Linear dispersion relation to = vq used in the Debye model. The high-frequency cutoff has wave vector q_D and frequency o>$_0$.

https://ebrary.net/196904/mathematics/einstein_model_specific_heat_solids

Dispersion Curve

$$\omega(q) = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

Angular frequency of vibrations as a function of wavevector, q



$-\pi/a < q < \pi/a$

First Brillouin Zone of the one-dimensional lattice

Longer wavevectors are smaller than the lattice

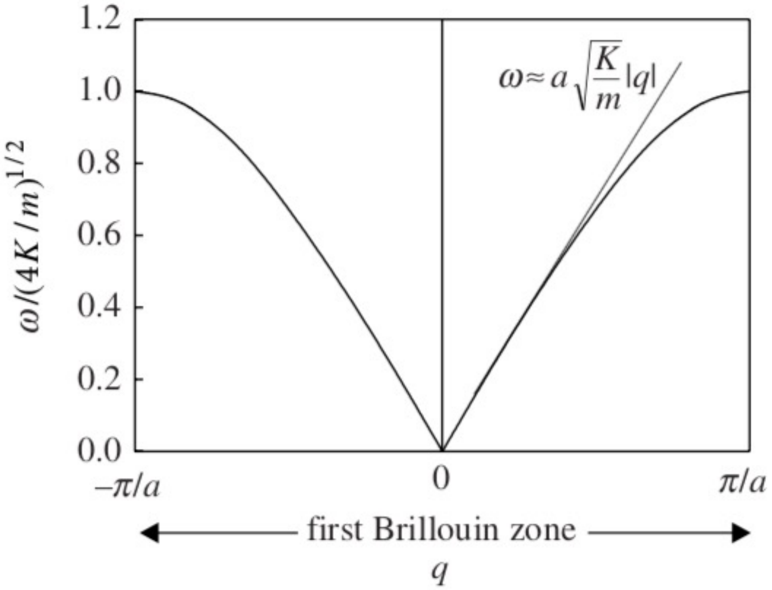
Figure 8.5 The dispersion curve for a one-dimensional monoatomic chain of atoms.

Dispersion Curve

$$\omega(q) = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

Angular frequency of vibrations as a function of wavevector, q

Slope is related to the modulus



$-\pi/a < q < \pi/a$

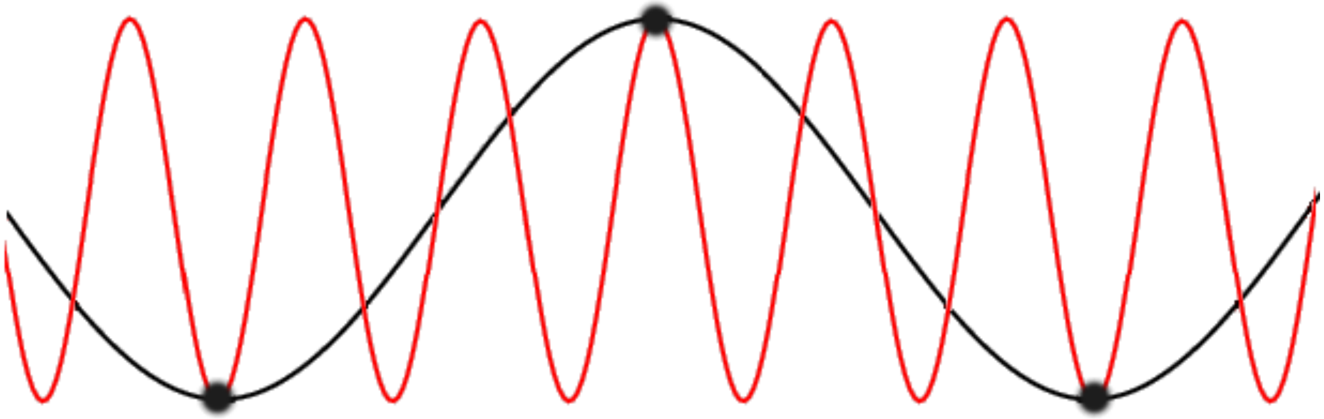
First Brillouin Zone of the one-dimensional lattice

Longer wavevectors are smaller than the lattice

Figure 8.5 The dispersion curve for a one-dimensional monoatomic chain of atoms.

Phonons

Two size scales, a and λ
If $\lambda \geq a$ you are within a Brillouin Zone
Wavevector $k = 2\pi/\lambda$



k-vectors exceeding the first Brillouin zone (red) do not carry any more information than their counterparts (black) in the first Brillouin zone.

Dispersion Curve

$$\omega(q) = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

Angular frequency of vibrations as a function of wavevector, q

For small wave vectors (**long wavelength**) sin(θ) => θ

Acoustic or Ultrasonic range

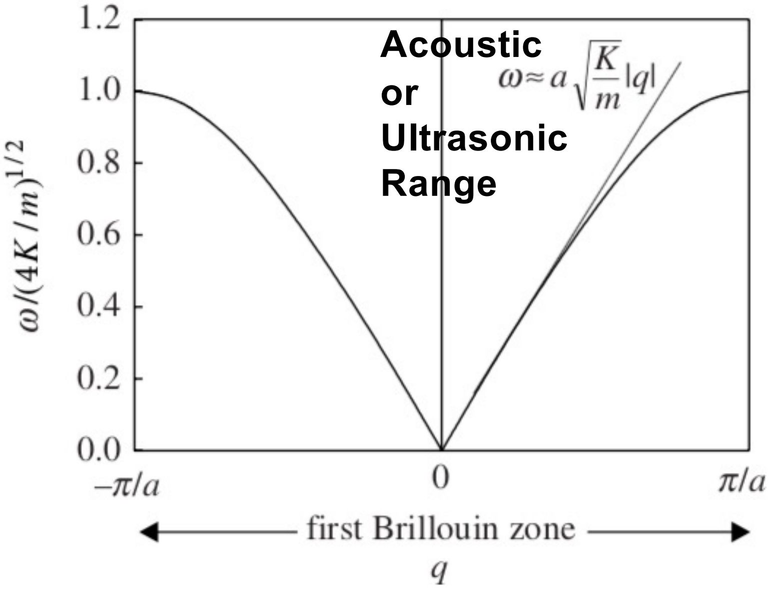
$$\omega \approx a\sqrt{\frac{K}{m}}\,|q|$$

wave vector $q = 2\pi/\lambda$

Long wavelengths

Group Velocity = dω/dq = a√(K/m)
Speed of sound in the solid

Material is a continuum at these large distances



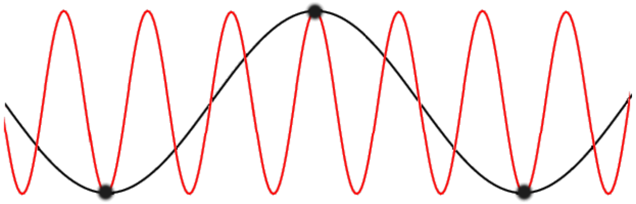
Dispersion Curve

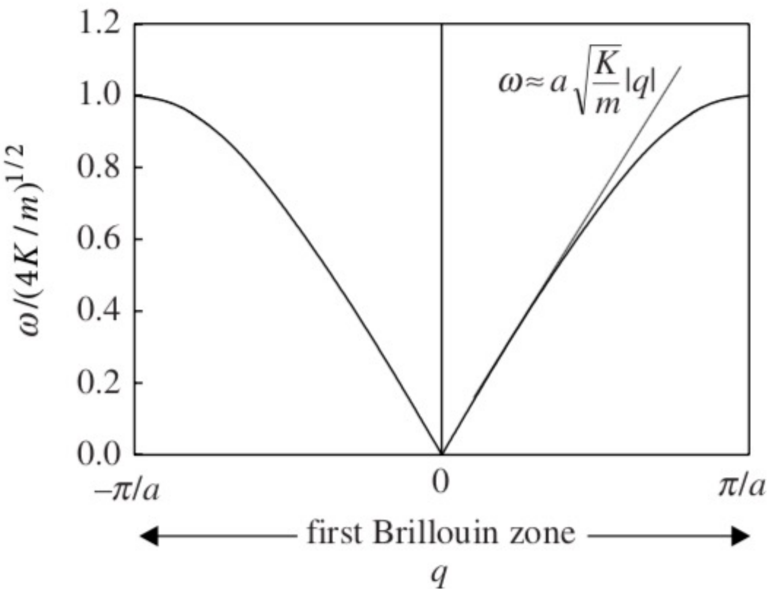
$$\omega(q) = \sqrt{\frac{4K}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|$$

Angular frequency of vibrations as a function of wavevector, q

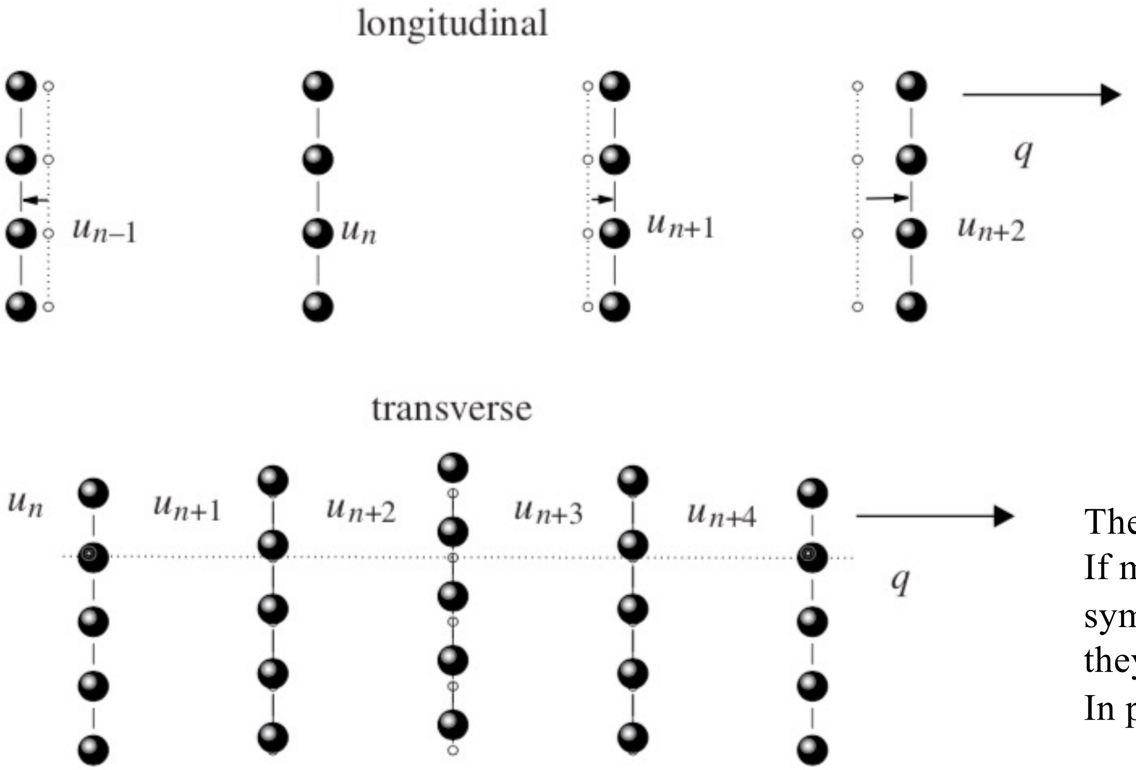
For large wave vectors (**short wavelengths**)

Dispersion region
ω isn't proportional to q
For larger q velocity drops until it
stops at the Brillouin zone boundary
Standing Wave



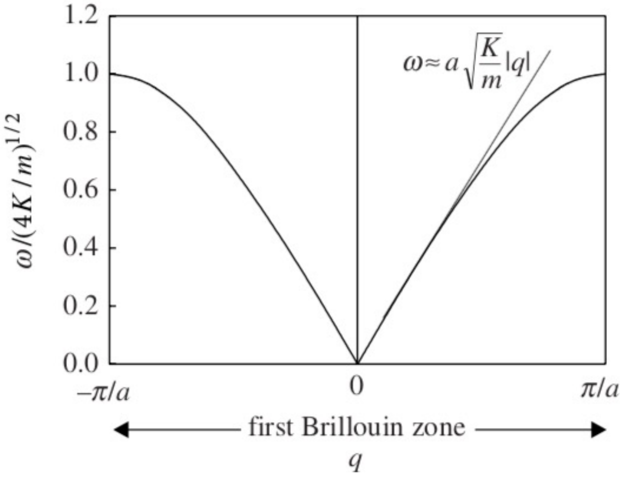


Longitudinal versus Transverse Waves



There are 2 transverse waves
If material is isotropic or for
symmetric crystal planes
they are degenerate
In plane and out of plane

Figure 8.6 Schematic representation of transverse and longitudinal collective vibrational waves.



Longitudinal and Transverse dispersion relationships for [100],[110], and [111] for lead

Transverse degenerate for [100] and [111] (4- and 3-fold rotation axis)

Not for [110] (two-fold rotation axis)

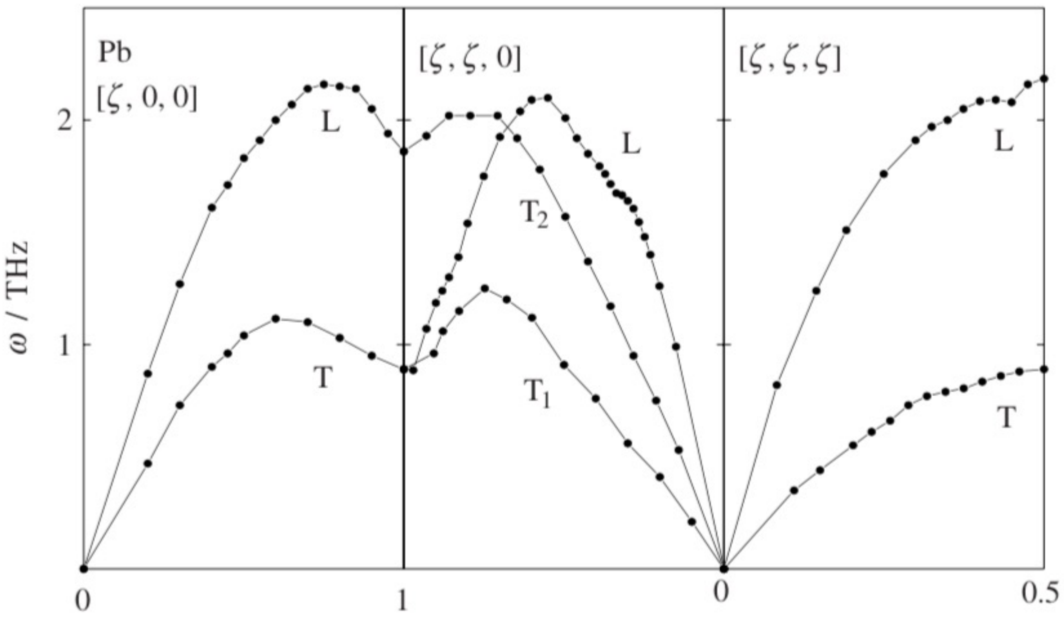


Figure 8.7 Experimental dispersion relations for acoustic modes for lead at 100 K [2]. Reproduced by permission of B. N. Brockhouse and the American Physical Society.

Diatomic Chain Model

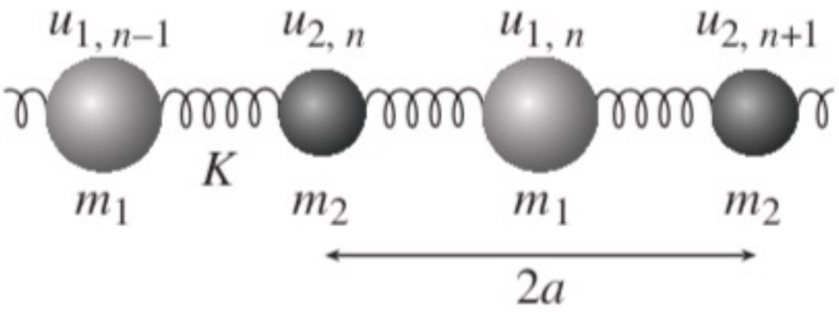


Figure 8.8 One-dimensional diatomic chain with lattice parameter $2a$ and force constant K.

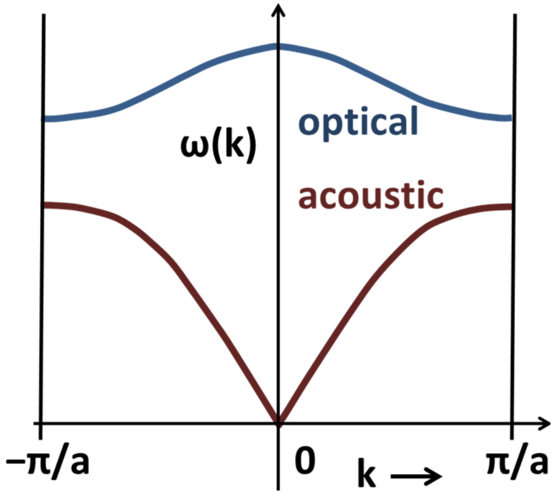
Acoustic and Optical modes

$$\omega_a^2 = K\left[\left(\frac{m_1+m_2}{m_1 m_2}\right) - \frac{\sqrt{(m_1-m_2)^2 + 4m_1 m_2 \cos^2 qa}}{m_1 m_2}\right]$$

Minus Acoustic

$$\omega_o^2 = K\left[\left(\frac{m_1+m_2}{m_1 m_2}\right) + \frac{\sqrt{(m_1-m_2)^2 + 4m_1 m_2 \cos^2 qa}}{m_1 m_2}\right]$$

Plus Optical



2.1.3 Normal Modes of a One-Dimensional Chain with a Basis

We consider a one-dimensional Bravais lattice of lattice constant a with two ions or atoms of masses M_1 and M_2 per unit cell. This is shown in Figure 2.6. The basic assumption is that each ion interacts only with the nearest neighbors, which are at a distance $a/2$ from each other, and $M_1 > M_2$. Thus, the lattice constant of the linear chain is a.

If K is the force constant, from Eq. (2.21) we obtain

$$V^{harm} = \frac{K}{2}\sum_s [u_1(sa) - u_2(sa)]^2 + \frac{K}{2}\sum_s [u_2(sa) - u_1[s+1]a]^2, \tag{2.32}$$

where $u_1(sa)$ is the displacement of the ion that oscillates about the site sa and $u_2(sa)$ is the displacement of the ion that oscillates around $sa + d$. The equations of motion are

$$\begin{aligned} M_1\, \ddot{u}_1(sa) &= -\frac{\partial V^{harm}}{\partial u_1(sa)} = -K[2u_1(sa) - u_2(sa) - u_2([s-1]a)], \\ M_2\, \ddot{u}_2(sa) &= -\frac{\partial V^{harm}}{\partial u_2(sa)} = -K[2u_2(sa) - u_1(sa) - u_1([s+1]a)]. \end{aligned} \tag{2.33}$$

The solutions of Eq. (2.33) are of the type

$$u_1(sa, t) = \in_1 e^{i(qsa-\omega t)}$$

and

$$u_2(sa, t) = \in_2 e^{i(qsa-\omega t)}. \tag{2.34}$$

Substituting Eq. (2.34) in Eq. (2.33), we obtain

$$-\omega^2 M_1 \in_1 e^{i(qsa-\omega t)} = K(\in_2 - 2\in_1 + \in_2 e^{-iqa})\, e^{i(qsa-\omega t)}$$

and

$$-\omega^2 M_2 \in_2 e^{i(qsa-\omega t)} = K(\in_1 e^{iqa} - 2\in_2 + \in_1)\, e^{i(qsa-\omega t)}. \tag{2.35}$$

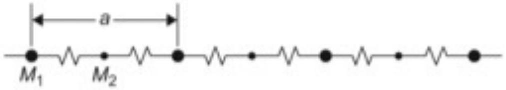


FIGURE 2.6

Diatomic linear chain of masses M_1 and M_2.

We cancel the $e^{i(qsa-\omega t)}$ term from both sides and solve the determinantal equation

$$\begin{vmatrix} 2K - M_1\omega^2 & -K(1+e^{-iqa}) \\ -K(1+e^{iqa}) & 2K - M_2\omega^2 \end{vmatrix} = 0. \tag{2.36}$$

There are two roots of the solution of Eq. (2.36), which yields (Problem 2.4)

$$\omega_{\pm}^2 = K\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm K\sqrt{\left[\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4\sin^2(qa/2)}{M_1M_2}\right]}. \tag{2.37}$$

The two solutions of Eq. (2.37) are the two branches of the phonon dispersion relation. For small q, the two roots of Eq. (2.37) are

$$\omega_- = \sqrt{\frac{K}{2(M_1+M_2)}}qa \tag{2.38}$$

and

$$\omega_+ = \sqrt{\frac{2K(M_1+M_2)}{M_1M_2}}. \tag{2.39}$$

We also note from Eq. (2.37) that if $qa = \pm\pi$ (the Brillouin zone boundary), the expressions for $\omega_{\pm}$ reduce to

$$\omega_{\pm}^2 = \left(K\left[\frac{1}{M_1} + \frac{1}{M_2}\right] \pm K\left[\frac{1}{M_2} - \frac{1}{M_1}\right]\right). \tag{2.40}$$

Thus, we obtain

$$\omega_+ = \sqrt{\frac{2K}{M_2}} \tag{2.41}$$

and

$$\omega_- = \sqrt{\frac{2K}{M_1}}. \tag{2.42}$$

At the Brillouin zone boundary, $q = \pm\frac{\pi}{a}$. We also note that because $M_1 > M_2$, $\omega_+ > \omega_-$. Another interesting point to note is that from Eq. (2.34), u_1 and u_2 are periodic with $q = \pm 2\pi/a$. Therefore, the dispersion relation repeats itself for each Brillouin zone. From the previous discussions, we obtain the following results.

The vibrational frequency of a diatomic linear chain of mass M_1 and M_2 is shown in Figure 2.7.

The first branch, ω_-, which tends to become zero at $q = 0$, is known as the acoustic mode.

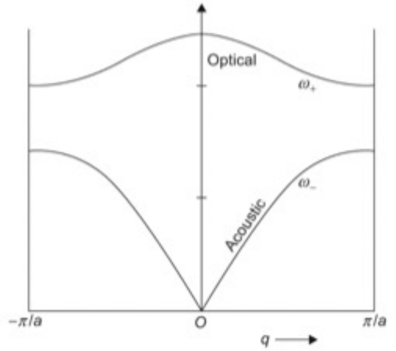


FIGURE 2.7

Optical and acoustic phonon branches of a diatomic linear chain.

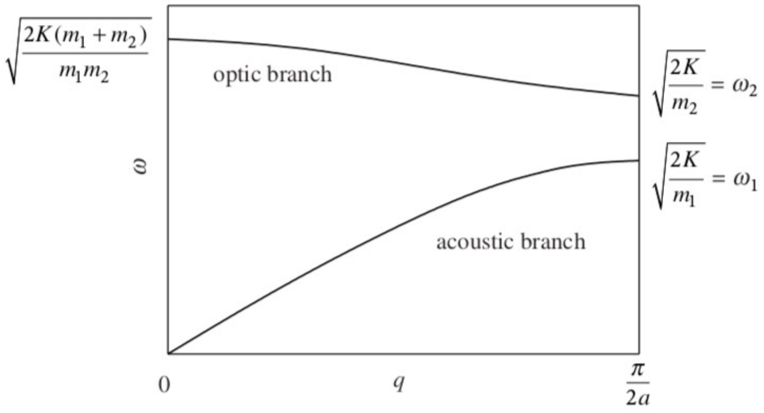
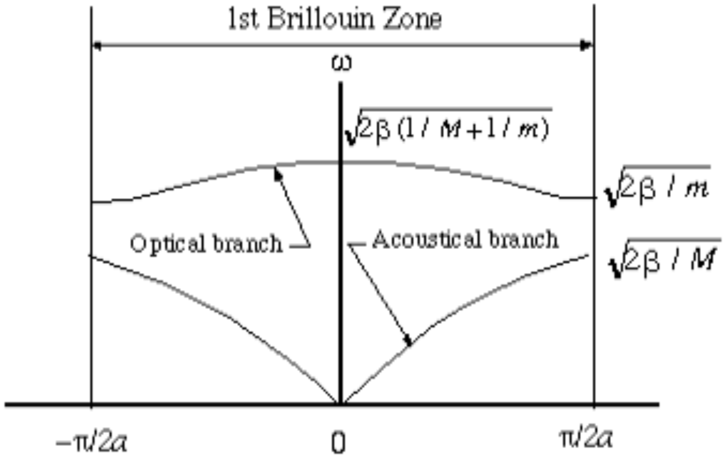


Figure 8.9 The dispersion curve for a one-dimensional diatomic chain of atoms. $m_2 < m_1$.

$$\omega_a \approx a\sqrt{\frac{2K}{m_1+m_2}}\,|\,q\,|$$

$$\omega_o(q=0) = \sqrt{\frac{2K(m_1+m_2)}{m_1 m_2}}$$

http://www.chembio.uoguelph.ca/educmat/chm729
/Phonons/optical.htm



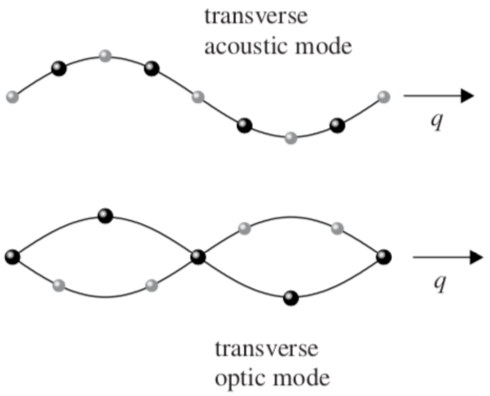


Figure 8.10 Transverse acoustic and optic modes of motion in a one-dimensional diatomic chain at the same wavelength.

Phonons

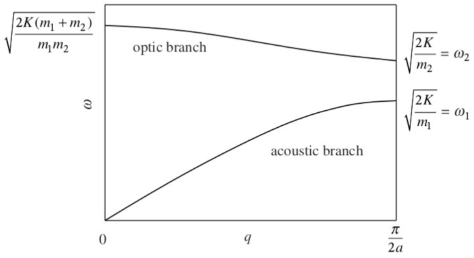


Figure 8.9 The dispersion curve for a one-dimensional diatomic chain of atoms. $m_2 < m_1$.

Short sizes (long wavelengths) are high energy (frequency)

Dispersion relationship is how the energy or frequency of vibrations related to the size scale or wavelengths or what happens to vibrational energy in the crystal, i.e., modulus.

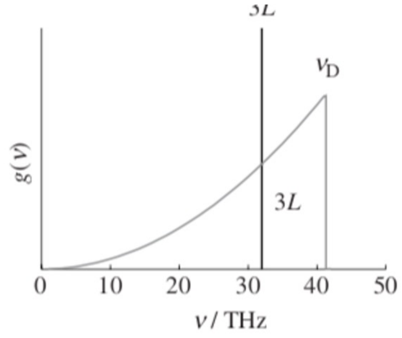
$$E = 2\hbar\omega_0 \left|\sin\left(\frac{ka}{2}\right)\right|$$

Probability of energy going to different frequencies due to the structure

Density of states is how the total energy is distributed to different frequencies of vibration. This is related to what happens at different wavenumbers to different wavelength phonons.

$$D(E) = \frac{1}{V} \cdot \frac{\mathrm{d}Z_m(E)}{\mathrm{d}E} \qquad \mathcal{Z} = \sum_{N=0}^{\infty} \exp(N(\mu - \varepsilon)/k_{\mathrm{B}}T)$$

N is an integer related to the vibrational state k



Convert dispersion relation to DOS for a 1D wave in the continuum limit

q= wave number: $q = \frac{2\pi}{\lambda}$, A= amplitude, ω= the frequency, v_s= the velocity of sound

$$\omega = v_s q$$

This is a kind of **dispersion relation** relating energy or frequency to wave vector

Wave equation

$$u = Ae^{i(qx-\omega t)}$$

Density of states doesn't depend on time so use: $u = Ae^{i(qx)}$

Choose periodic boundary condition $u(x = 0) = u(x = L)$

Apply boundary conditions to $u = Ae^{i(qx)}$ Yields $e^{iqL} = 1$

That is qL = n 2π

This only occurs if: $q = n\frac{2\pi}{L}$ Since: $e^{ix} = \cos(x) + i\sin(x)$

n are the modes or the number of waves for a given frequency and the maximum number is how many atoms on a line.

https://eng.libretexts.org/Bookshelves/Materials_Science/Supplemental_Modules_(Materials_Science)/Electronic_Properties/Density_of_States

Convert Dispersion relation to DOS For a 1D wave in the continuum limit

the number of modes in an interval dq in q-space equals:

$$q = n\frac{2\pi}{L}$$

$$\mathrm{d}n = \frac{dq}{\frac{2\pi}{L}} = \frac{L}{2\pi}dq$$

This number is the density of states (DOS) at a frequency ω

$$g(\omega)d\omega = \frac{L}{2\pi}dq \text{ which we turn into: } g(\omega) = (\tfrac{L}{2\pi})/(\tfrac{d\omega}{dq})$$

Using **dispersion relation** $\omega = v_s q$

$$\frac{d\omega}{dq} = v_s \quad g(\omega) = \left(\frac{L}{2\pi}\right)\frac{1}{v_s}$$

For modes in positive and negative “q=space”

$$g(\omega) = 2\left(\frac{L}{2\pi}\frac{1}{v_s}\right) \qquad g(\omega) = \frac{L}{\pi}\frac{1}{v_s}$$

A constant **density of states** like the Einstein Model

https://eng.libretexts.org/Bookshelves/Materials_Science/Supplemental_Modules_(Materials_Science)/Electronic_Properties/Density_of_States

$$E = 2\hbar\omega_0 \left|\sin\left(\frac{ka}{2}\right)\right|$$

$$D(E) = \frac{1}{V} \cdot \frac{\mathrm{d}Z_m(E)}{\mathrm{d}E}$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} \exp(N(\mu - \varepsilon)/k_{\mathrm{B}}T)$$

Dispersion Relationship

Density of States

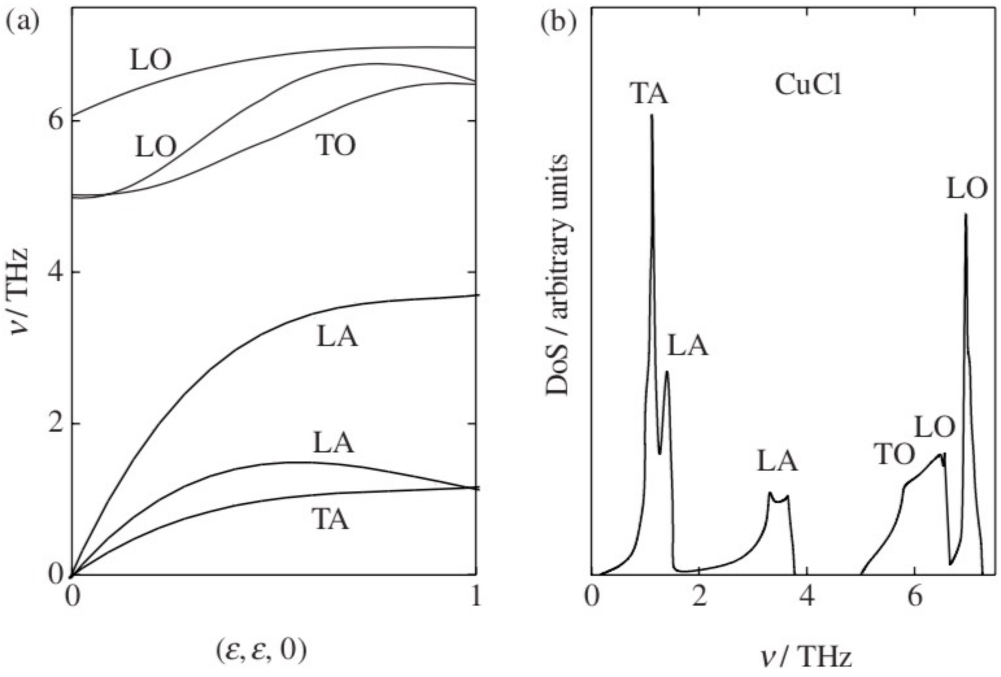


Figure 8.11 (a) Dispersion curve for CuCl(s) along [110] of the cubic unit cell. (b) Density of vibrational modes [3]. Here L, T, A and O denote longitudinal, transverse, acoustic and optic. Reproduced by permission of B. Hennion and The Institute of Physics.

Number of vibrational modes

$$3N_{\mathrm{A}}\, g(\nu)\mathrm{d}\nu \quad \text{where} \quad \int_0^{\infty} g(\nu)\mathrm{d}\nu = 1$$

$$\begin{aligned} c_V &= \left(\frac{\partial E}{\partial T}\right)_V \\ &= \sum \hbar\omega \frac{\partial n}{\partial T} \\ &= \sum k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2} \end{aligned}$$

3-d Crystal

Transverse and longitudinal optical and acoustic modes exist for 3d crystals.

Dispersion Relationship

Density of States

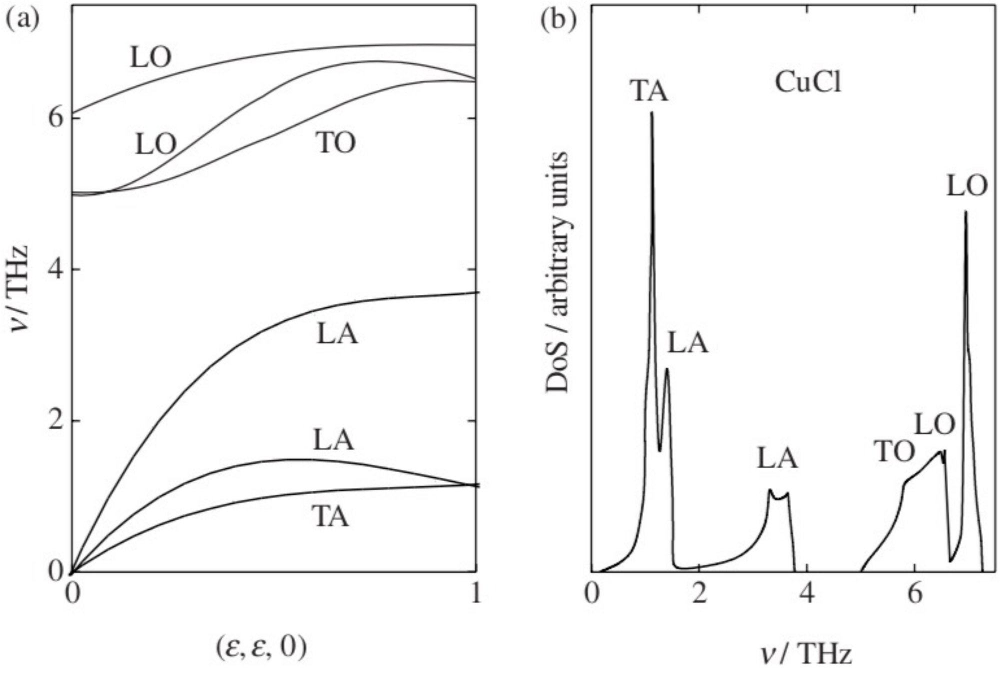


Figure 8.11 (a) Dispersion curve for CuCl(s) along [110] of the cubic unit cell. (b) Density of vibrational modes [3]. Here L, T, A and O denote longitudinal, transverse, acoustic and optic. Reproduced by permission of B. Hennion and The Institute of Physics.

n atoms in unit cell

$3N_A n$ vibrational modes

$3N_A$ acoustic modes (Unit cell vibrates as an entity)

$3N_A(n-1)$ optical modes (deformation of unit cell)

At high T each mode has k_BT (2 springs for each Cartesian coordinate in two directions)

So, heat capacity is 3R

Number of vibrational modes

$$3N_A\, g(\nu)\mathrm{d}\nu \quad \text{where} \quad \int_0^\infty g(\nu)\mathrm{d}\nu = 1$$

Debye Model

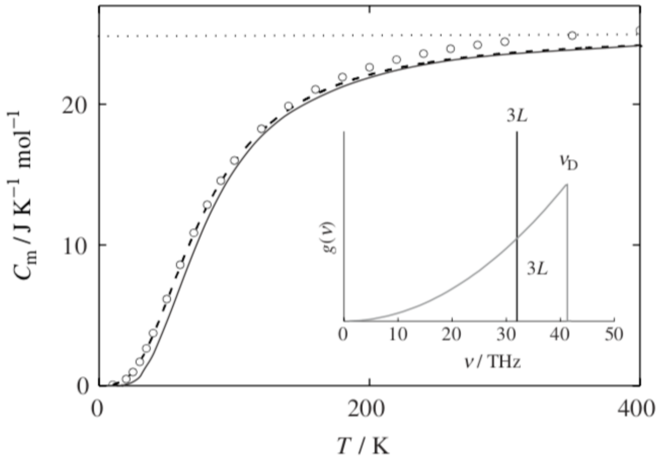


Figure 8.12 Experimental heat capacity of Cu at constant pressure compared with the Debye and Einstein $C_{V,m}$ calculated by using $\Theta_E = 244$ K and $\Theta_D = 314$ K. The vibrational density of states according to the two models is shown in the insert.

At low temperature

Low energy, low frequency vibrations are excited

These are acoustic mode vibrations

Unit cell vibrates as an entity

Long distances compared to a unit cell

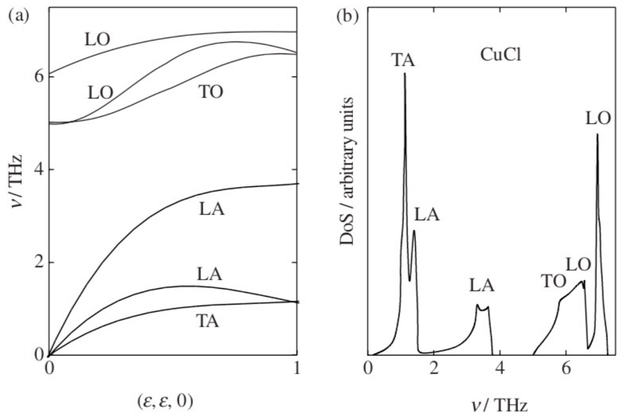


Figure 8.11 (a) Dispersion curve for CuCl(s) along [110] of the cubic unit cell. (b) Density of vibrational modes [3]. Here L, T, A and O denote longitudinal, transverse, acoustic and optic. Reproduced by permission of B. Hennion and The Institute of Physics.

Debye Model Derivation

https://eng.libretexts.org/Bookshelves/Materials_Science/Supplemental_Modules_(Materials_Science)/Electronic_Properties/Debye_Model_For_Specific_Heat

Debye Model

$$U \approx \int_0^{\sqrt[3]{N}} \int_0^{\sqrt[3]{N}} \int_0^{\sqrt[3]{N}} E(n)\, \bar{N}\left(E(n)\right)\, dn_x\, dn_y\, dn_z$$

$$\langle N \rangle_{BE} = \frac{1}{e^{E/kT} - 1} \qquad \bar{N}(E) = \frac{3}{e^{E/kT} - 1}$$

One Longitudinal Two Transverse

$$U = \int_0^{\sqrt[3]{N}} \int_0^{\sqrt[3]{N}} \int_0^{\sqrt[3]{N}} E(n)\, \frac{3}{e^{E(n)/kT} - 1}\, dn_x\, dn_y\, dn_z$$

$$(n_x, n_y, n_z) = (n \sin\theta \cos\phi, n \sin\theta \sin\phi, n \cos\theta)$$

Convert to Spherical Coordinates

https://en.wikipedia.org/wiki/Debye_model

Debye Model

$$U \approx \int_0^{\pi/2}\int_0^{\pi/2}\int_0^R E(n)\,\frac{3}{e^{E(n)/kT}-1}n^2\sin\theta\,dn\,d\theta\,d\phi$$

$$N = \frac{1}{8}\frac{4}{3}\pi R^3 \qquad R = \sqrt[3]{\frac{6N}{\pi}}$$

There are 8 cubes worth of particles in the sphere

$$U = \frac{3\pi}{2}\int_0^R \frac{hc_s n}{2L}\frac{n^2}{e^{hc_s n/2LkT}-1}\,dn$$

$$E_n^2 = p_n^2 c_\mathrm{s}^2 = \left(\frac{hc_\mathrm{s}}{2L}\right)^2 (n_x^2+n_y^2+n_z^2)$$

$$T_\mathrm{D}^{-3} \propto c_\mathrm{eff}^{-3} := (1/3)c_\mathrm{long}^{-3} + (2/3)c_\mathrm{trans}^{-3}$$

https://en.wikipedia.org/wiki/Debye_model

Debye Model

$$U = \frac{3\pi}{2}kT\left(\frac{2LkT}{hc_{\rm s}}\right)^3 \int_0^{hc_{\rm s}R/2LkT} \frac{x^3}{e^x - 1}\,dx.$$

$$x = \frac{hc_{\rm s}n}{2LkT}$$

$$T_{\rm D} \stackrel{\rm def}{=} \frac{hc_{\rm s}R}{2Lk} = \frac{hc_{\rm s}}{2Lk}\sqrt[3]{\frac{6N}{\pi}} = \frac{hc_{\rm s}}{2k}\sqrt[3]{\frac{6}{\pi}\frac{N}{V}}$$

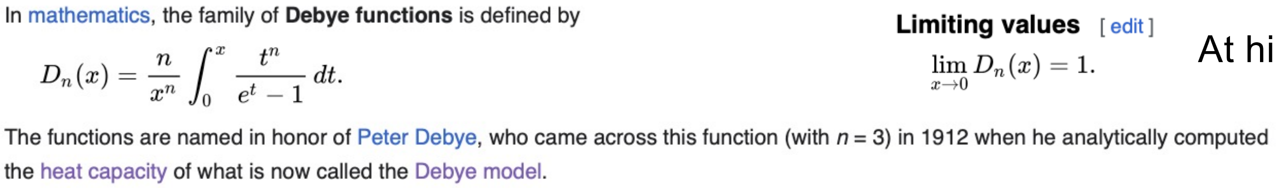
$$\frac{U}{Nk} = 9T\left(\frac{T}{T_{\rm D}}\right)^3 \int_0^{T_{\rm D}/T} \frac{x^3}{e^x - 1}\,dx = 3TD_3\left(\frac{T_{\rm D}}{T}\right)$$

$$\frac{C_V}{Nk} = 9\left(\frac{T}{T_{\rm D}}\right)^3 \int_0^{T_{\rm D}/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2}\,dx$$

https://en.wikipedia.org/wiki/Debye_model

Debye Model

$$\frac{U}{Nk} = 9T\left(\frac{T}{T_{\rm D}}\right)^3 \int_0^{T_{\rm D}/T} \frac{x^3}{e^x - 1}\,dx = 3TD_3\left(\frac{T_{\rm D}}{T}\right)$$



In mathematics, the family of **Debye functions** is defined by

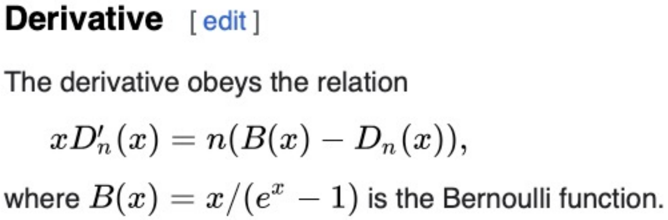
$$D_n(x) = \frac{n}{x^n}\int_0^x \frac{t^n}{e^t - 1}\,dt.$$

The functions are named in honor of Peter Debye, who came across this function (with $n = 3$) in 1912 when he analytically computed the heat capacity of what is now called the Debye model.

Limiting values [edit]

$$\lim_{x\to 0} D_n(x) = 1.$$

At high T (Dulong-Petit)



Derivative [edit]

The derivative obeys the relation

$$xD_n'(x) = n(B(x) - D_n(x)),$$

where $B(x) = x/(e^x - 1)$ is the Bernoulli function.

So far I can't do this

$$\frac{C_V}{Nk} = 9\left(\frac{T}{T_{\rm D}}\right)^3 \int_0^{T_{\rm D}/T} \frac{x^4 e^x}{(e^x - 1)^2}\,dx$$

https://en.wikipedia.org/wiki/Debye_model

Debye Model

$$U = \frac{3\pi}{2} kT \left(\frac{2LkT}{hc_{\mathrm{s}}} \right)^3 \int_0^{hc_{\mathrm{s}} R/2LkT} \frac{x^3}{e^x - 1} \, dx.$$

$$x = \frac{hc_{\mathrm{s}} n}{2LkT}$$

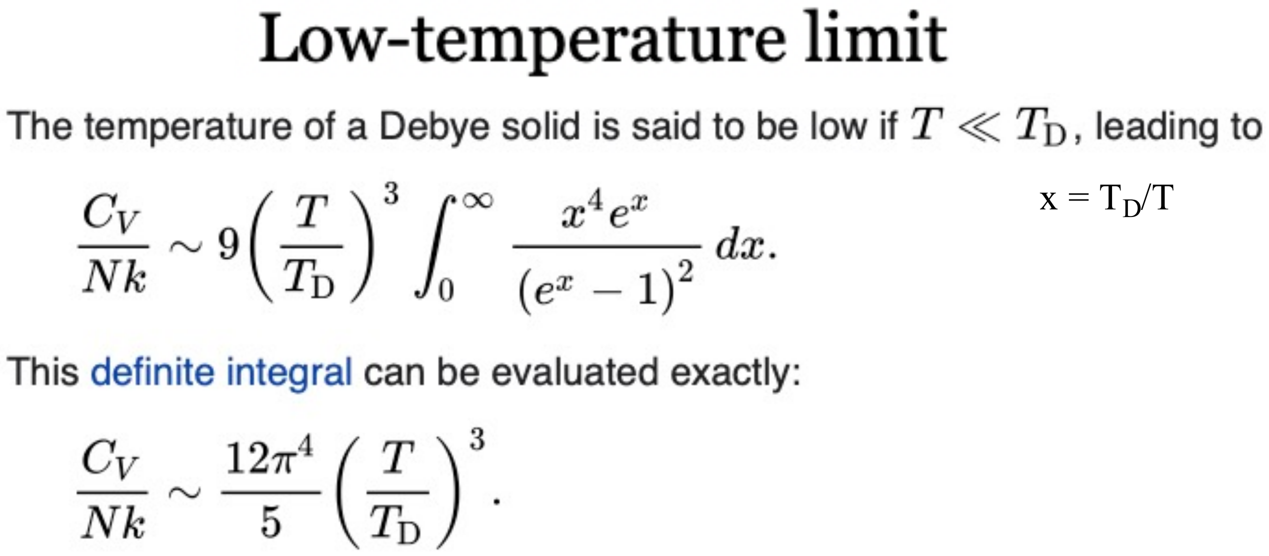
$$T_{\mathrm{D}} \overset{\text{def}}{=} \frac{hc_{\mathrm{s}} R}{2Lk} = \frac{hc_{\mathrm{s}}}{2Lk} \sqrt[3]{\frac{6N}{\pi}} = \frac{hc_{\mathrm{s}}}{2k} \sqrt[3]{\frac{6}{\pi} \frac{N}{V}}$$

$$\frac{U}{Nk} = 9T \left(\frac{T}{T_{\mathrm{D}}} \right)^3 \int_0^{T_{\mathrm{D}}/T} \frac{x^3}{e^x - 1} \, dx = 3T D_3 \left(\frac{T_{\mathrm{D}}}{T} \right)$$

$$\frac{C_V}{Nk} = 9 \left(\frac{T}{T_{\mathrm{D}}} \right)^3 \int_0^{T_{\mathrm{D}}/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} \, dx$$

https://en.wikipedia.org/wiki/Debye_model

Debye Model



Low-temperature limit

The temperature of a Debye solid is said to be low if $T \ll T_{\rm D}$, leading to

$$\frac{C_V}{Nk} \sim 9\left(\frac{T}{T_{\rm D}}\right)^3 \int_0^\infty \frac{x^4 e^x}{\left(e^x - 1\right)^2}\, dx.$$

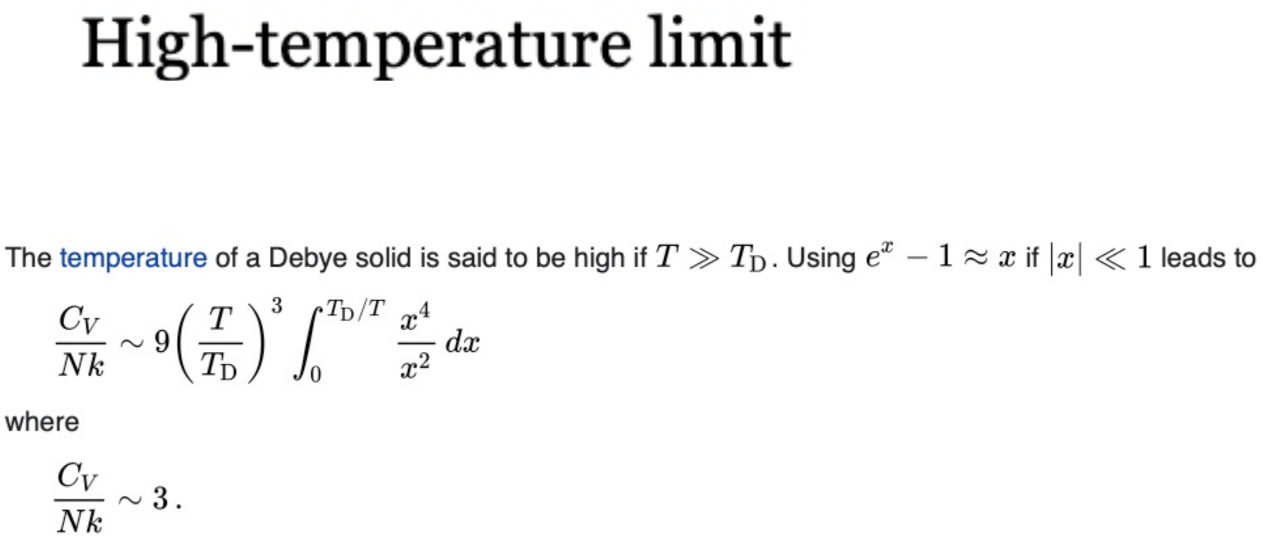
$x = T_D/T$

This definite integral can be evaluated exactly:

$$\frac{C_V}{Nk} \sim \frac{12\pi^4}{5}\left(\frac{T}{T_{\rm D}}\right)^3.$$

https://en.wikipedia.org/wiki/Debye_model

Debye Model



High-temperature limit

The temperature of a Debye solid is said to be high if $T \gg T_{\rm D}$. Using $e^x - 1 \approx x$ if $|x| \ll 1$ leads to

$$\frac{C_V}{Nk} \sim 9\left(\frac{T}{T_{\rm D}}\right)^3 \int_0^{T_{\rm D}/T} \frac{x^4}{x^2}\,dx$$

where

$$\frac{C_V}{Nk} \sim 3\,.$$

https://en.wikipedia.org/wiki/Debye_model

Debye Model

Debye

$$\frac{C_V}{Nk} = 9\left(\frac{T}{T_{\mathrm{D}}}\right)^3 \int_0^{T_{\mathrm{D}}/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2}\, dx$$

Einstein

$$C_V = 3Nk\left(\frac{\epsilon}{kT}\right)^2 \frac{e^{\epsilon/kT}}{\left(e^{\epsilon/kT} - 1\right)^2}$$

$$T_{\mathrm{D}} \stackrel{\mathrm{def}}{=} \frac{hc_{\mathrm{s}}}{2k}\sqrt[3]{\frac{6}{\pi}\frac{N}{V}}$$

$$T_{\mathrm{E}} = \frac{\epsilon}{k} = \frac{h\nu}{k} = \frac{hc_{\mathrm{s}}}{2k}\sqrt[3]{\frac{N}{V}}$$

$$\frac{T_{\mathrm{E}}}{T_{\mathrm{D}}} = \sqrt[3]{\frac{\pi}{6}} = 0.805995977...$$

https://en.wikipedia.org/wiki/Debye_model

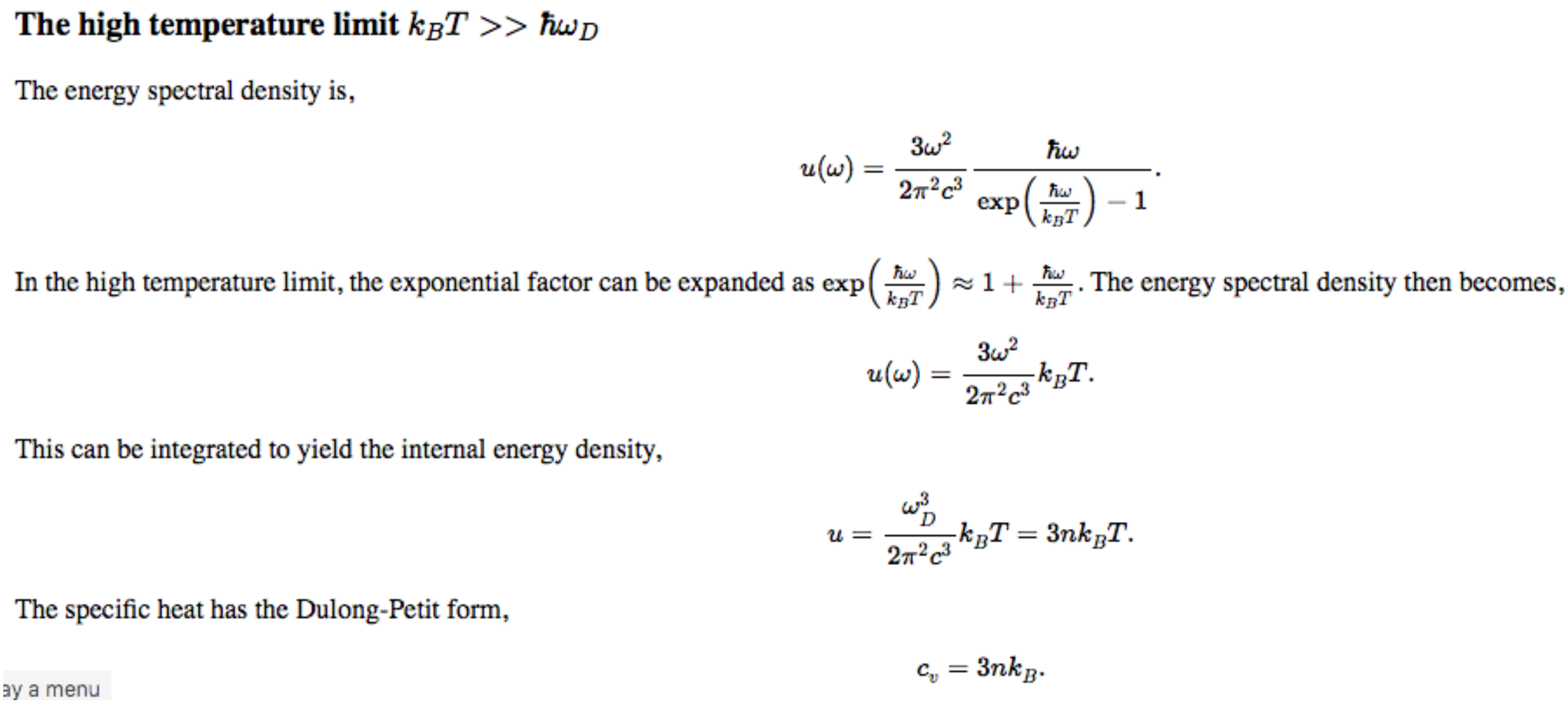
Debye Model

	Debye	Einstein	Dulong Petit
Low T	$\frac{C_V}{Nk} \sim \frac{12\pi^4}{5}\left(\frac{T}{T_{\mathrm{D}}}\right)^3$	Exponential approach to T = 0 $C_V = 3Nk\left(\frac{\epsilon}{kT}\right)^2 \frac{1}{e^{\epsilon/kT}}$	$\frac{C_V}{Nk} \sim 3$
High T	$\frac{C_V}{Nk} \sim 3$	$\frac{C_V}{Nk} \sim 3$	$\frac{C_V}{Nk} \sim 3$

$$\frac{T_{\mathrm{E}}}{T_{\mathrm{D}}} = \sqrt[3]{\frac{\pi}{6}} = 0.805995977...$$

https://en.wikipedia.org/wiki/Debye_model

https://lampx.tugraz.at/~hadley/ss1/phonons/table/dosdebye.html



The high temperature limit $k_BT >> \hbar\omega_D$

The energy spectral density is,

$$u(\omega) = \frac{3\omega^2}{2\pi^2c^3}\frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_BT}\right)-1}.$$

In the high temperature limit, the exponential factor can be expanded as $\exp\left(\frac{\hbar\omega}{k_BT}\right) \approx 1 + \frac{\hbar\omega}{k_BT}$. The energy spectral density then becomes,

$$u(\omega) = \frac{3\omega^2}{2\pi^2c^3}k_BT.$$

This can be integrated to yield the internal energy density,

$$u = \frac{\omega_D^3}{2\pi^2c^3}k_BT = 3nk_BT.$$

The specific heat has the Dulong-Petit form,

$$c_v = 3nk_B.$$

Phonon density of states of the Debye model

https://lampx.tugraz.at/~hadley/ss1/phonons/table/dosdebye.html

In the Debye model, the dispersion relation is linear, ω = c|k|, and the density of states is quadratic as it is in the long wavelength limit.

$$D(\omega)=\frac{3\omega^2}{2\pi^2c^3}\quad [\text{s rad}^{-1}\ \text{m}^{-3}].$$

Here c is the speed of sound. This holds up to a maximum frequency called the Debye frequency ω_D. In three dimensions there are 3 degrees of freedom per atom so the total number of phonon modes is $3n$.

$$3n=\int_0^{\omega_D} D(\omega)d\omega.$$

Here n is the atomic density. There are no phonon modes with a frequency above the Debye frequency. The Debye freqency is $\omega_D^3=6\pi^2nc^3$.

The form below generates a table of where the first column is the angular frequency ω in rad/s and the second column is the density of states $D(\omega)$ in units of s/(rad m³).

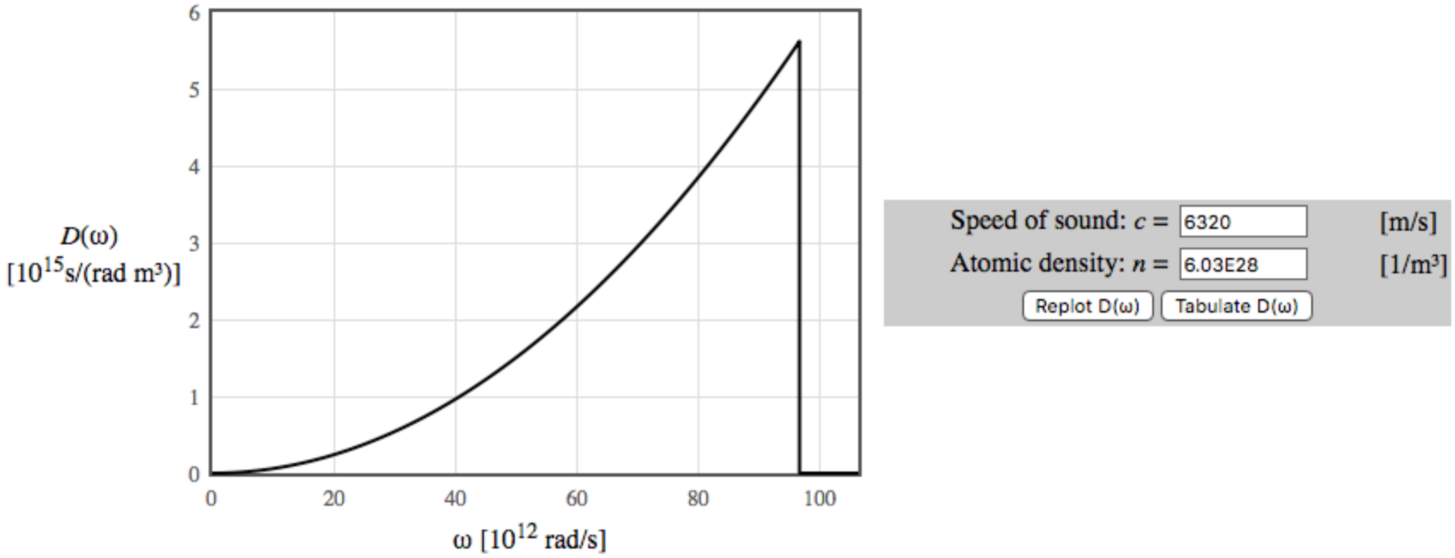
$$u(\omega)=\frac{3\omega^2}{2\pi^2c^3}\frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_BT}\right)-1}.$$

$$\exp\left(\frac{\hbar\omega}{k_BT}\right)\approx 1+\frac{\hbar\omega}{k_BT}$$

$$u(\omega)=\frac{3\omega^2}{2\pi^2c^3}k_BT.$$

$$u=\frac{\omega_D^3}{2\pi^2c^3}k_BT=3nk_BT.$$

$$c_v=3nk_B.$$



Speed of sound: c = 6320 [m/s]

Atomic density: n = 6.03E28 [1/m³]

Debye Model

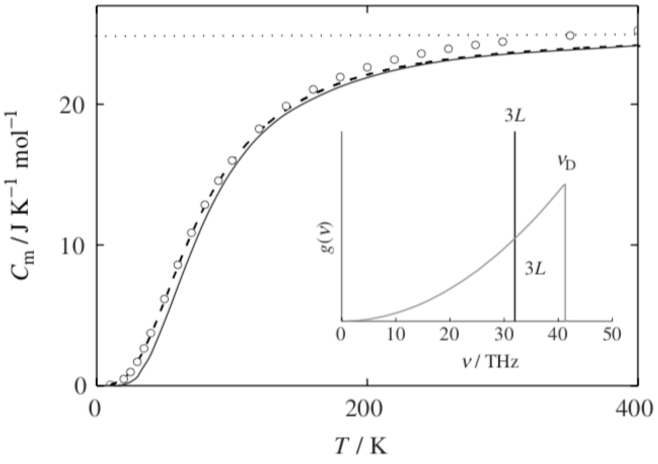


Figure 8.12 Experimental heat capacity of Cu at constant pressure compared with the Debye and Einstein $C_{V,m}$ calculated by using $\Theta_E = 244$ K and $\Theta_D = 314$ K. The vibrational density of states according to the two models is shown in the insert.

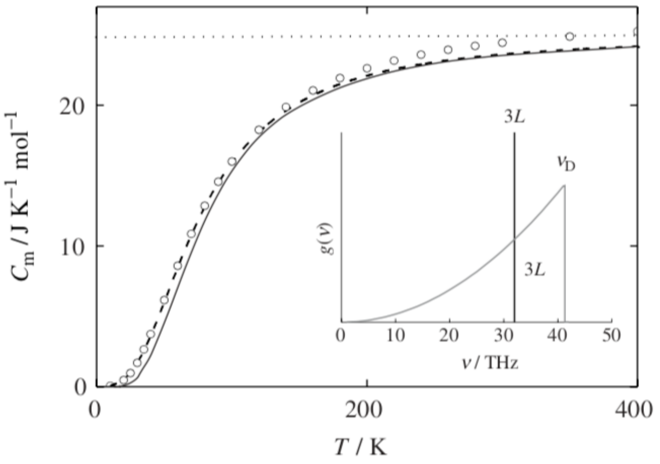
At low temperature
Low energy, low frequency vibrations are excited
These are acoustic mode vibrations
Unit cell vibrates as an entity
Long distances compared to a unit cell

Distribution of frequencies, g(ω), above a cutoff frequency, ω_D

$$g(\omega) = \frac{3\omega^2}{\omega_D^3} \quad \text{for} \quad \omega_D \geq \omega$$

$$g(\omega) = 0 \quad \text{for} \quad \omega > \omega_D$$

Debye Model



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At low temperature
Low energy, low frequency vibrations are excited
These are acoustic mode vibrations
Unit cell vibrates as an entity
Long distances compared to a unit cell

Quantized energy levels

$$\varepsilon = \hbar\omega$$

Energy also equals kT
This defines the Debye temperature, θ_D

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = 2\pi\,\frac{h\nu_D}{k_B}$$

Debye Model

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = 2\pi\frac{h\nu_D}{k_B}$$

Einstein Model

$$C_{V,m} = \left(\frac{d\bar{U}}{dT}\right)_V = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T)-1]^2}$$

Einstein temperature: $\Theta_E = \frac{\hbar\omega_E}{k_B}$

Heat Capacity is given by,

$$C_{V,m} = 9R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{e^x}{(e^x-1)^2} x^4 dx$$

At Low T this reduces to, $C_V = \frac{12\pi^4}{5}R\left(\frac{T}{\Theta_D}\right)^3$

The T^3 dependence is seen experimentally

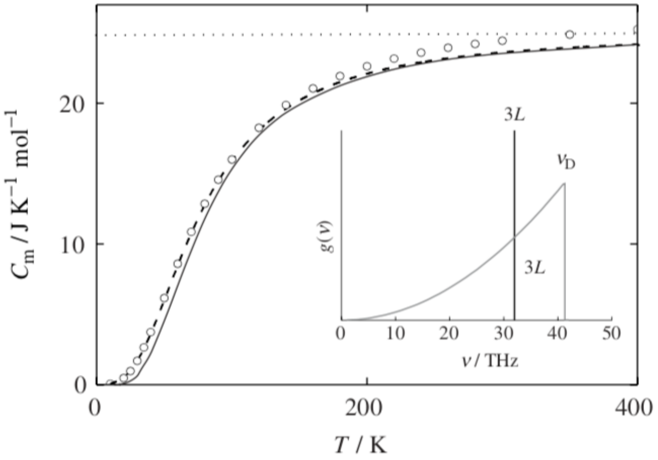
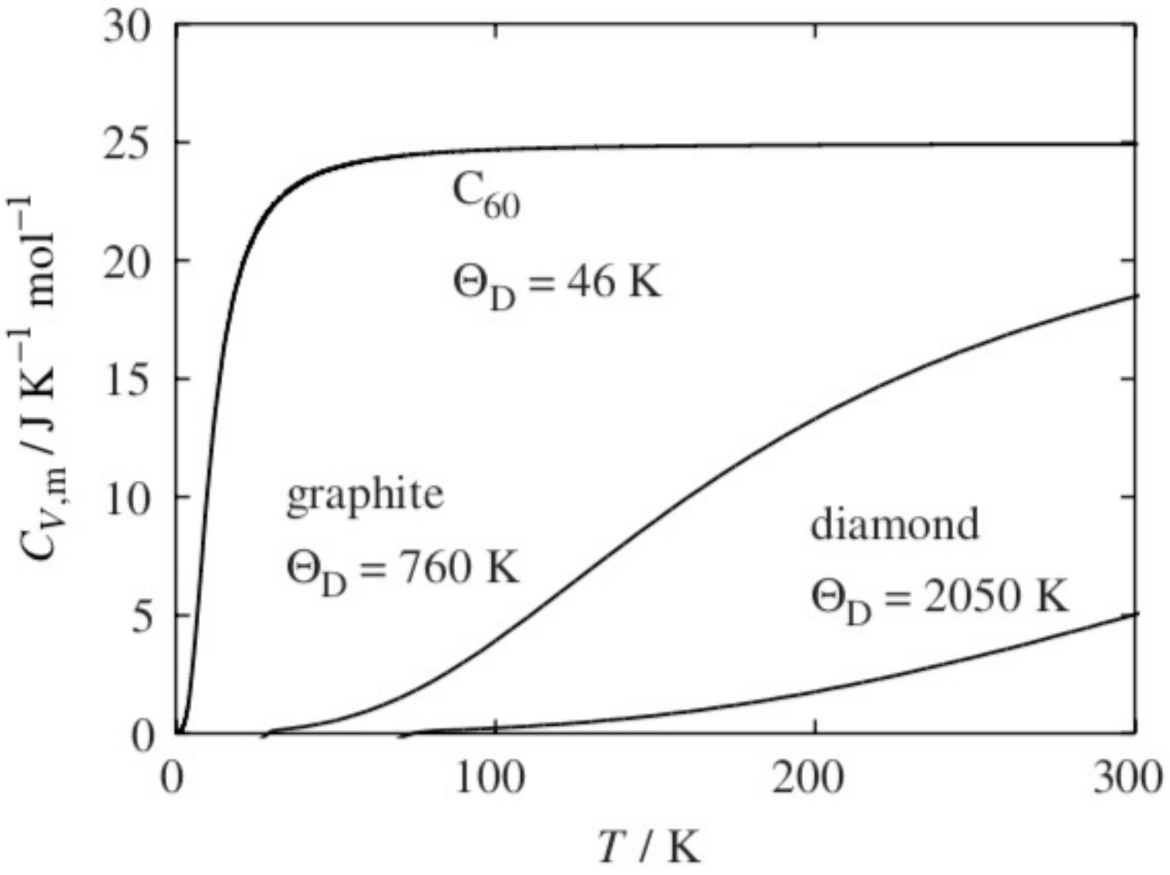


Figure 8.12 Experimental heat capacity of Cu at constant pressure compared with the Debye and Einstein $C_{V,m}$ calculated by using $\Theta_E = 244$ K and $\Theta_D = 314$ K. The vibrational density of states according to the two models is shown in the insert.

$$\Theta_D = 315 \text{ K}$$
$$\Theta_E = 244 \text{ K}$$

Higher Characteristic T
represents stronger bonds



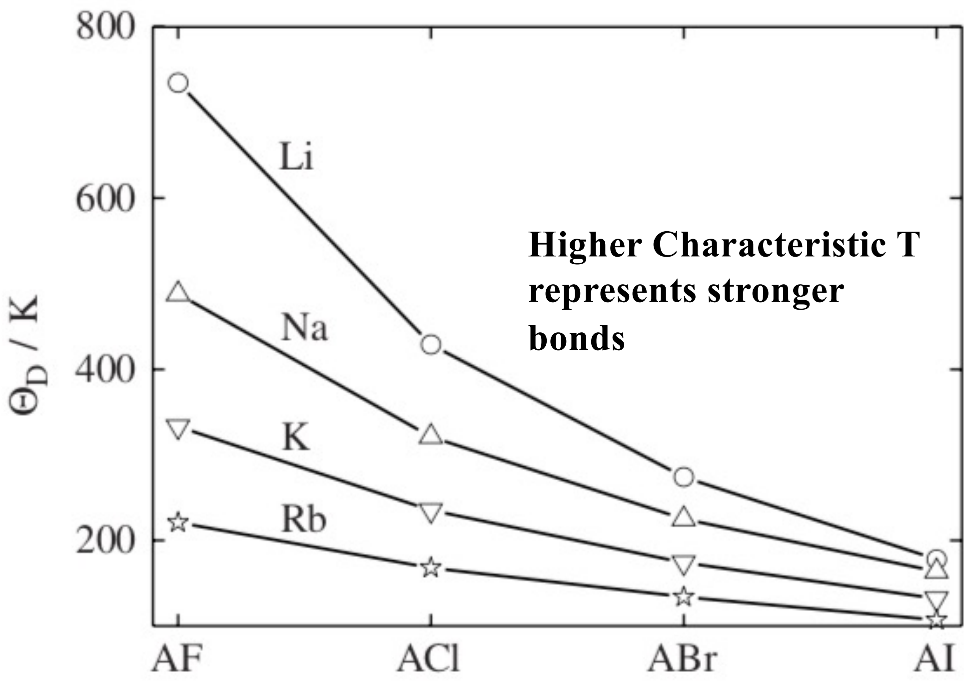
Higher Characteristic T
represents stronger bonds

Figure 8.13 Lattice heat capacity of three different polymorphs of carbon; C_{60} [5], graphite and diamond.

Table 8.2. Debye temperature (Θ_D in K) and electronic heat capacity coefficient (see Section 8.4) (γ in mJ K^{-1} mol^{-1}) of the elements.

Li 344 18	Be 1440 2						A Θ_D γ					B	C 2050 0	N	O	F	Ne 75
Na 158 14	Mg 400 14											Al 428 14	Si 645	P	S	Cl	Ar 92
K 91 21	Ca 230 77	Sc 360	Ti 420 36	V 380 92	Cr 630 16	Mn 410 180	Fe 470 50	Co 445 48	Ni 450 73	Cu 315 7	Zn 327 6	Ga 320 6	Ge 374	As 282	Se 90	Br	Kr 72
Rb 56 24	Sr 147 37	Y 280	Zr 291 30	Nb 275 88	Mo 450 21	Tc	Ru 600 34	Rh 480 49	Pd 274 100	Ag 225 6	Cd 209 7	In 108 18	Sn 200 18	Sb 211	Te 153	I	Xe 64
Cs 33 32	Ba 110 27	La 142	Hf 252 26	Ta 240 59	W 400 12	Re 430 25	Os 500 24	Ir 420 31	Pt 240 66	Au 165 7	Hg 72 19	Tl 79 15	Pb 105 34	Bi 119	Po	At	Rn

Higher Characteristic T represents stronger bonds

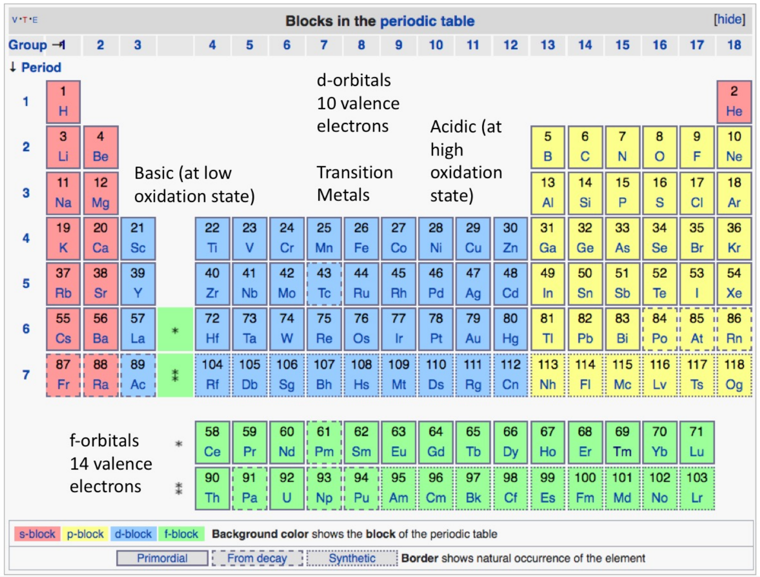


Higher Characteristic T represents stronger bonds

Figure 8.14 Debye temperature of the alkali halides.

Basic

s-orbitals
2 valence
electrons
(more
basic to
right)



Blocks in the periodic table

Group → / ↓ Period	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	‡	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				‡	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

s-block p-block d-block f-block **Background color** shows the **block** of the periodic table

Primordial From decay Synthetic **Border** shows natural occurrence of the element

d-orbitals
10 valence
electrons

Basic (at low
oxidation state)

Transition
Metals

Acidic (at
high
oxidation
state)

f-orbitals
14 valence
electrons

Acidic

p-orbitals
6 valence
electrons
(more
acidic to
right)

Modulus and Heat Capacity

$\sigma = E\,\varepsilon$

$F/A = E\,\Delta d/d$

$F = K\,\Delta d$

$K = F/\Delta d = E\,A/d$

At large q, $\omega = \sqrt{(4K/m)}$

This yields ω_D from E

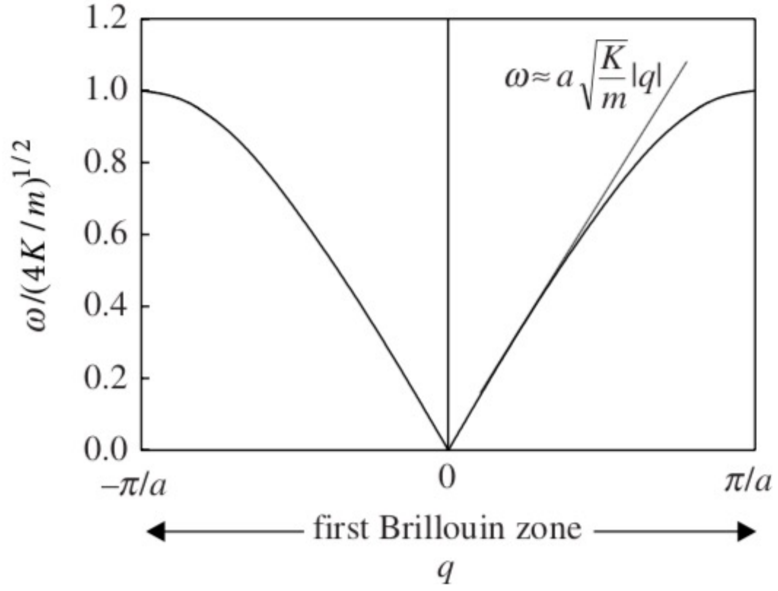
For Cu, $\theta_D = 344\text{K}$

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = 2\pi\frac{h\nu_D}{k_B}$$

$\omega_D = 32\ \text{THz}$

$K = 13.4\ \text{N/m}$

$\omega_D = 18\ \text{THz}$



Modulus and Heat Capacity

The Debye Temperature reflects the highest energy, lowest wave vector vibrations so the linear part of the dispersion curve

$$\Theta_{\mathrm{D}} = \frac{\hbar\omega_{\mathrm{D}}}{k_{\mathrm{B}}} = 2\pi\,\frac{h\nu_{\mathrm{D}}}{k_{\mathrm{B}}}$$

Pergamon Acta mater. 49 (2001) 947–961 www.elsevier.com/locate/actamat

CALCULATION OF DEBYE TEMPERATURE FOR
CRYSTALLINE STRUCTURES—A CASE STUDY ON Ti, Zr, AND
Hf

Q. CHEN† and B. SUNDMAN

Department of Materials Science and Engineering, Royal Institute of Technology, S-10044 Stockholm, Sweden

$$\theta_D(0) = 1.15k(0.43)\frac{\hbar}{k_B}(48\pi^5)^{1/6}\sqrt{\frac{r_0B}{M}} \qquad (15)$$
$$= 0.5\frac{\hbar}{k_B}(48\pi^5)^{1/6}\sqrt{\frac{r_0B}{M}}.$$

$$\theta_D(0) = 0.86k^{Hex}\frac{\hbar}{k_B}(48\pi^5)^{1/6}\sqrt{\frac{r_0B}{M}} \qquad (19)$$
$$= 0.70\frac{\hbar}{k_B}(48\pi^5)^{1/6}\sqrt{\frac{r_0B}{M}}.$$

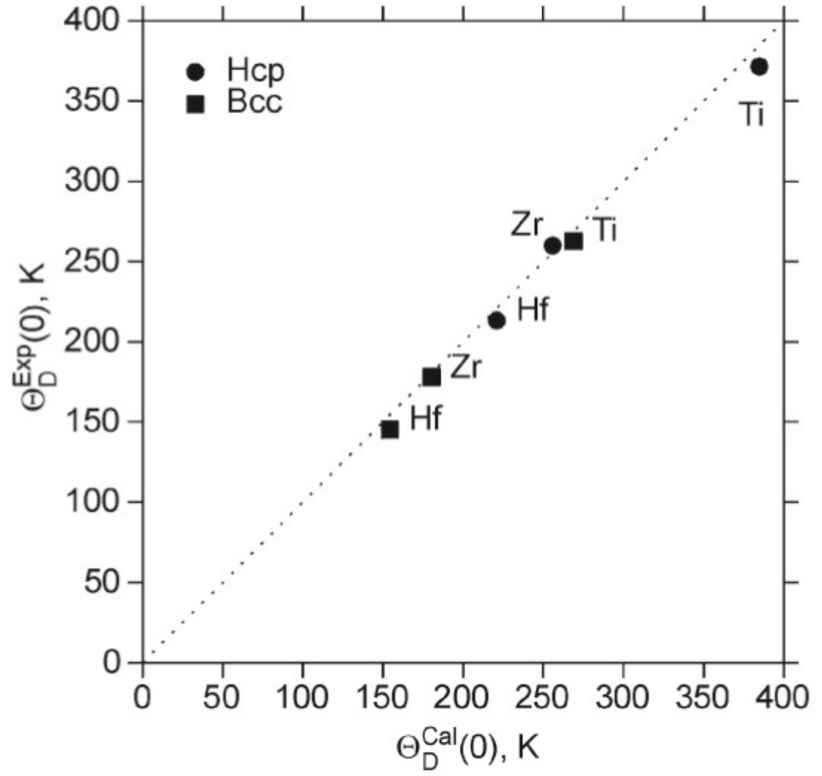


Fig. 13. Comparison of the calculated and experimental high temperature entropy–Debye temperature $\theta_D(0)$ for hcp and bcc Ti, Zr, and Hf.

Table 8.3 Comparison of Debye temperatures derived from heat capacity data and from elastic properties.

	Ag	Cu	Al	NaCl	KBr	LiF
Θ_D(Elastic)	226.4	344.4	428.2	321.9	182.8	834.1
Θ_D(CV)	226.2	345.1	426	320	184	838

How to obtain C_p from calculated C_V?

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{\alpha^2 VT}{\kappa_T}$$

At low T
$C_V = C_p$

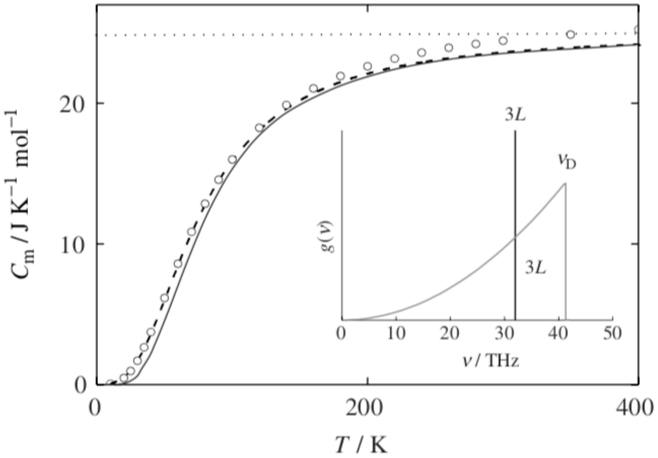
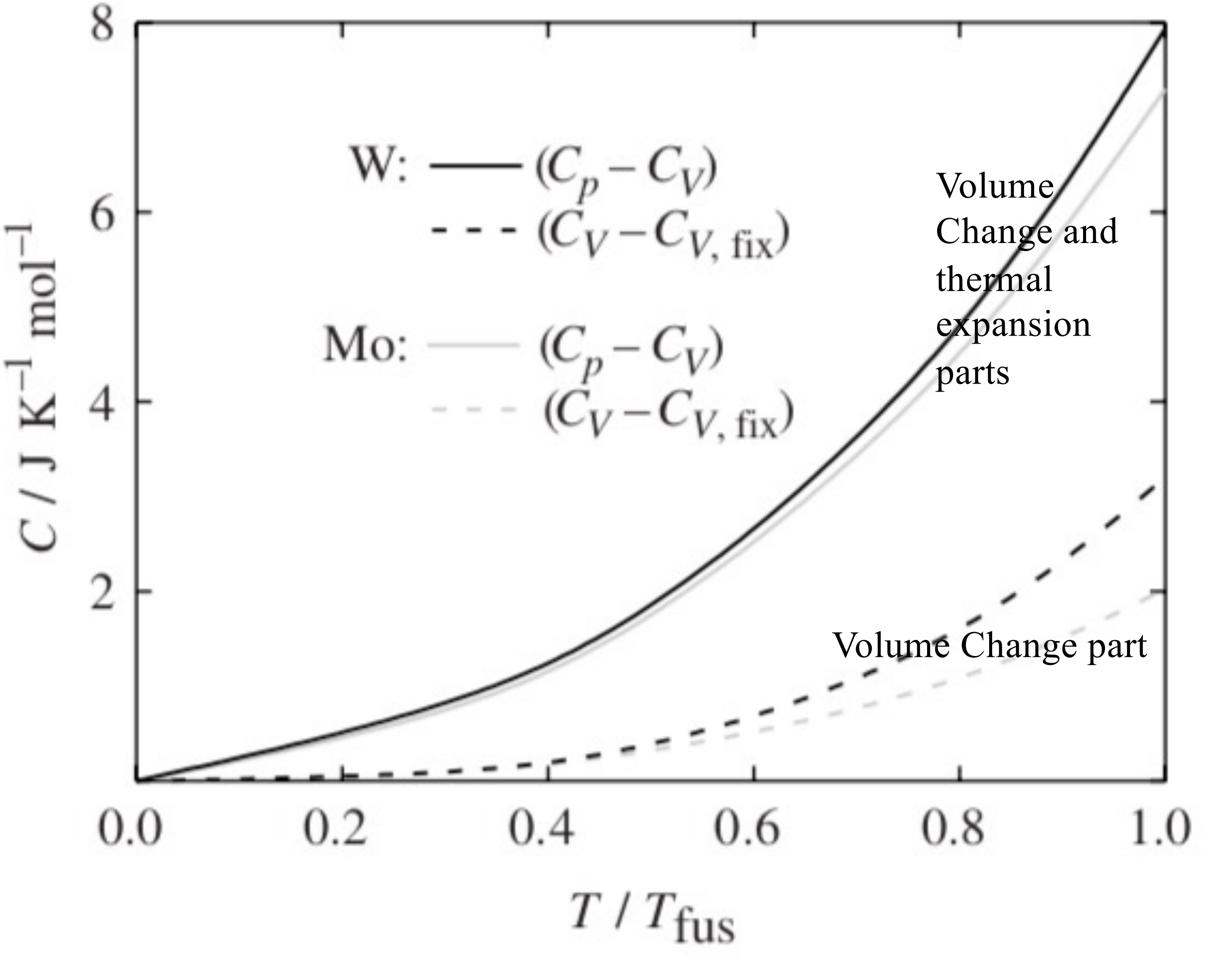


Figure 8.12 Experimental heat capacity of Cu at constant pressure compared with the Debye and Einstein $C_{V,\mathrm{m}}$ calculated by using $\Theta_E = 244$ K and $\Theta_D = 314$ K. The vibrational density of states according to the two models is shown in the insert.

The harmonic oscillator model assumes constant volume
So, deviations for constant pressure are related to "anharmonic" vibrations
Anharmonic vibrations contribute to the heat capacity
They also lead to a finite thermal expansion coefficient



Volume Change and thermal expansion parts

Volume Change part

Anharmonic vs Harmonic Contributions to Heat Capacity (due to thermal expansion and thermal conductivity)

Figure 8.15 $C_{p,\mathrm{m}} - C_{V,\mathrm{m}}$ and $C_{V,\mathrm{m}} - C_{V,\mathrm{m},\mathrm{fix}}$ for Mo and W [6

Approximate relationships for C_p - C_V

Nernst–Lindeman relationship *If you don't know the thermal expansion coefficient*

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{V\alpha^2}{\kappa_T C_{p,\mathrm{m}}^2} C_{p,\mathrm{m}}^2 T = A C_{p,\mathrm{m}}^2 T$$

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{\alpha^2 VT}{\kappa_T}$$

If you know the thermal expansion coefficient,

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \gamma_{\mathrm{G}} \alpha C_{V,\mathrm{m}} T$$

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \frac{\alpha^2 VT}{\kappa_T}$$

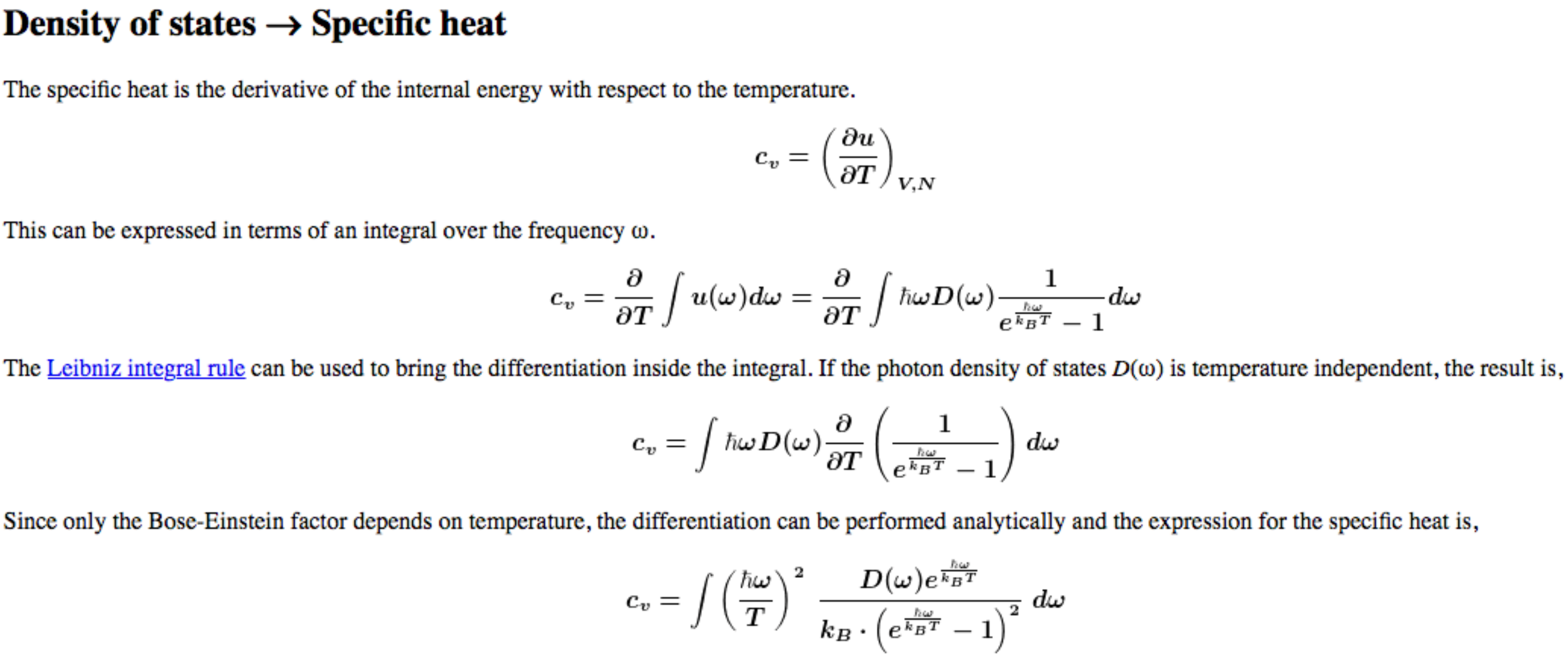
$$\gamma_{\mathrm{G}} = \left[\frac{\partial p}{\partial (U/V)}\right]_V = \frac{\alpha V}{\kappa_T C_{V,\mathrm{m}}}$$

Grüneisen parameter

How does the frequency of vibration change with specific volume of a unit cell

$$\gamma_i = -\frac{V}{\omega_i}\frac{\partial \omega_i}{\partial V}$$

http://lampx.tugraz.at/~hadley/ss1/dbr/dos2cv.html



Density of states → Specific heat

The specific heat is the derivative of the internal energy with respect to the temperature.

$$c_v = \left(\frac{\partial u}{\partial T}\right)_{V,N}$$

This can be expressed in terms of an integral over the frequency ω.

$$c_v = \frac{\partial}{\partial T}\int u(\omega)d\omega = \frac{\partial}{\partial T}\int \hbar\omega D(\omega)\frac{1}{e^{\frac{\hbar\omega}{k_BT}}-1}d\omega$$

The Leibniz integral rule can be used to bring the differentiation inside the integral. If the photon density of states $D(\omega)$ is temperature independent, the result is,

$$c_v = \int \hbar\omega D(\omega)\frac{\partial}{\partial T}\left(\frac{1}{e^{\frac{\hbar\omega}{k_BT}}-1}\right)d\omega$$

Since only the Bose-Einstein factor depends on temperature, the differentiation can be performed analytically and the expression for the specific heat is,

$$c_v = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega)e^{\frac{\hbar\omega}{k_BT}}}{k_B\cdot\left(e^{\frac{\hbar\omega}{k_BT}}-1\right)^2}d\omega$$

Spectroscopy measures vibrations, this can be used to calculate the density of states, this can be integrated to obtain the heat capacity

Number of vibrational modes $3N_A g(\nu)\mathrm{d}\nu$ where $\int_0^\infty g(\nu)\mathrm{d}\nu = 1$

IR: High Polarity
Motion of charged atoms under electromagnetic field

NaCl

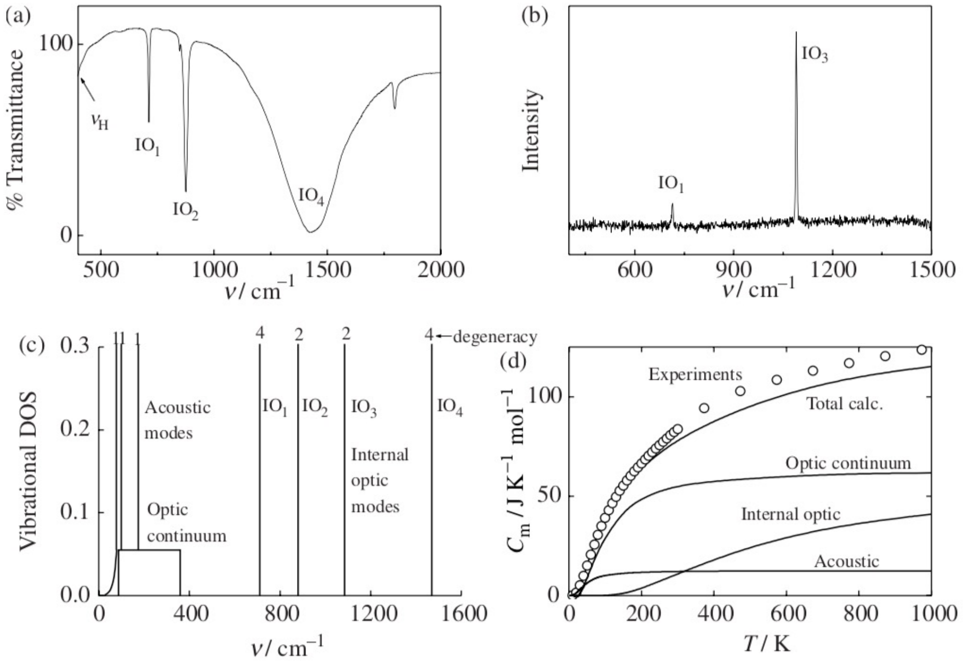
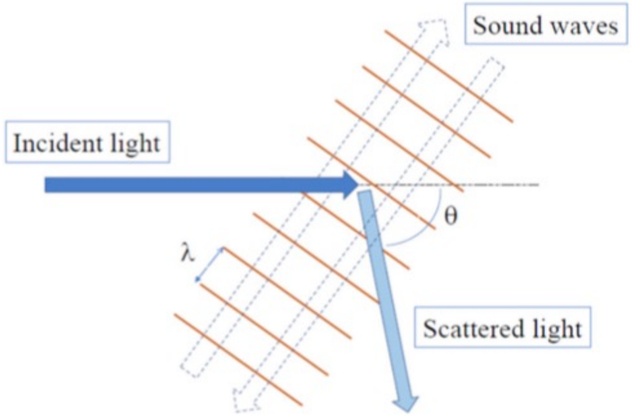


Figure 8.16 (a) IR and (b) Raman spectra for the mineral calcite, $CaCO_3$. The estimated density of vibrational states is given in (c) while the deconvolution of the total heat capacity into contributions from the acoustic and internal optic modes as well as from the optic continuum is given in (d).

Raman: High Polarizability
Motion of electrons in polarizable bonds under electromagnetic field

Benzene, Graphene, Nanotubes,

Spectroscopy measures vibrations, this can be used to calculate the density of states, this can be integrated to obtain the heat capacity




materials

Review

100th Anniversary of Brillouin Scattering: Impact on Materials Science

Seiji Kojima

Materials **2022**, *15*, 3518.

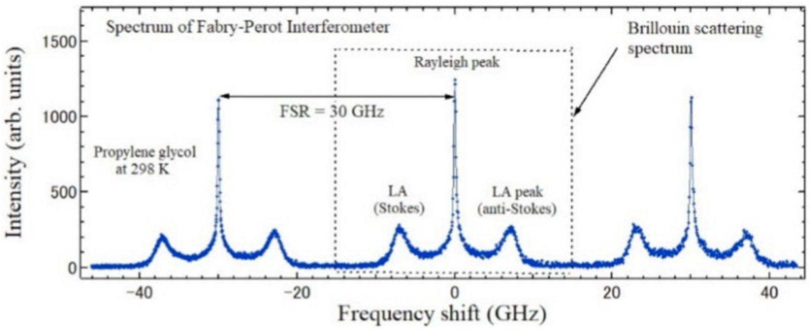


Figure 2. The spectrum of an angular dispersive Fabry-Perot interferometer of propylene glycol in a liquid phase at 298 K with the free spectral range of 30 GHz.

Spectroscopy measures vibrations, this can be used to calculate the density of states, this can be integrated to obtain the heat capacity

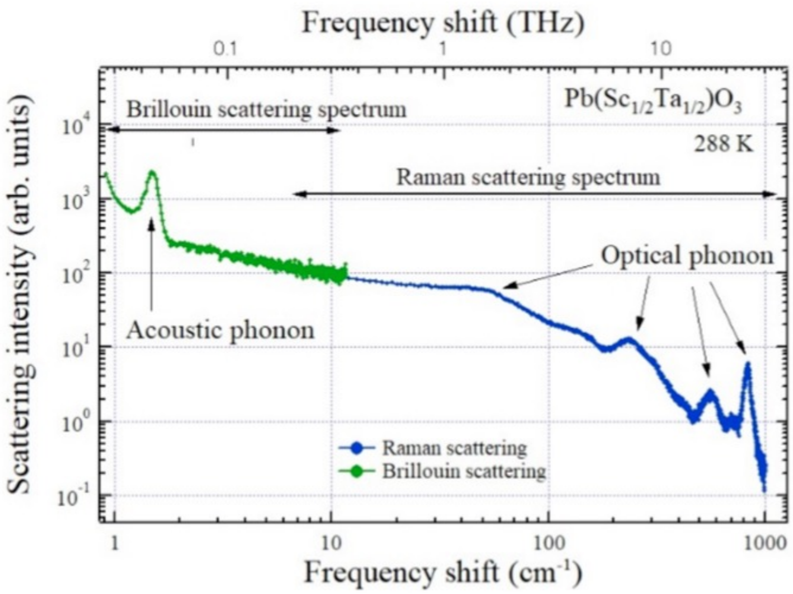
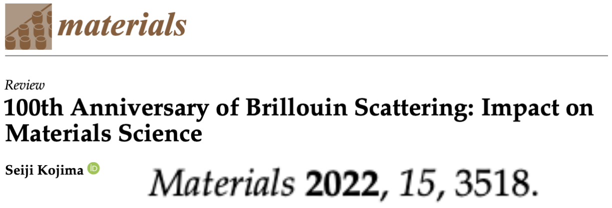


Figure 3. Broadband inelastic light scattering spectrum of a ferroelectric Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ crystal. Brillouin and Raman scattering spectra were measured by a tandem multi-pass FPI and triple-grating spectrometer, respectively [22].


materials

Review

100th Anniversary of Brillouin Scattering: Impact on Materials Science

Seiji Kojima

Materials **2022**, *15*, 3518.

Entropy from Heat Capacity

-SUV
 H   A
-pGT

$C_V = (dU/dT)_V$
From the Thermodynamic Square
$dU = TdS – pdV$ so $C_V = (dU/dT)_V = T\ (dS/dT)_V - p\ (dV/dT)_V$
Second term is 0 dV at constant V is 0
$(dS/dT)_V = C_V/T$
Similarly
$C_p = (dH/dT)_p$
From the Thermodynamic Square
$dH = TdS + Vdp$ so $C_p = (dH/dT)_p = T\ (dS/dT)_p - V\ (dp/dT)_p$
Second term is 0 dp at constant p is 0
$(dS/dT)_p = C_p/T$

Integrate $C_p/T\ dT$ or Integrate $C_V/T\ dT$ to obtain S

Low Temperatures Solve Numerically
High Temperatures Series Expansion

$$S = 3R\left[\frac{4}{3} + \ln\left(\frac{T}{\theta_i}\right) + \frac{1}{40}\left(\frac{\theta_i}{T}\right)^2 - \frac{1}{2240}\left(\frac{\theta_i}{T}\right)^4 + \dots\right]$$

$$C_{V,\mathrm{m}} = 3R\left(\frac{\Theta_\mathrm{E}}{T}\right)^2 \frac{\exp(\Theta_\mathrm{E}/T)}{[\exp(\Theta_\mathrm{E}/T) - 1]^2}$$

$$S_\mathrm{E} = 3R\left[\frac{\Theta_\mathrm{E}/T}{[\exp(\Theta_\mathrm{E}/T) - 1]} - \ln[1 - \exp(-\Theta_\mathrm{E}/T)]\right]$$

$$\theta_\mathrm{E} = \hbar\omega_\mathrm{E}/k_\mathrm{B}$$

$$C_{V,\mathrm{m}} = 9R\left(\frac{T}{\Theta_\mathrm{D}}\right)^3 \int_0^{\Theta_\mathrm{D}/T} \frac{e^x}{(e^x - 1)^2} x^4\,\mathrm{d}x$$

$$S_\mathrm{D} = 3R\left[\frac{4T^3}{\Theta_\mathrm{D}^3} \int_0^{\Theta_\mathrm{D}/T} \frac{x^3\,\mathrm{d}x}{[\exp(x) - 1]} - \ln[1 - \exp(-\Theta_\mathrm{D}/T)]\right]$$

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

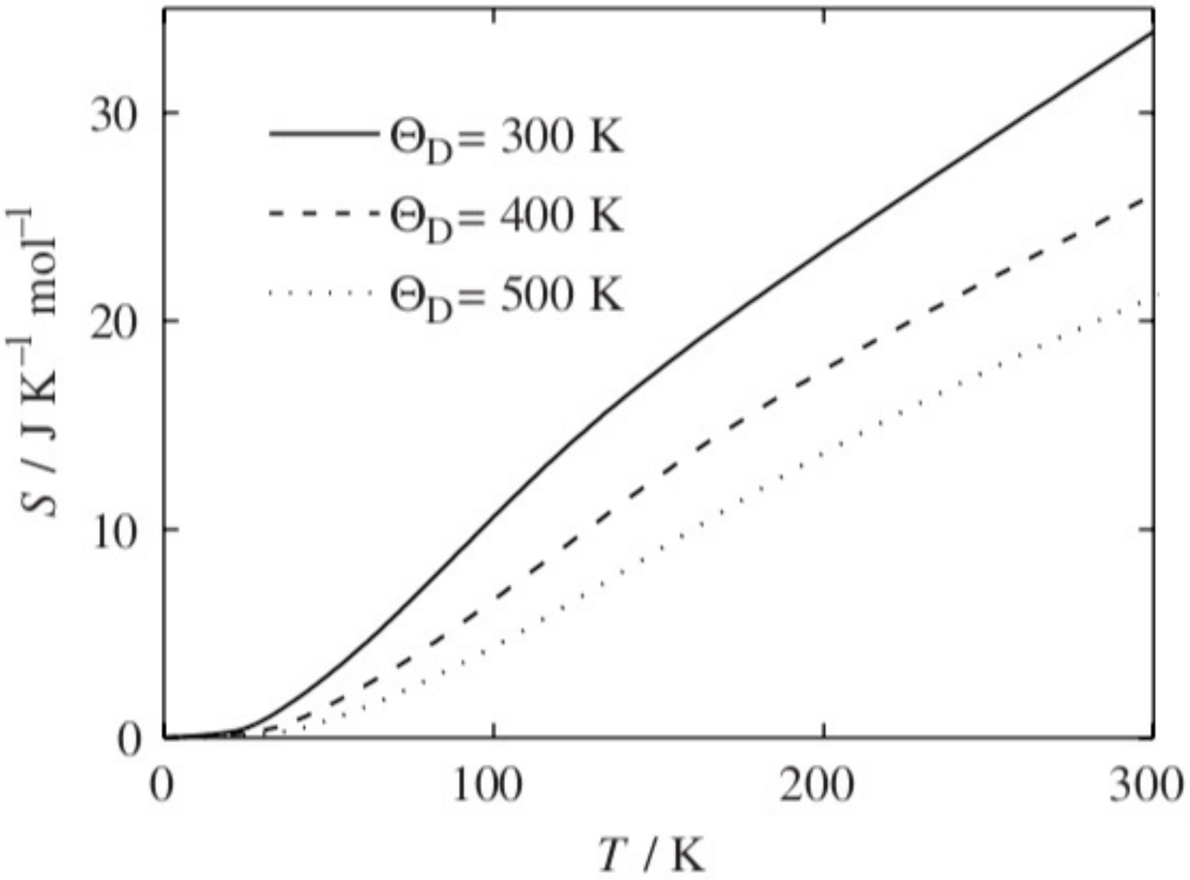


Figure 8.17 Entropy of a monoatomic solid for different values of the Debye temperature, Θ_D.

Calorimetrically determine S at high temperature then find the Debye temperature that makes the calculation of S match

$$S = 3R\left[\frac{4}{3} + \ln\left(\frac{T}{\theta_i}\right) + \frac{1}{40}\left(\frac{\theta_i}{T}\right)^2 - \frac{1}{2240}\left(\frac{\theta_i}{T}\right)^4 + \ldots\right]$$

Large θ_D means more stable

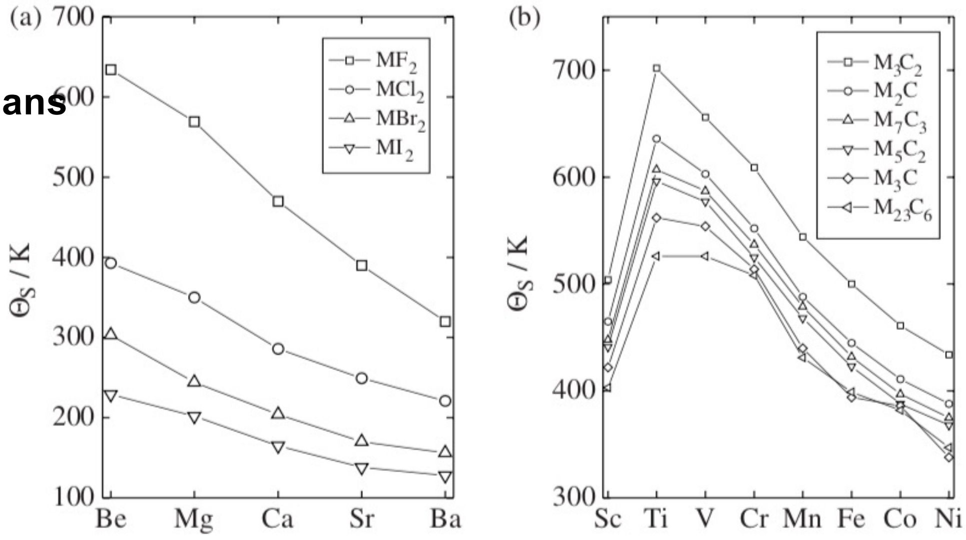
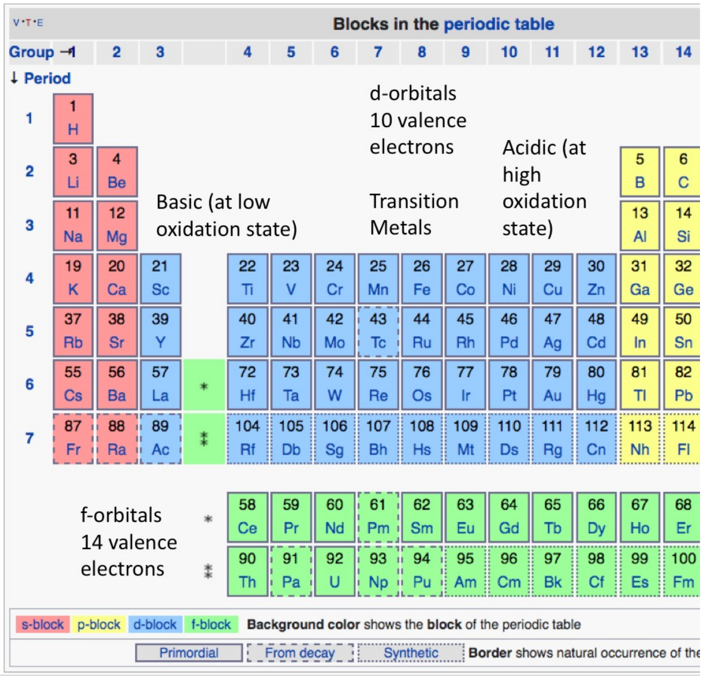


Figure 8.18 Entropy Debye temperature, Θ_S, for (a) alkali earth dihalides [10] and series transition metal carbides [11].

Basic

s-orbitals 2 valence electrons (more basic to right)



Period	1	2	3		4	5	6	7	8	9	10	11	12	13	14
1	1 H														
2	3 Li	4 Be												5 B	6 C
3	11 Na	12 Mg												13 Al	14 Si
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb
7	87 Fr	88 Ra	89 Ac	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl
				*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er
				**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm

s-block p-block d-block f-block **Background color** shows the **block** of the periodic table

Primordial From decay Synthetic **Border** shows natural occurrence of the

d-orbitals 10 valence electrons

Acidic (at high oxidation state)

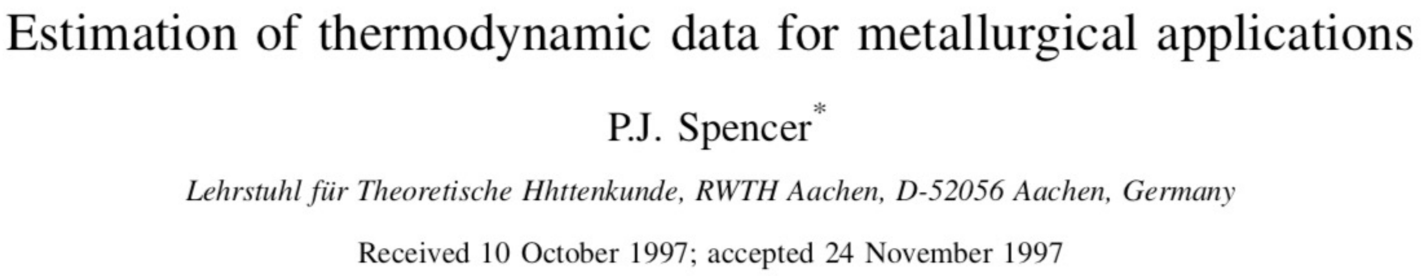
Basic (at low oxidation state)

Transition Metals

f-orbitals 14 valence electrons

Group Contribution Method for Entropy and Heat Capacity

Sum the component entropy and heat capacities



Estimation of thermodynamic data for metallurgical applications

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Received 10 October 1997; accepted 24 November 1997

-SUV
 H   A
-pGT

Entropy correlates with molar volume

Maxwell $(dS/dV)_T = (dp/dT)_V$
Triple product $(dp/dT)_V = -(dV/dT)_P\ (dP/dV)_T$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa_T}$$

or

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial \Theta}{\partial V}\right)_T \left(\frac{\partial S}{\partial \Theta}\right)_T$$

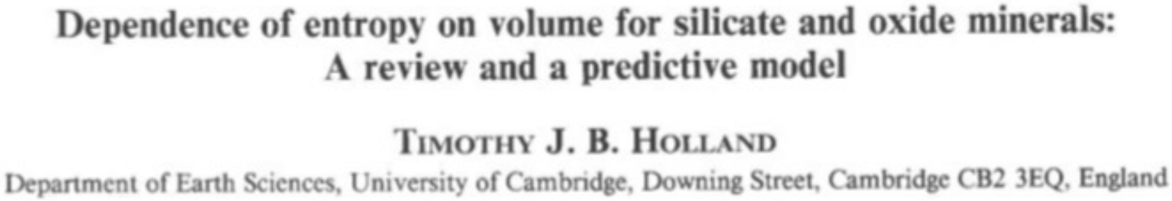
$$\Theta = \Theta_o \left(\frac{V_o}{V}\right)^{1/3}$$

Θ_0 is characteristic T at V_0

$(dS/d\theta)_T$ from

$$S_E = 3R\left[\frac{\Theta_E/T}{[\exp(\Theta_E/T)-1]} - \ln[1-\exp(-\Theta_E/T)]\right]$$

$$S_D = 3R\left[\frac{4T^3}{\Theta_D^3}\int_0^{\Theta_D/T}\frac{x^3\,dx}{[\exp(x)-1]} - \ln[1-\exp(-\Theta_D/T)]\right]$$



Dependence of entropy on volume for silicate and oxide minerals: A review and a predictive model

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$dG = -SdT + Vdp$
For a transition $\Delta G = 0$
And
$dp/dT = \Delta S/\Delta V$
ΔS and ΔV have the same sign

-SUV
H A
-pGT

This isn't true with a change in oxidation state or coordination number

Tetrahedral Si Octahedral Si 50% Octahedral Si
pyroxene > perovskite > garnet > ilmenite entropy

Tetrahedral Si 50% Octahedral Si Octahedral Si
pyroxene < garnet < ilmenite < perovskite Density = mass/volume

All the Si atoms are tetrahedrally coordinated in pyroxene, while 50% are tetrahedrally coordinated and 50% octahedrally coordinated in garnet. In the ilmenite and perovskite modifications all Si atoms are octahedrally coordinated.

Electronic Heat Capacity

Electrons that escape from the valence band to the conduction band have three degrees of freedom so contribute (3/2)R to the heat capacity (Drude Model of conduction)
For monovalent Cu we expect Dulong Petit 3R plus 3/2 R (but we see only 3R so where is the 3/2 R?)

For Cu, (3 + 3/2)R this isn't seen due to quantization of the electron energy level

Fermi Level = Electron energy level that at equilibrium is 50% occupied

Electrons above this energy are free electrons on average

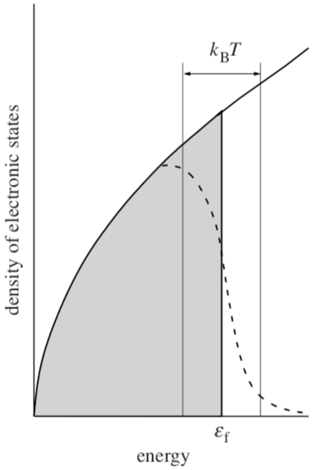
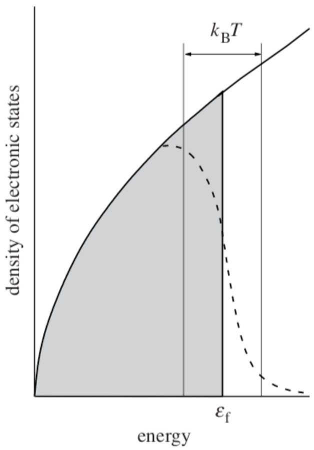


Figure 8.19 Energy distribution for a free electron gas at 0 K (shaded) and an elevated temperature (dashed line), *T*.

Free electron gas at 0 K (shaded)

Excited at T (dashed line)



Heat from 0K to T

$$\Delta U = N_1 k_B T$$

N_1 is the number of electrons excited by kT
These occupy electronic states in a band of kT about the Fermi level

$$N_1 = n(\varepsilon_F) k_B T$$

$n(\varepsilon_F)$ is the number of electrons at the Fermi level

$$\Delta U = n(\varepsilon_F) k_B^2 T^2$$

$$C_E = \frac{\partial \Delta U}{\partial T} = 2n(\varepsilon_F) k_B^2 T$$

$$C_E = \gamma T$$

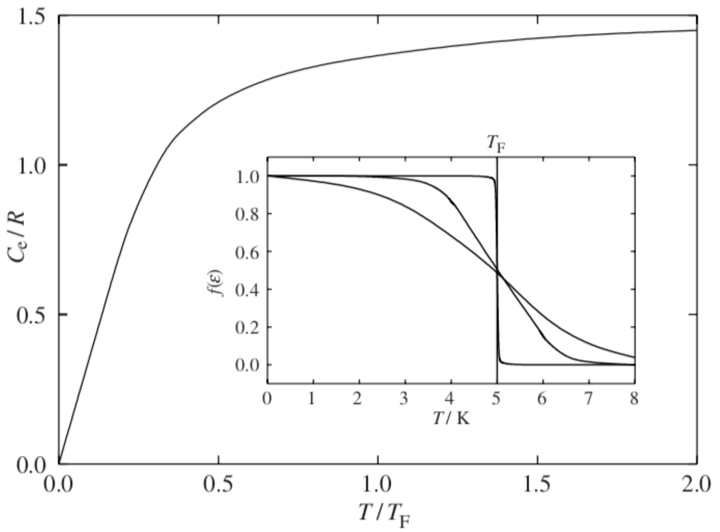


Figure 8.20 Heat capacity of a free electron gas. The population of the electronic states at different temperatures is shown in the insert. T_F is typically of the order of 10^5 K.

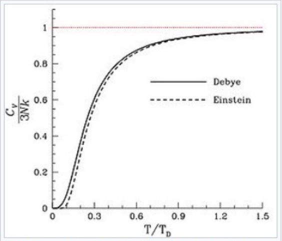
γ is the electronic heat capacity coefficient

γ is 0 for an insulator and has a value for a metal

Table 8.2. Debye temperature (Θ_D in K) and electronic heat capacity coefficient (see Section 8.4) (γ in mJ K^{-1} mol^{-1}) of the elements.

A
Θ_D
γ

Li 344 18	Be 1440 2											B	C 2050 0	N	O	F	Ne 75
Na 158 14	Mg 400 14											Al 428 14	Si 645	P	S	Cl	Ar 92
K 91 21	Ca 230 77	Sc 360	Ti 420 36	V 380 92	Cr 630 16	Mn 410 180	Fe 470 50	Co 445 48	Ni 450 73	Cu 315 7	Zn 327 6	Ga 320 6	Ge 374	As 282	Se 90	Br	Kr 72
Rb 56 24	Sr 147 37	Y 280	Zr 291 30	Nb 275 88	Mo 450 21	Tc	Ru 600 34	Rh 480 49	Pd 274 100	Ag 225 6	Cd 209 7	In 108 18	Sn 200 18	Sb 211	Te 153	I	Xe 64
Cs 33 32	Ba 110 27	La 142	Hf 252 26	Ta 240 59	W 400 12	Re 430 25	Os 500 24	Ir 420 31	Pt 240 66	Au 165 7	Hg 72 19	Tl 79 15	Pb 105 34	Bi 119	Po	At	Rn



Debye vs. Einstein. Predicted heat capacity as a function of temperature.

$$C_E = \gamma T$$

$$C_{V,m} = 9R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{e^x}{(e^x-1)^2} x^4 \, dx$$

For T < 10K

$$C_V = \beta T^3 + \gamma T$$

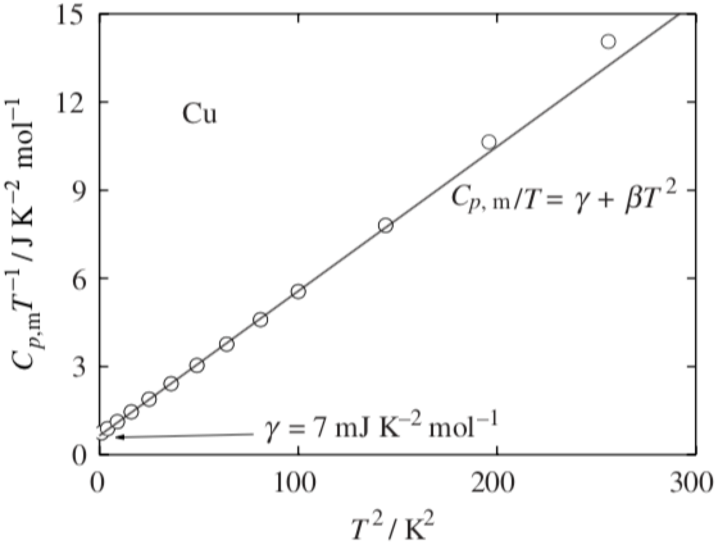
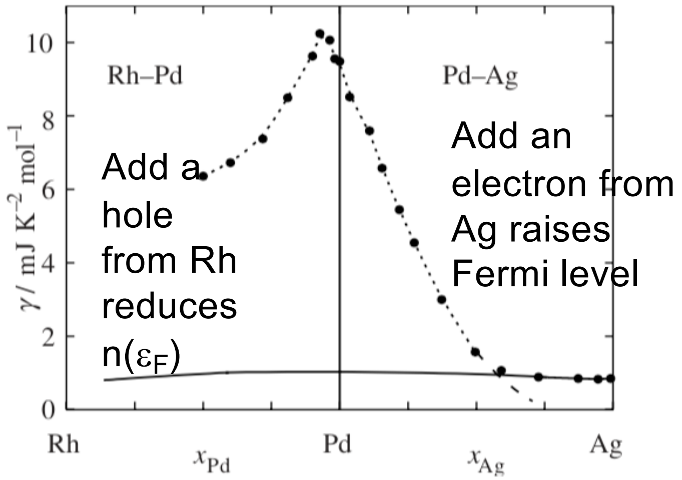


Figure 8.21 Heat capacity of Cu plotted as $C_{p,\mathrm{m}} \cdot T^{-1}$ versus T^2.



Add a hole from Rh reduces n(ε_F)

Add an electron from Ag raises Fermi level

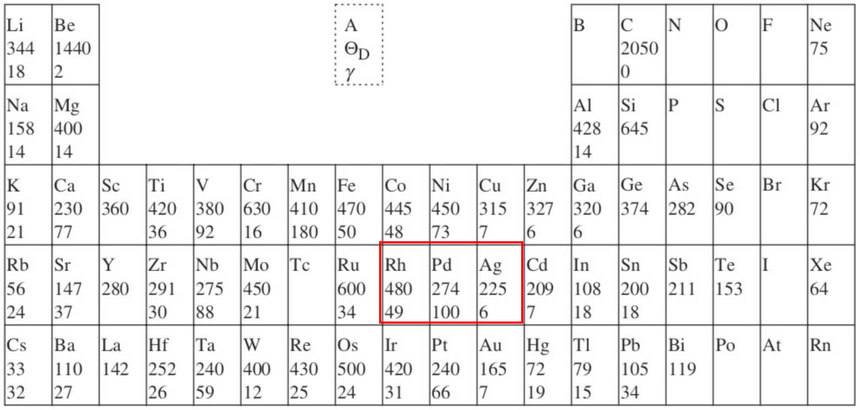
$$C_{\mathrm{E}} = \frac{\partial \Delta U}{\partial T} = 2n(\varepsilon_{\mathrm{F}})k_{\mathrm{B}}^2 T$$

$$C_{\mathrm{E}} = \gamma T$$

Figure 8.22 Variation of the electronic heat capacity coefficient with composition for the alloys Rh–Pd and Pd–Ag [17]. Solid and dotted lines represent the electronic DoS for the 5s and 4d bands, respectively.

A striking example is the electronic heat capacity coefficients observed for Rh–Pd–Ag alloys given in Figure 8.22 [17]. In the rigid band approach, the addition of Ag to Pd gives an extra electron per atom of silver and these electrons fill the band to a higher energy level. Correspondingly, alloying with Rh gives an electron hole per Rh atom and the Fermi level is moved to a lower energy. The variation of the electronic heat capacity coefficient with composition of the alloy maps approximately the shape of such an electron band.

Table 8.2. Debye temperature (Θ_D in K) and electronic heat capacity coefficient (see Section 8.4) (γ in mJ K^{-1} mol^{-1}) of the elements.



Li 344 18	Be 1440 2						A Θ_D γ					B	C 2050 0	N	O	F	Ne 75
Na 158 14	Mg 400 14											Al 428 14	Si 645	P	S	Cl	Ar 92
K 91 21	Ca 230 77	Sc 360	Ti 420 36	V 380 92	Cr 630 16	Mn 410 180	Fe 470 50	Co 445 48	Ni 450 73	Cu 315 7	Zn 327 6	Ga 320 6	Ge 374	As 282	Se 90	Br	Kr 72
Rb 56 24	Sr 147 37	Y 280	Zr 291 30	Nb 275 88	Mo 450 21	Tc	Ru 600 34	Rh 480 49	Pd 274 100	Ag 225 6	Cd 209 7	In 108 18	Sn 200 18	Sb 211	Te 153	I	Xe 64
Cs 33 32	Ba 110 27	La 142	Hf 252 26	Ta 240 59	W 400 12	Re 430 25	Os 500 24	Ir 420 31	Pt 240 66	Au 165 7	Hg 72 19	Tl 79 15	Pb 105 34	Bi 119	Po	At	Rn

Magnetic Heat Capacity

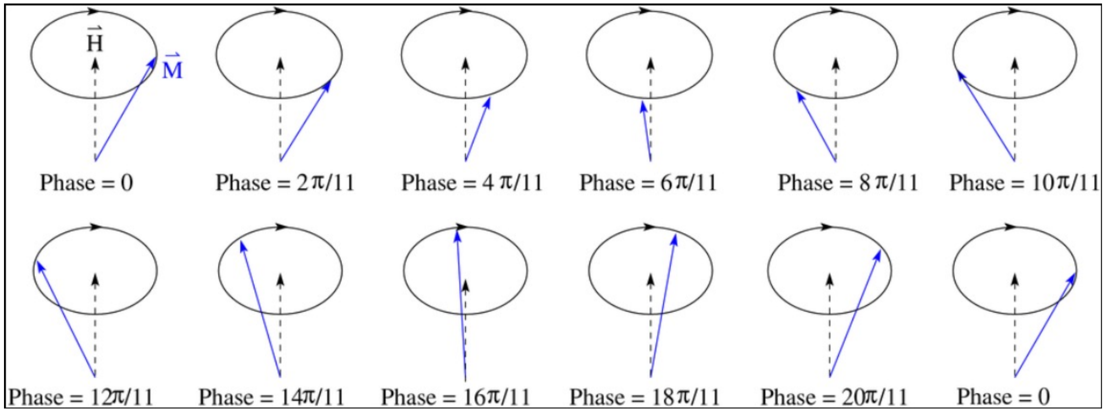
Slide 93 for density of states

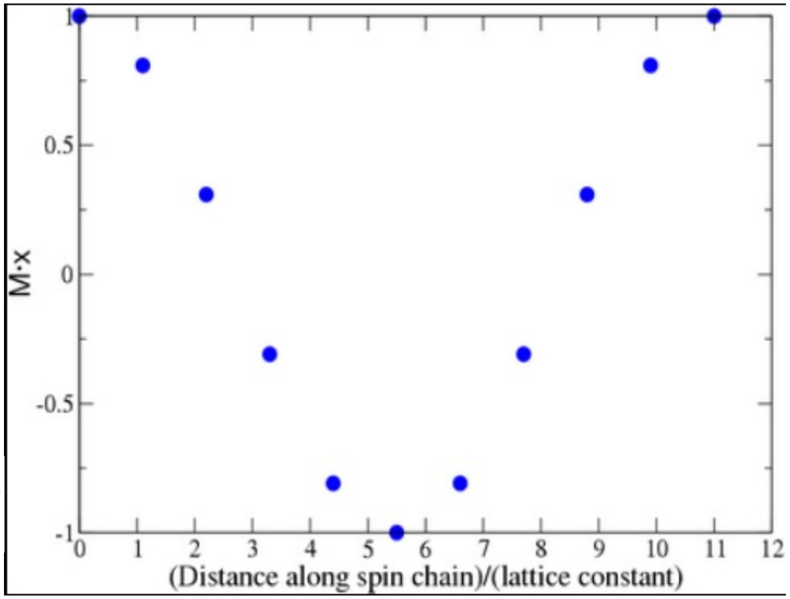
$$c_v = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega)e^{\frac{\hbar\omega}{k_B T}}}{k_B \cdot \left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2}\, d\omega$$

Magnetic excitation
Magnon
Spin waves

$\nu(q)$ $\quad g_{\text{magn}}(\nu)$

Spin waves are propagating disturbances in the ordering of magnetic materials.

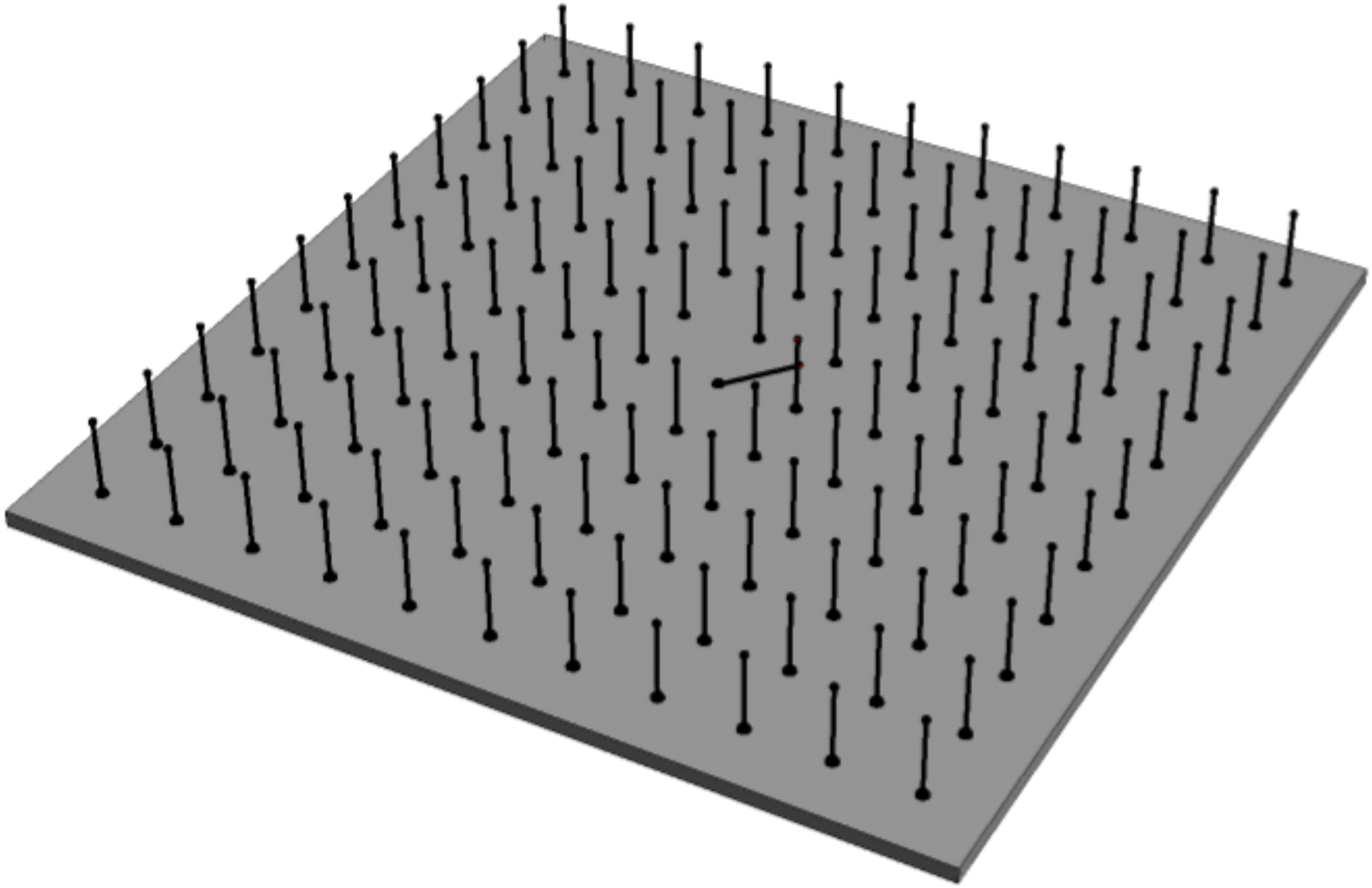




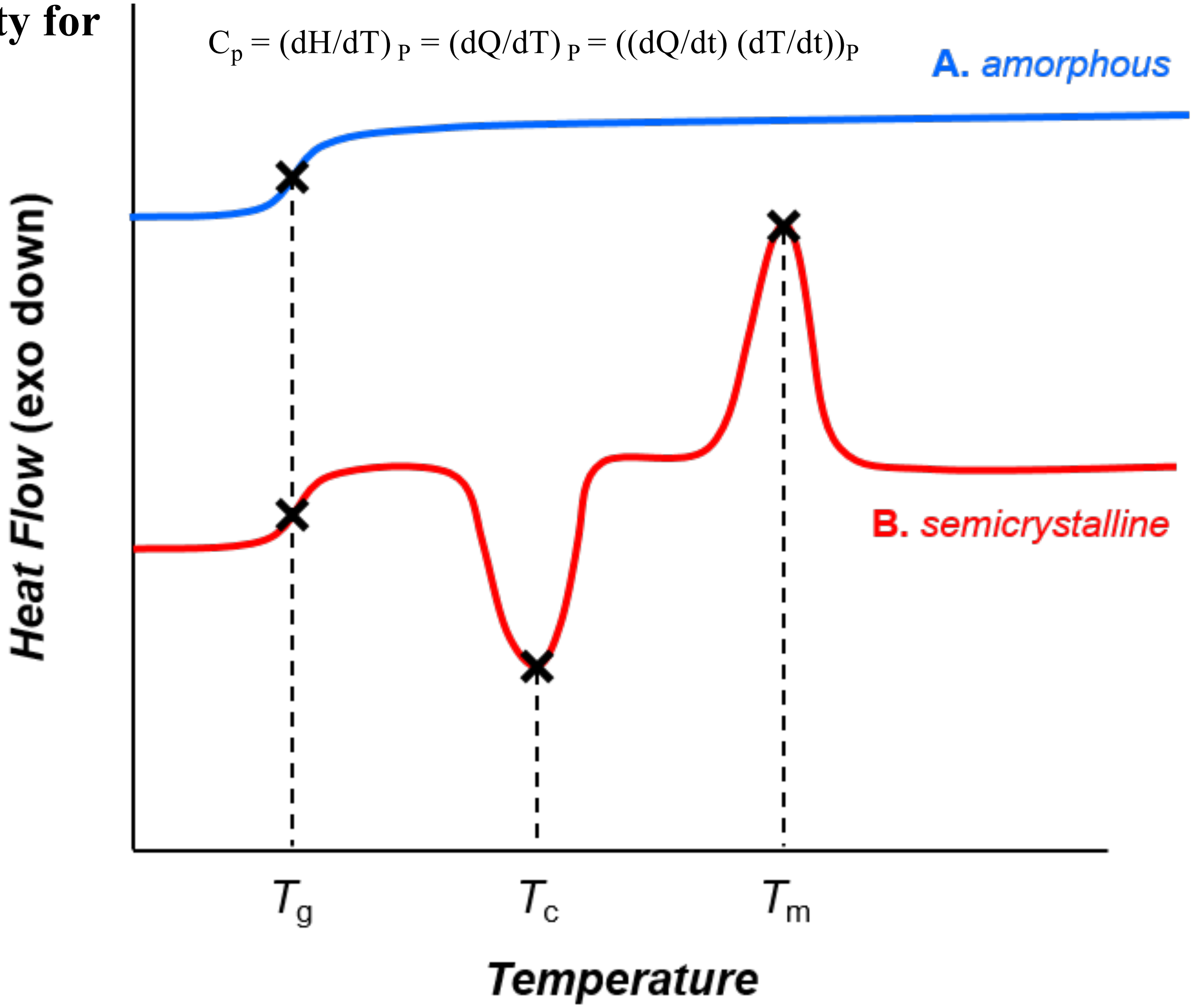
$$C_{\text{magn}} = R\int \frac{x^2 e^x}{(e^x - 1)^2} g_{\text{magn}}(\omega)\mathrm{d}\omega$$

$$x = \hbar\omega / k_B T$$

Ferromagnet $T^{3/2}$ at low T

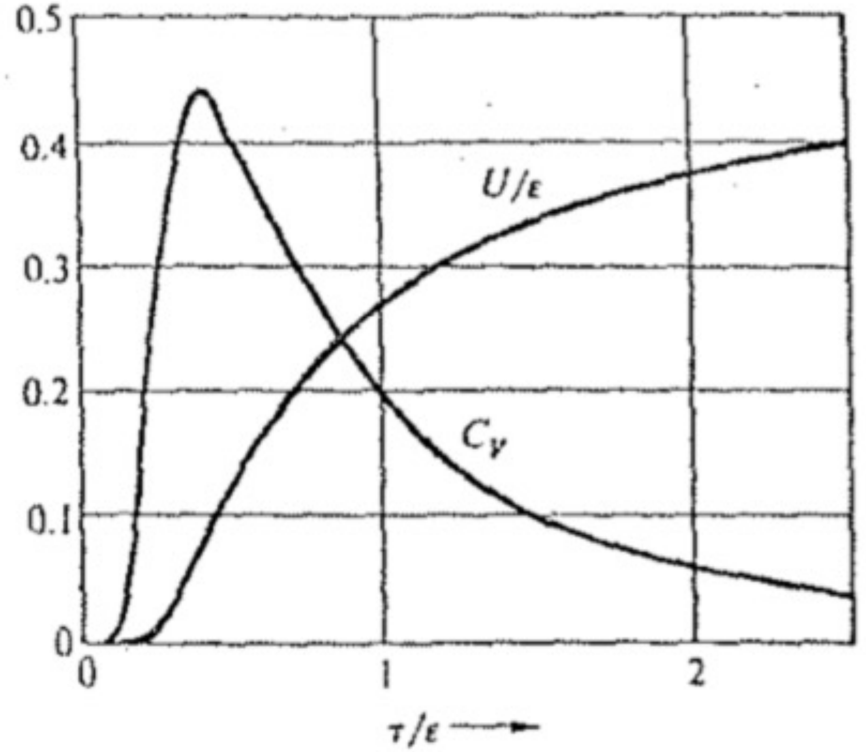


Heat Capacity for Systems that Display a Transition



$C_p = (dH/dT)_P = (dQ/dT)_P = ((dQ/dt)\ (dT/dt))_P$

Heat Capacity for Systems that Display a Transition



Rate of entropy change with T, $C_v = T(dS/dT)_V$,

-increases as kT approaches the transition temperature.

-At high temperatures all states are active so the change in entropy is small.

This results in a peak in C_v and C_p

From Kittel and Kroemer Thermal Physics Chapter 2

For a system with quantized energy and two states ε_1 and ε_2, the ratio of the probabilities of the two states is given by the Boltzmann potentials, (τ is the temperature k_BT)

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}.$$

If state ε_2 is the ground state, $\varepsilon_2 = 0$, and the sum of exponentials is called the partition function Z, and the sum of probabilities equals 1 then,

$Z = \exp(-\varepsilon_2/\tau) + 1$

$$U \equiv \langle \varepsilon \rangle = \frac{\varepsilon \exp(-\varepsilon/\tau)}{Z} = \varepsilon \frac{\exp(-\varepsilon/\tau)}{1 + \exp(-\varepsilon/\tau)}.$$

$$C_V \equiv (\partial U/\partial \tau)_V.$$

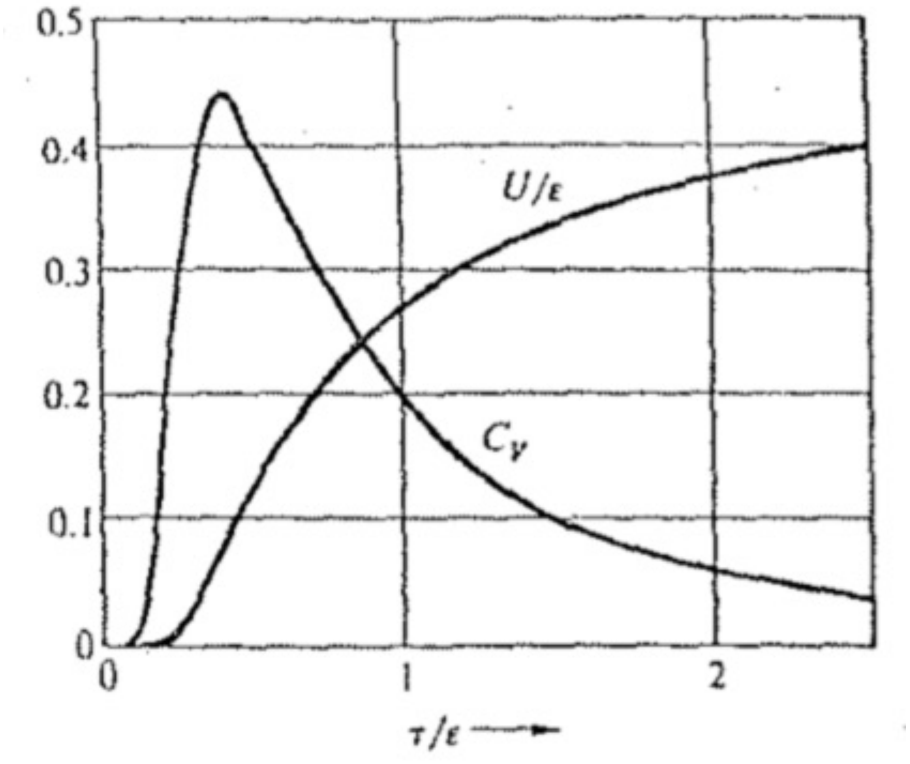
Z normalizes the probability for a state “s”

$$C_V = k_B \left(\frac{\varepsilon}{k_BT}\right)^2 \frac{\exp(\varepsilon/k_BT)}{[\exp(\varepsilon/k_BT) + 1]^2}.$$

$P(\varepsilon_s) = \exp(-\varepsilon_s/\tau)/Z$

The average energy for the system is $U = {(\sum \varepsilon_i e^{-\varepsilon_i/\tau})}/{Z} = \tau^2 \left(\frac{d\ln Z}{d\tau}\right)$

From Kittel and Kroemer Thermal Physics Chapter 2



$$U \equiv \langle \varepsilon \rangle = \frac{\varepsilon \exp(-\varepsilon/\tau)}{Z} = \varepsilon \frac{\exp(-\varepsilon/\tau)}{1 + \exp(-\varepsilon/\tau)}.$$

$$C_V = k_B \left(\frac{\varepsilon}{k_B T} \right)^2 \frac{\exp(\varepsilon/k_B T)}{[\exp(\varepsilon/k_B T) + 1]^2}.$$

First term decays with $(\varepsilon/kT)^2$

Second term increases with ~ $\exp(-\varepsilon/kT)$

Metal-Insulator Transition

First order transition at T_{trs} between an insulator $\gamma = 0$ and a metal $\gamma = \gamma_{met}$

A quantum transition, critical quantum behavior

$$\Delta_{\text{ins-met}} S_m = \gamma_{met} T_{trs}$$

Transition can occur on doping of an oxide like Fe_2O_3
Temperature or Pressure Changes

$$(dS/dT)_p = C_p / T$$

Magnetic Order-Disorder Transition

At the Curie temperature material goes from a ferromagnet to a paramagnet and loses magnetic order

This impacts the entropy and heat capacity

Maximum total order-disorder entropy can be calculated, ΔS

N_{un} unpaired electrons

total spin quantum number $\mathscr{S} = \Sigma \frac{1}{2} N_{\mathrm{un}}$

$(2\mathscr{S} + 1)$ quantized orientations

$k_B \ln(2\mathscr{S} + 1)$ per particle

$$\Delta S = R \ln(2\mathscr{S} + 1)$$

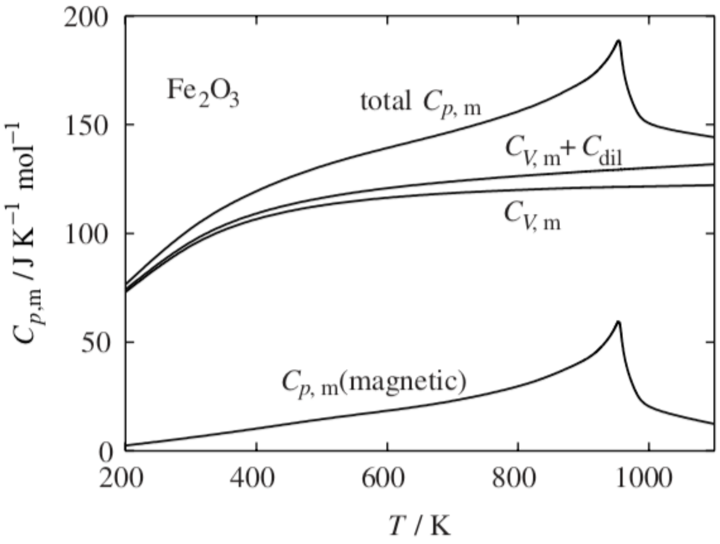
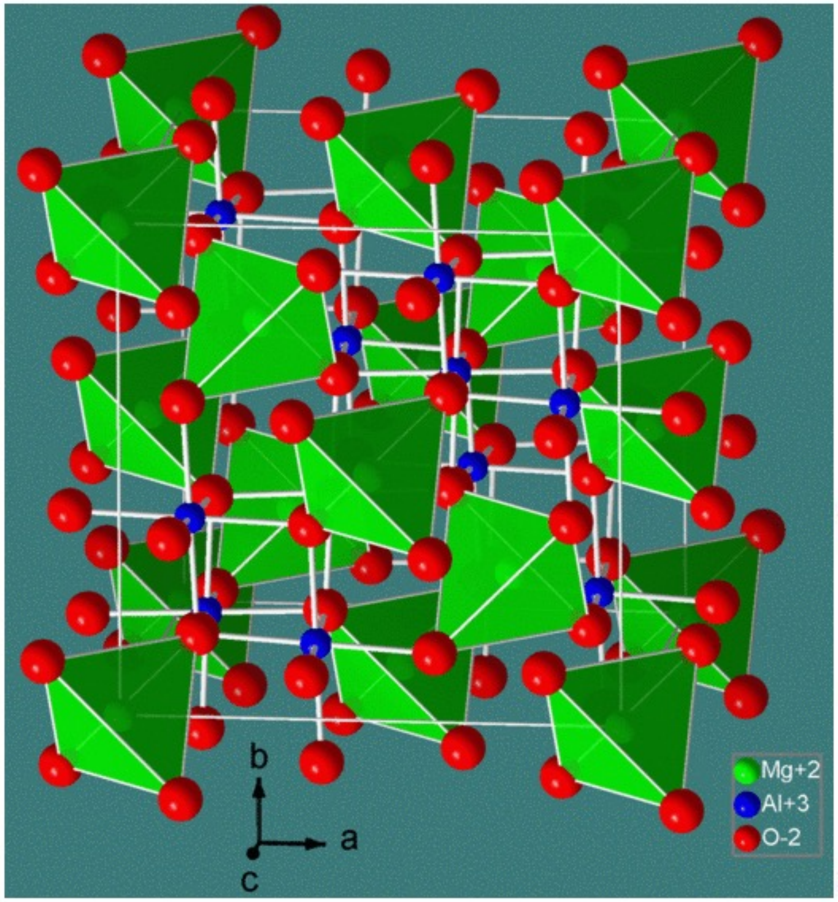


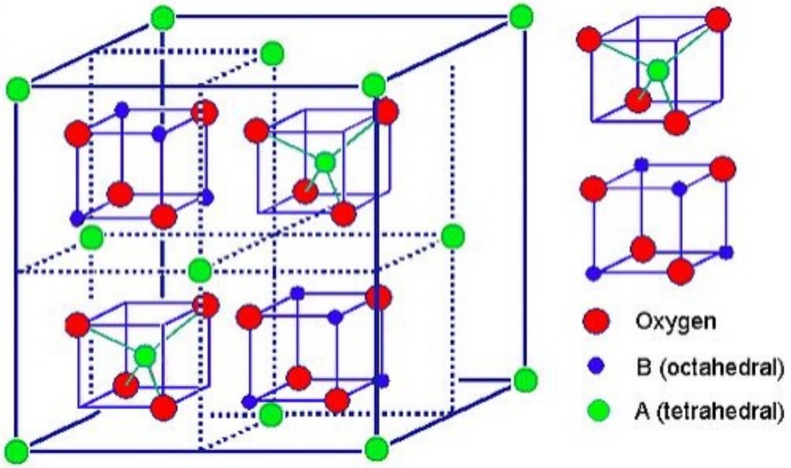
Figure 8.23 Heat capacity of Fe_2O_3 [18]. The heat capacity is deconvoluted to show the relative magnitude of the main contributions. $C_{\mathrm{dil}} = C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \alpha^2 TV/\kappa_T$.

$(dS/dT)_p = C_p/T$

Co_3O_4 Transitions

Cathode in Li^+ batteries or blue pigment for pottery





The **spinel structure** is formulated MM'_2X_4, where M and M' are tetrahedrally and octahedrally coordinated cations, respectively, and X is an anion (typically O or F). The structure is named after the mineral $MgAl_2O_4$, and oxide spinels have the general formula AB_2O_4.

Co_3O_4 Transitions

The normal spinel contains Co^{2+} at tetrahedral sites and low-spin Co^{3+} at octahedral sites. The heat capacity effect observed at *T* β 900K is in part a low- to high-spin transition of the Co^{3+} ions and in part a partial transition from normal toward random distribution of Co^{3+} and Co^{2+} on the tetrahedral and octahedral sites of the spinel structure. The insert to the figure shows the magnetic order–disorder transition of Co_3O_4 at around 30 K.

$$(dS/dT)_p = C_p/T$$

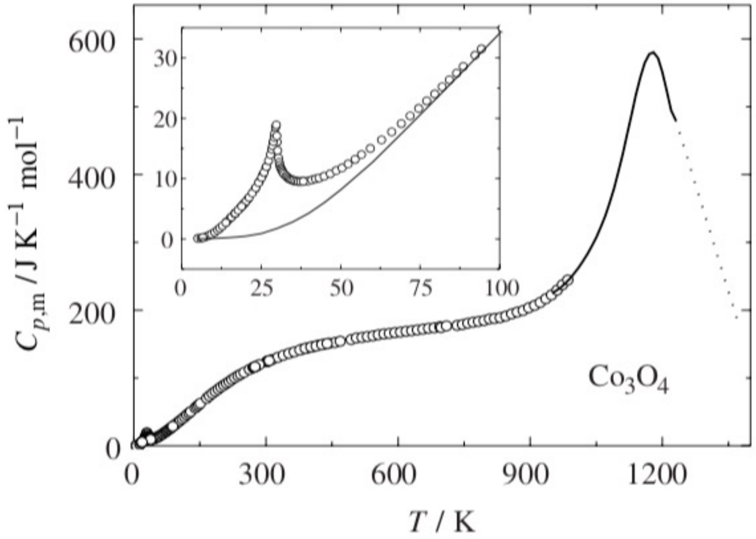
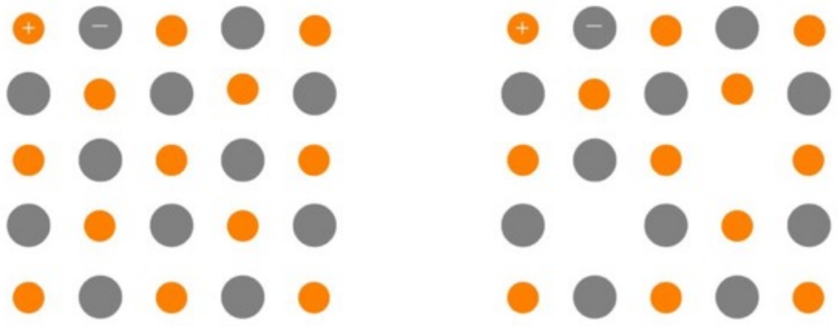
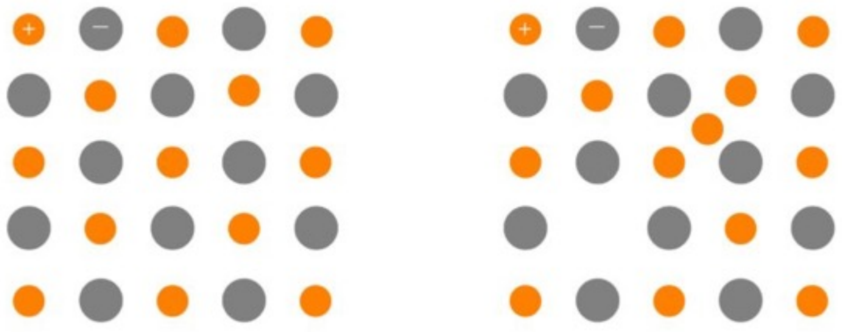


Figure 8.24 Heat capacity of Co_3O_4 [23–25]. The insert shows the magnetic order–disorder transition at around 30 K [24] in detail.



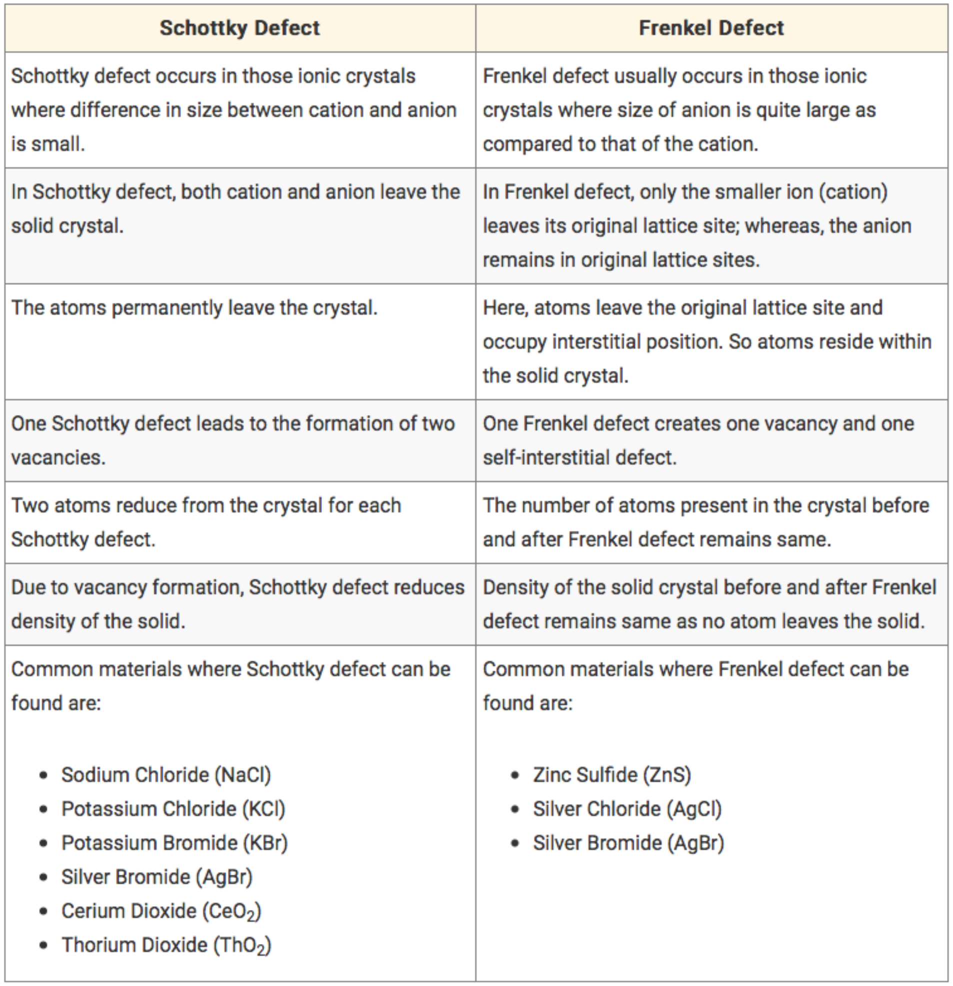
Perfect Crystal

Schottky Defect



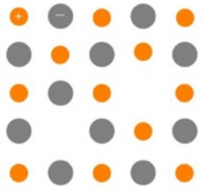
Perfect Crystal

Frenkel Defect



Schottky Defect	Frenkel Defect
Schottky defect occurs in those ionic crystals where difference in size between cation and anion is small.	Frenkel defect usually occurs in those ionic crystals where size of anion is quite large as compared to that of the cation.
In Schottky defect, both cation and anion leave the solid crystal.	In Frenkel defect, only the smaller ion (cation) leaves its original lattice site; whereas, the anion remains in original lattice sites.
The atoms permanently leave the crystal.	Here, atoms leave the original lattice site and occupy interstitial position. So atoms reside within the solid crystal.
One Schottky defect leads to the formation of two vacancies.	One Frenkel defect creates one vacancy and one self-interstitial defect.
Two atoms reduce from the crystal for each Schottky defect.	The number of atoms present in the crystal before and after Frenkel defect remains same.
Due to vacancy formation, Schottky defect reduces density of the solid.	Density of the solid crystal before and after Frenkel defect remains same as no atom leaves the solid.
Common materials where Schottky defect can be found are: • Sodium Chloride (NaCl) • Potassium Chloride (KCl) • Potassium Bromide (KBr) • Silver Bromide (AgBr) • Cerium Dioxide (CeO_2) • Thorium Dioxide (ThO_2)	Common materials where Frenkel defect can be found are: • Zinc Sulfide (ZnS) • Silver Chloride (AgCl) • Silver Bromide (AgBr)

$(dS/dT)_p = C_p/T$



Schottky Defect

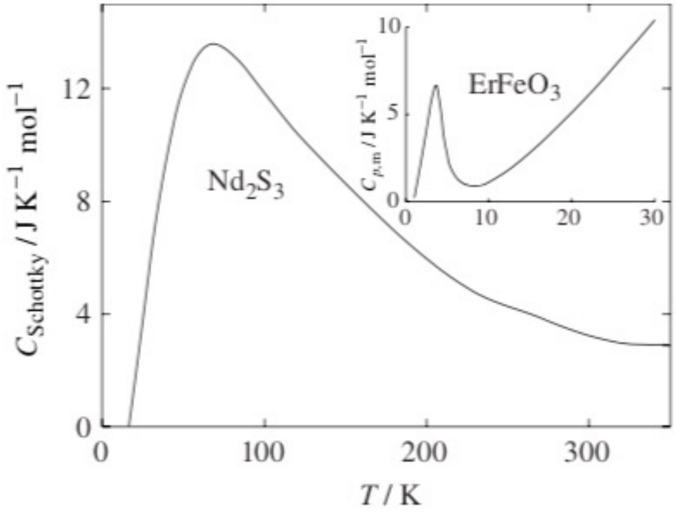


Figure 8.25 The Schottky-type heat capacity of Nd_2S_3 [28]. The insert shows the total heat capacity of $ErFeO_3$ [29].

Two levels with energy spacing ε/k_B
$T > \varepsilon/k_B$ both levels occupied equally
$T < \varepsilon/k_B$ only lower level occupied
Boltzmann statistics yields

$$C_{\mathrm{sch}} = R\left(\frac{\varepsilon}{k_B T}\right)^2 \left(\frac{g_0}{g_1}\right)\left[\frac{\exp(\varepsilon/k_B T)}{\{1+(g_0/g_1)\exp(\varepsilon/k_B T)\}^2}\right]$$

g_0 and g_1 are the degeneracies of the ground level and the excited level

Schottky Defects

Endothermic formation enthalpy
Entropy associated with disorder of defect location

$$C_{V,\mathrm{m}} = \frac{1}{RT^2}\left[\Delta_{\mathrm{vac}}H_{\mathrm{m}}^2 \exp\left(\frac{\Delta_{\mathrm{vac}}S_{\mathrm{m}}}{R}\right)\right]\exp\left(-\frac{\Delta_{\mathrm{vac}}H_{\mathrm{m}}}{RT}\right)$$

$$C_{\mathrm{sch}} = R\left(\frac{\varepsilon}{k_{\mathrm{B}}T}\right)^2\left(\frac{g_0}{g_1}\right)\left[\frac{\exp(\varepsilon/k_{\mathrm{B}}T)}{\{1+(g_0/g_1)\exp(\varepsilon/k_{\mathrm{B}}T)\}^2}\right]$$

$\Delta G = \Delta H - T\Delta S$

$(dS/dT)_V = C_V/T$

Fast Ion Conductors (solid oxide fuel cells high T)

Solid electrolytes for batteries and fuel cells

AgI, I lattice remains intact, Ag+ conductor becomes a liquid

Also, Cu_2S, Ag_2S. NaS battery

Heat Capacity drops with temperature

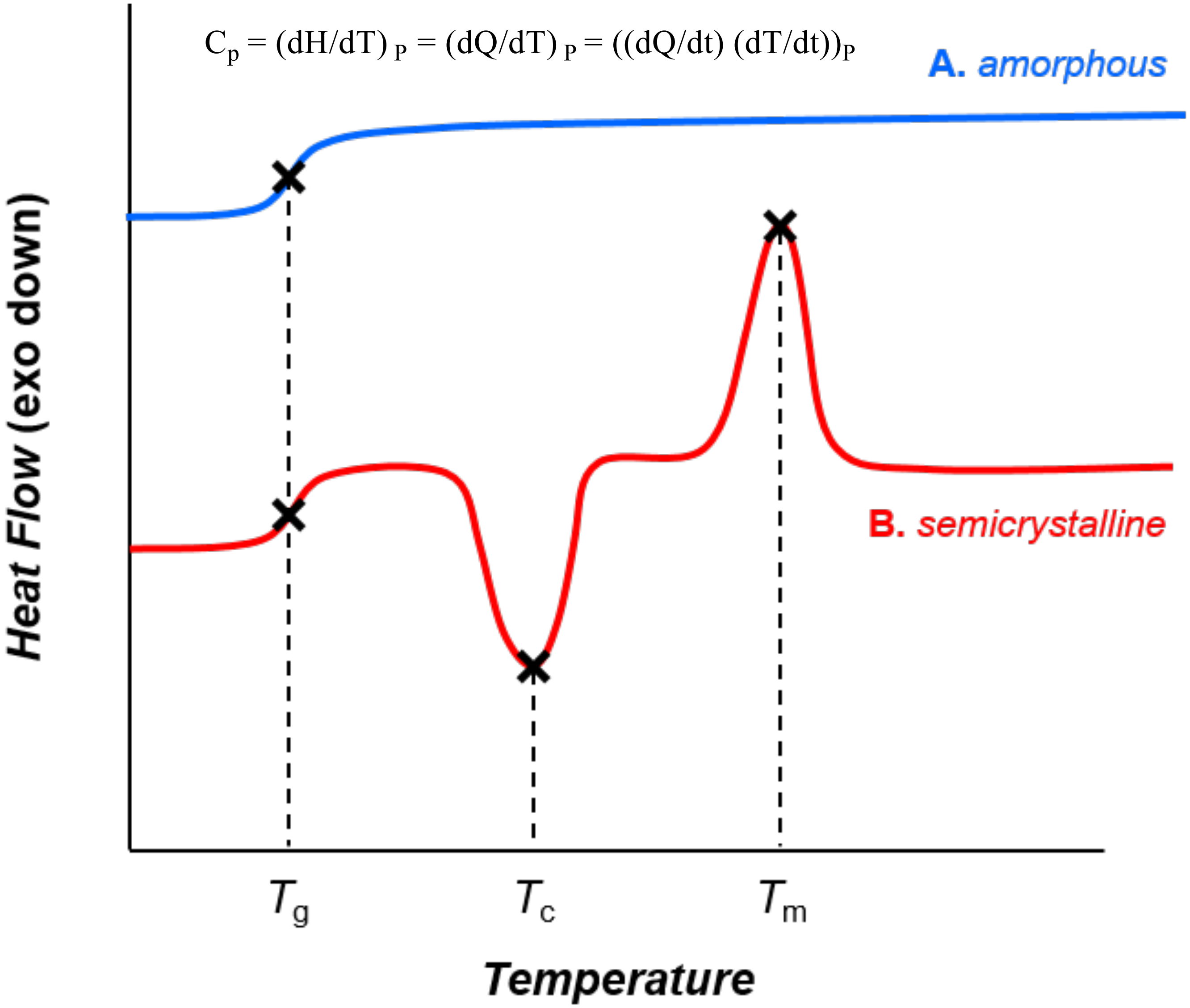
$$C_V = k_B\left(\frac{\varepsilon}{k_B T}\right)^2 \frac{\exp(\varepsilon/k_B T)}{[\exp(\varepsilon/k_B T) + 1]^2}.$$

First term decays with $(\varepsilon/kT)^2$

Second term increases with $\sim \exp(-\varepsilon/kT)$

Liquids and Glasses

$C_p = (dH/dT)_P = (dQ/dT)_P = ((dQ/dt)\ (dT/dt))_P$



Liquids and Glasses

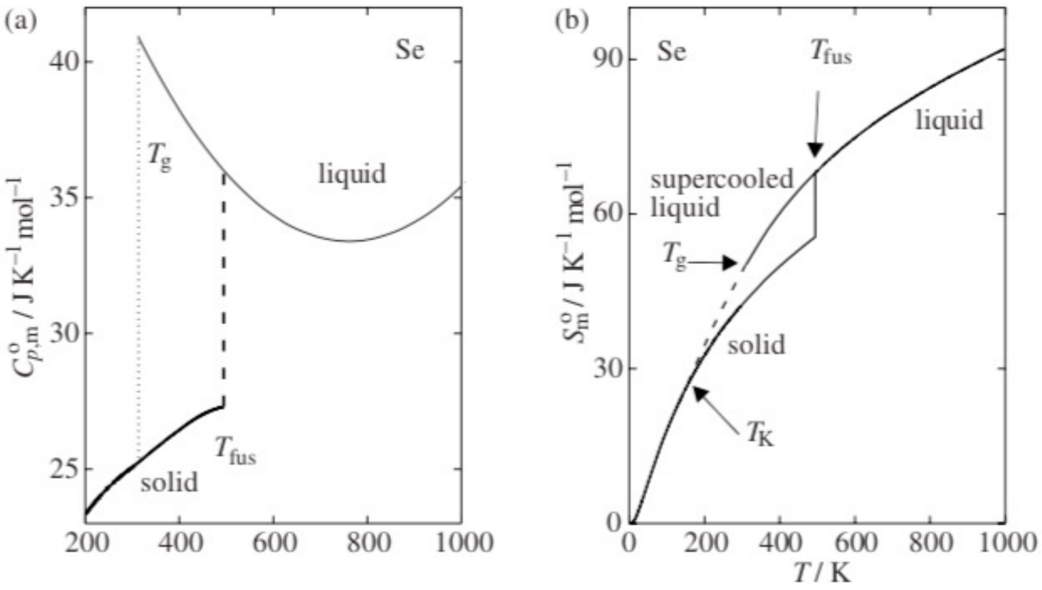


Figure 5.1 (a) Heat capacity of crystalline, liquid and supercooled liquid Se as a function of temperature [1–3]. (b) Entropy of crystalline, liquid and supercooled liquid Se as a function of temperature.

Broad minimum in heat capacity

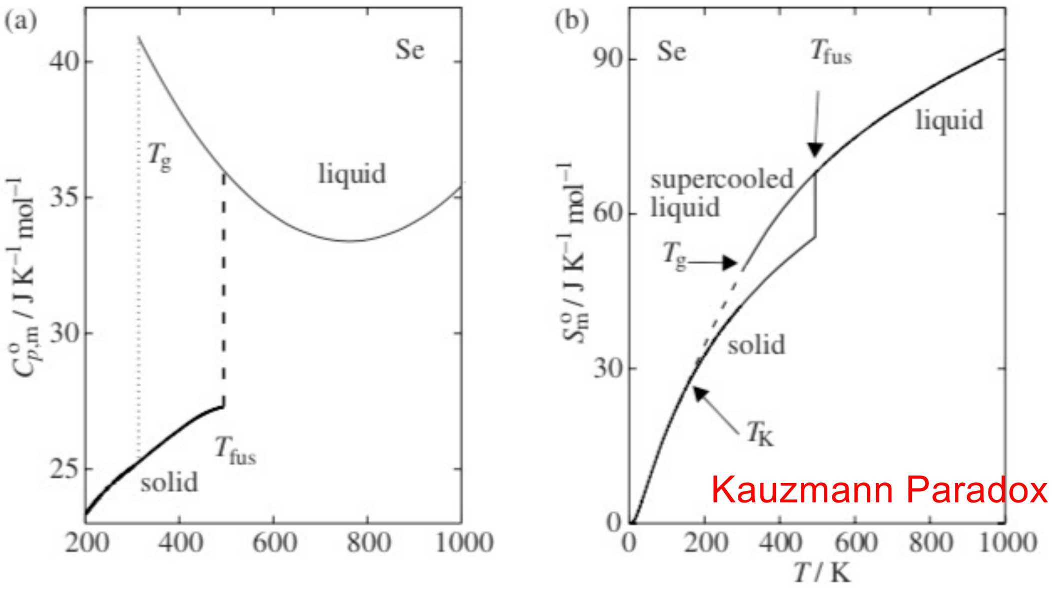
Loss of short-range order with rising T leads to drop in heat capacity

Initially, loss of vibrational degrees of freedom associated with short range order led to decrease in C_p

Later, S increases with T

$$T(dS/dT)_p = C_p$$

Liquids and Glasses



Kauzmann Paradox

Figure 5.1 (a) Heat capacity of crystalline, liquid and supercooled liquid Se as a function of temperature [1–3]. (b) Entropy of crystalline, liquid and supercooled liquid Se as a function of temperature.

Broad minimum in heat capacity

Loss of short-range order with rising T leads to drop in heat capacity

Initially, loss of vibrational degrees of freedom associated with short range order led to decrease in C_p

Later, S increases with T

$$T(dS/dT)_p = C_p$$

Anomalous behavior of glasses near absolute 0

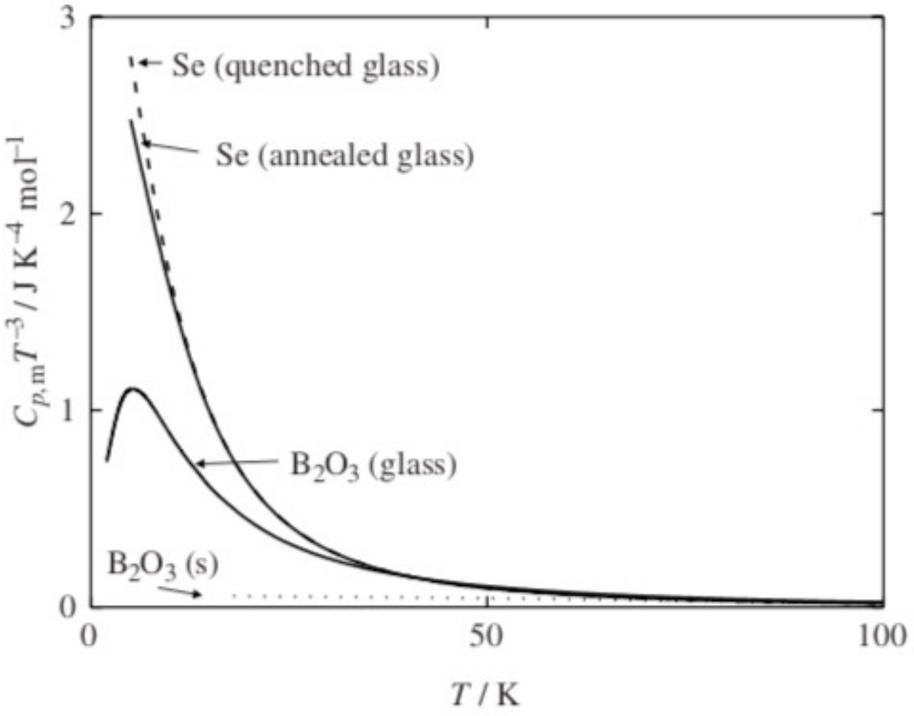


Figure 8.26 Heat capacity of glassy and crystalline B_2O_3 [42–44] and glassy Se [41] plotted as $C_{p,m} \cdot T^{-3}$ versus T.

Debye $C_V \sim T^3$ near 0 K

Behavior is due to
anharmonic vibrations
(Relaxation phenomena)

Pseudo-second order transition behavior of glasses

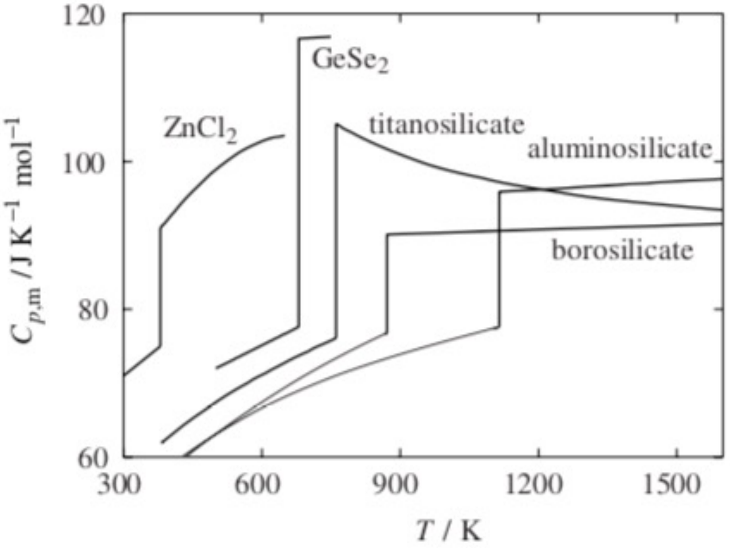


Figure 8.27 Heat capacity of some glass-forming liquids close to their glass transition temperatures: $ZnCl_2$ [45], $GeSe_2$ [46], and a selected titanosilicate [47], aluminosilicate [48] and borosilicate [49] system.

Relaxation phenomena
In glasses

Pseudo-second order transition behavior of glasses

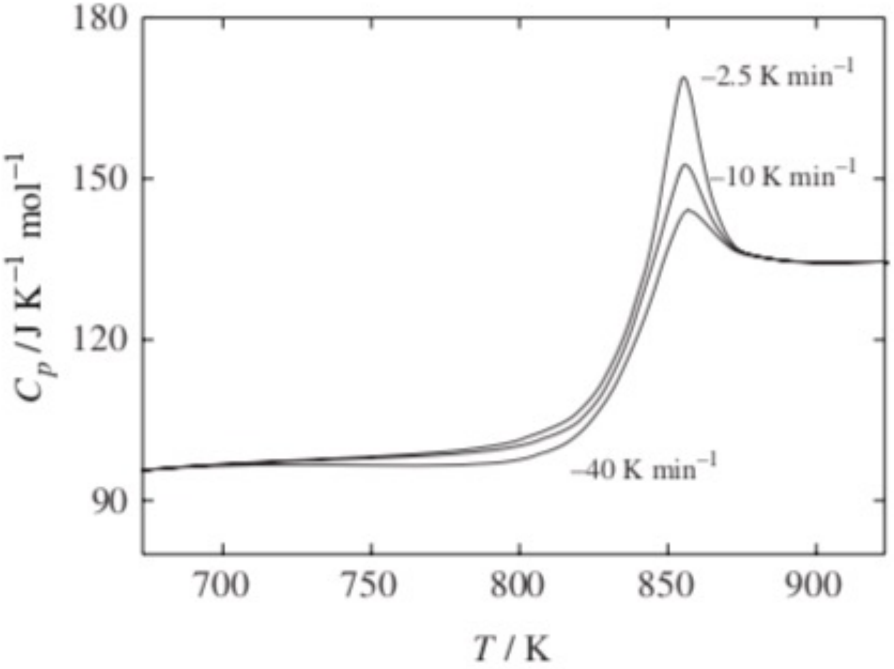


Figure 8.28 Heat capacity of glassy B_2O_3 at different heating rates [50].

Relaxation phenomena
In glasses

Pseudo-second order transition behavior of glasses

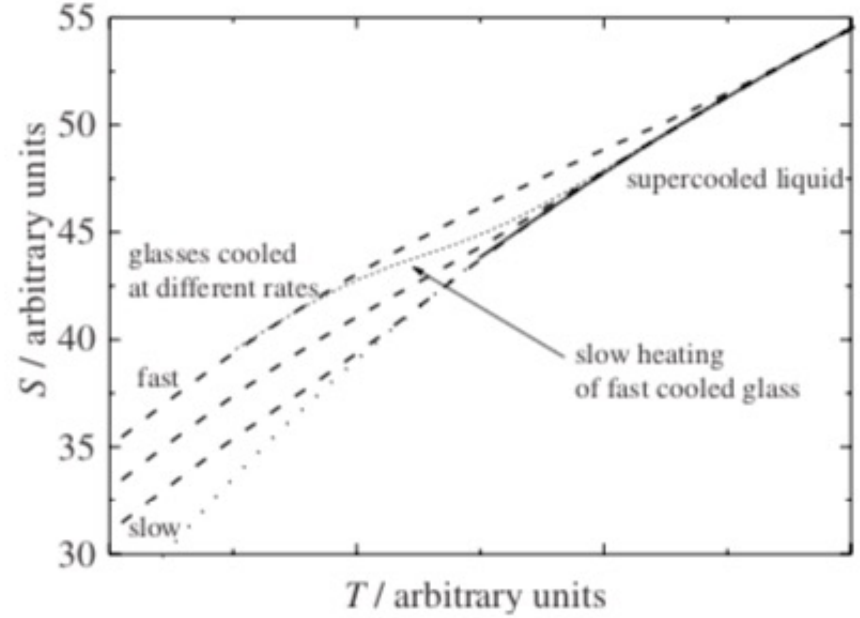
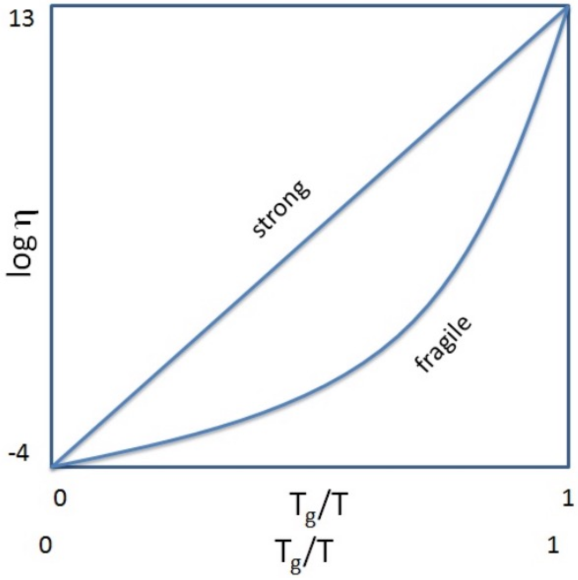


Figure 8.29 Entropy of a supercooled liquid and glasses formed by fast and slow cooling of this liquid (the different dashed lines). The short dashed line represents slow heating of a glass first prepared by fast cooling.

Relaxation phenomena
In glasses

Thermodynamic and Kinetic Fragility

Fragile versus strong glass



Kinetics: Deviation from Arrhenius behavior

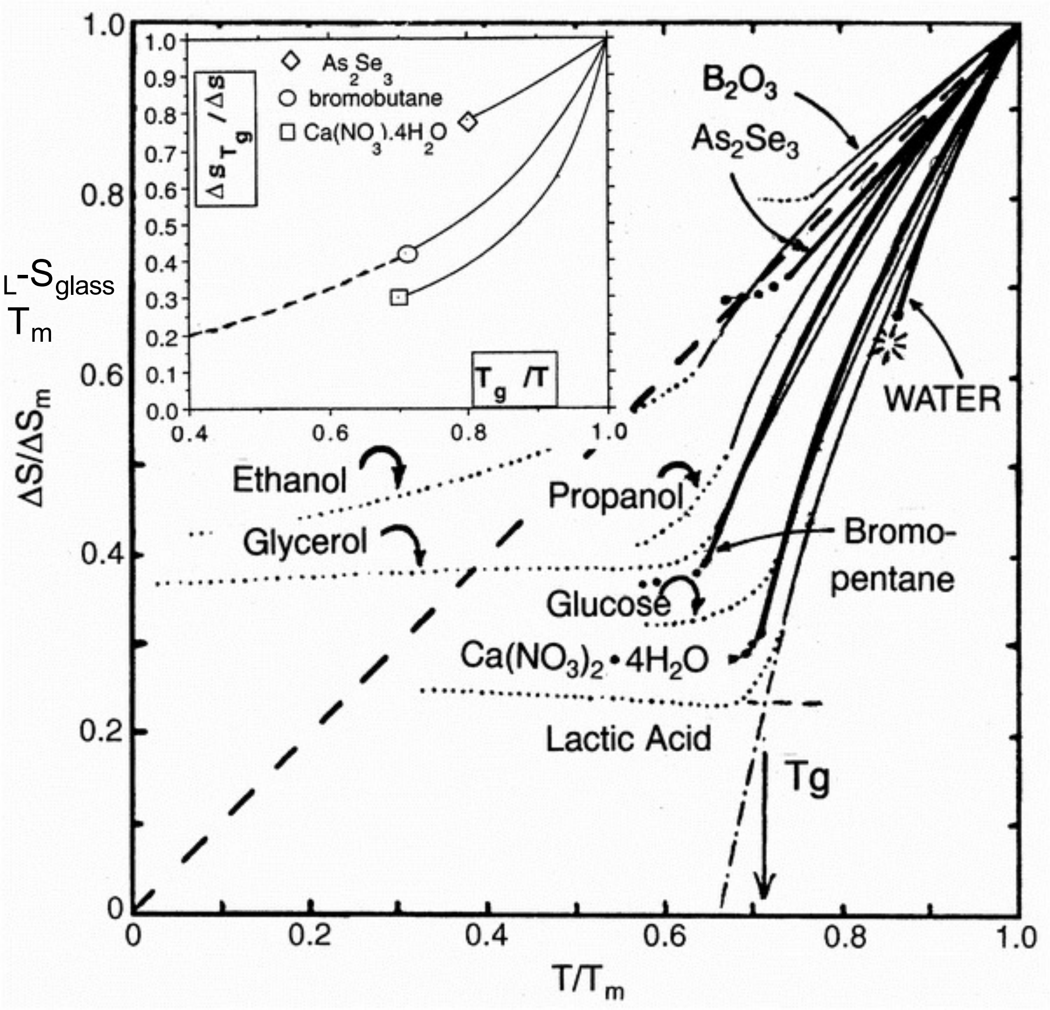
$\eta = \eta_0 \exp(-E_a/k_B T)$

Scaled Exponential

$\eta = \eta_0 \exp(-E_a/k_B T)^m$

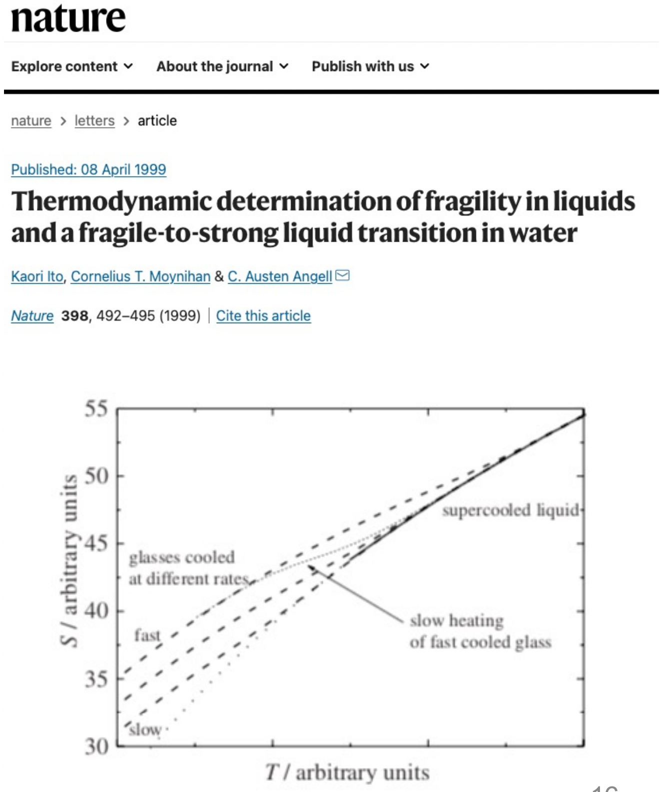
$$m := \left(\frac{\partial \log_{10} \eta}{\partial \left(T_g/T\right)}\right)_{T=Tg} = \frac{1}{\ln 10}\left(\frac{\partial \ln \eta}{\partial \left(T_g/T\right)}\right)_{T=Tg} = \frac{T_g}{\ln 10}\left(\frac{-\partial \ln \eta}{\partial T}\right)_{T=Tg}$$

Figure 1: Use of the Kauzmann plot to define thermodynamic fragility for glass-forming liquids.



$\Delta S = S_L - S_{glass}$

m is at T_m



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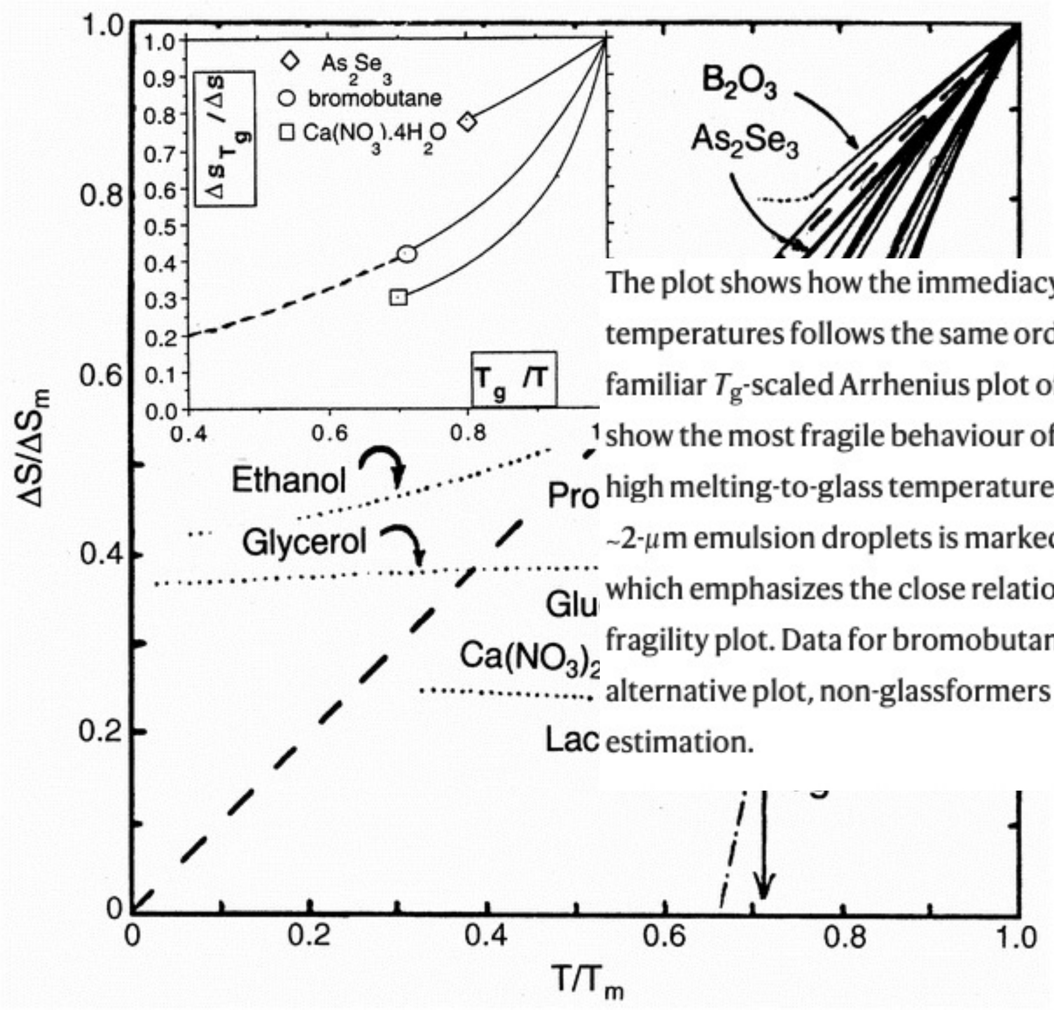
Thermodynamic determination of fragility in liquids and a fragile-to-strong liquid transition in water

Kaori Ito, Cornelius T. Moynihan & C. Austen Angell

Nature **398**, 492–495 (1999) | Cite this article

Figure 1: Use of the Kauzmann plot to define thermodynamic fragility for glass-forming liquids.



The plot shows how the immediacy of the entropy crisis for liquids cooled below their melting temperatures follows the same order as the fragilities of these liquids as determined from the familiar T_g-scaled Arrhenius plot of transport data. Data for supercooled water on the same plot show the most fragile behaviour of all, despite a distortion towards lower fragility caused by the high melting-to-glass temperature ratio for water. The temperature of homogeneous nucleation for $\sim$2-μm emulsion droplets is marked by a star. Inset, alternative representation of data in main panel, which emphasizes the close relation of thermodynamic fragility to the more familiar (kinetic) fragility plot. Data for bromobutane were extended beyond the melting point in ref. 8. In this alternative plot, non-glassformers are excluded unless the scaling temperature T_g is obtained by estimation.

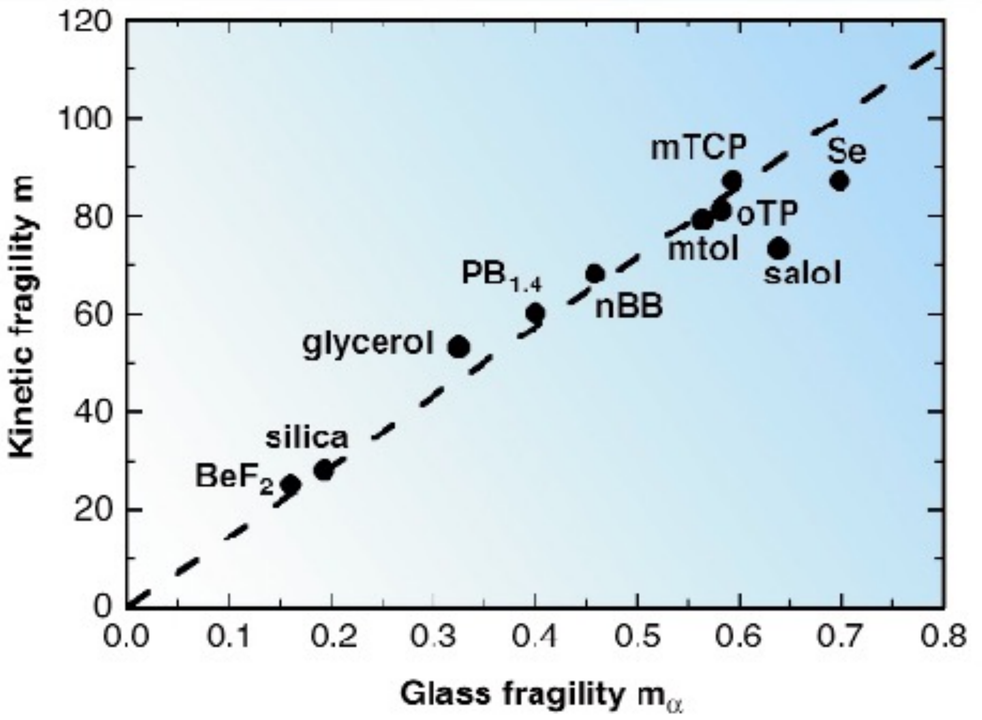
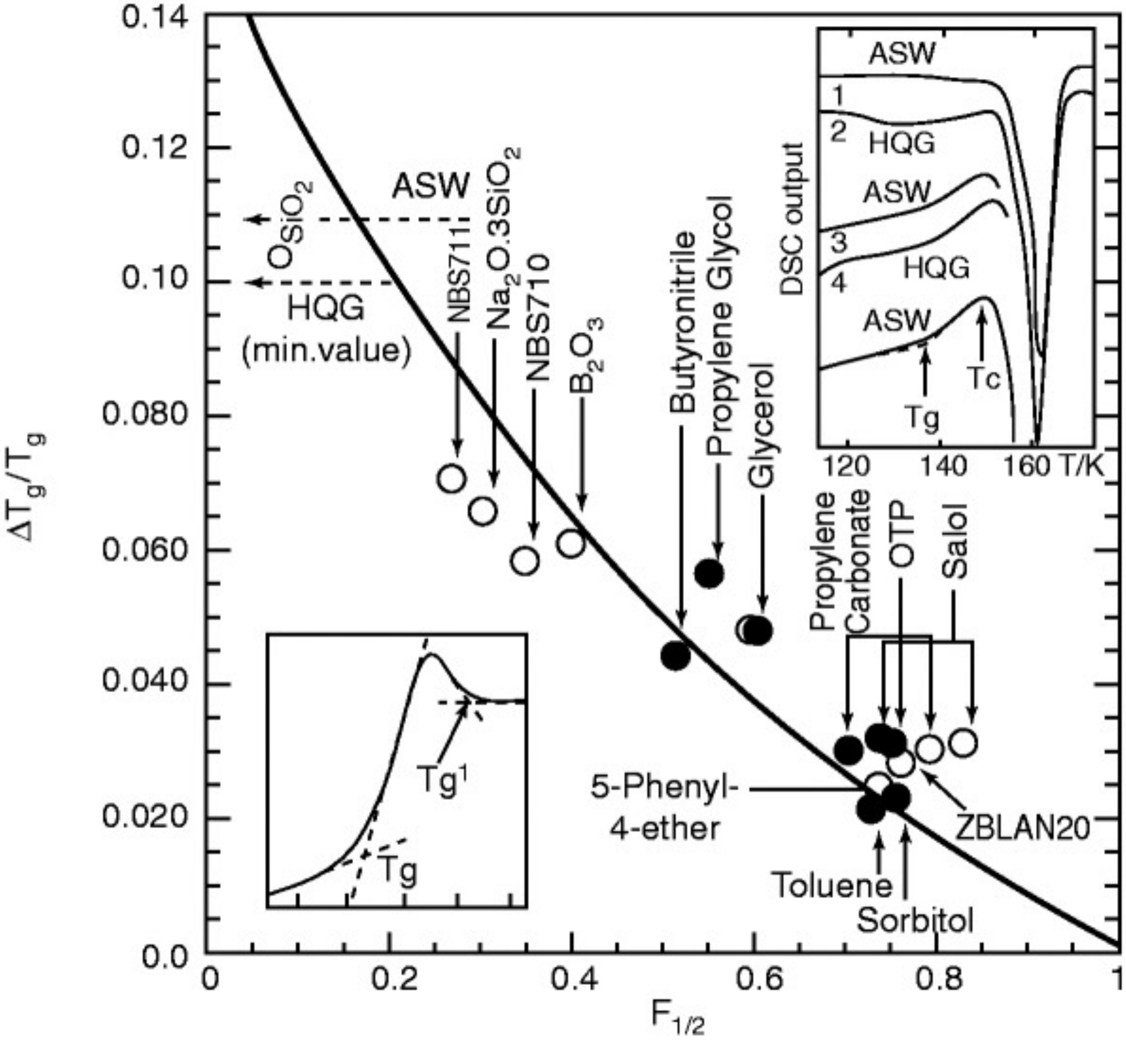


Fig. 13: Correlation of glass and liquid fragilities for an ensemble of glass-formers.

Figure 2: Correlation between fragility metrics $\Delta T_g / T_g$ and $F_{1/2}$.

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Heat Capacity of Polymers

Amorphous structure but with regular order along the chain
1-d vibrational structure

Einstein method works well above 100K

$$E(\theta/T) = [(\theta/T)^2 \exp(\theta/T)] / [\exp(\theta/T) - 1]^2$$

E is the heat capacity contribution for each vibration

$$C_E = Nk\sum_{N_E} E(\theta/T)$$

$$N_E = 3N_{Atoms} - N$$

N_{atoms} = number of atoms in a mer unit
3 for CH_2
N = number of skeletal modes of vibration
N = 2 for $-(CH_2)_n-$

$$C_{V,\mathrm{m}} = \left(\frac{\mathrm{d}\bar{U}}{\mathrm{d}T}\right)_V = 3R\left(\frac{\Theta_\mathrm{E}}{T}\right)^2 \frac{\exp(\Theta_\mathrm{E}/T)}{[\exp(\Theta_\mathrm{E}/T)-1]^2}$$

Einstein temperature: $\Theta_\mathrm{E} = \dfrac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}}$

Below 50K need more detailed breakup of 1d and 3d vibrations using Debye Approach

Weak Van der Waals interactions between chains described by 3d Debye function

$$\mathbf{D}_3(\theta/T_3) = 3\,(\theta/T_3)^3 \int_0^{\theta/T_3} \{[(\theta/T)^4 \exp(\theta/T)] \,/\, [\exp(\theta/T) - 1]^2\}\, d(\theta/T)$$

$$C_v / 3Nk = \mathbf{D}_3\,(\theta/T_3)$$

$\theta_3 = h\, v_3 / k$ For skeletal modes normal to the chain

Strong covalent interactions along chains described by 1d Debye function

$$\mathbf{D}_1(\theta/T_1) = (\theta/T_1) \int_0^{\theta/T_1} \{[(\theta/T)^2 \exp(\theta/T)] \,/\, [\exp(\theta/T) - 1]^2\}\, d(\theta/T)$$

$$C_v / 3Nk = \mathbf{D}_1(\theta/T_1)$$

$\theta/T = h\, v_1 / k$ For skeletal vibrations in the chain axis

Linear heat capacity increase from 0 to 200K

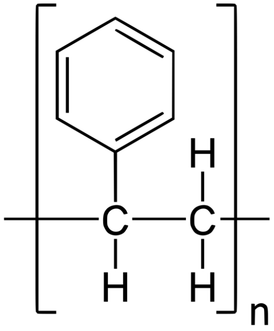
$$C_V(\text{Tarasov}) = NR/3 \cdot \{\mathbf{D}_1(\theta_1/T) - (\theta_3/\theta_1)[\mathbf{D}_1(\theta_3/T) - \mathbf{D}_3(\theta_3/T)]\}$$

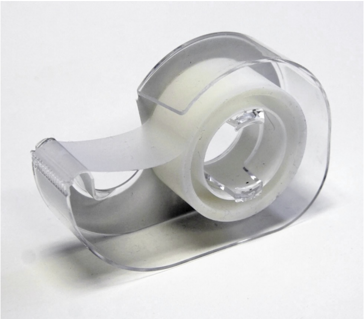
At low frequency 3d vibrations, at high frequency 1d vibrations

1d Tasarov simplification (generates about 1% error versus experimental)

$$C_T = Nk/3\ [\ (6.7T/\theta_1)^2 / (1 + (6.7T/\theta_1)^2)]$$

Polystyrene





N_{atoms} = 16 atoms per unit

N = 6 skeletal mode vibrations

$N_E = 3N_{Atoms} - N$

N_E = 42

θ_1 = 285 K

42 total atomic group modes of vibration

θ	Number	θ	Number
4000	8	700	2
2000	10	500	1
1500	12	350	1
1000	8	-	-

$$\mathbf{E}(\theta/T) = [(\theta/T)^2 \exp(\theta/T)] / [\exp(\theta/T) - 1]^2$$

$$C_E = Nk\sum_{N_E} \mathbf{E}(\theta/T)$$

Or calculate with the Tasarov Equation $C_T = 6\,R\,[\,(T/42.5)^2 / (1 + (T/42.5)^2)]$

$C_P - C_V = -\mathrm{T}\,(\mathrm{d}V/\mathrm{d}T)^2{}_P\,/\,(\mathrm{d}V/\mathrm{d}P)^2{}_T = V\alpha^2 BT$

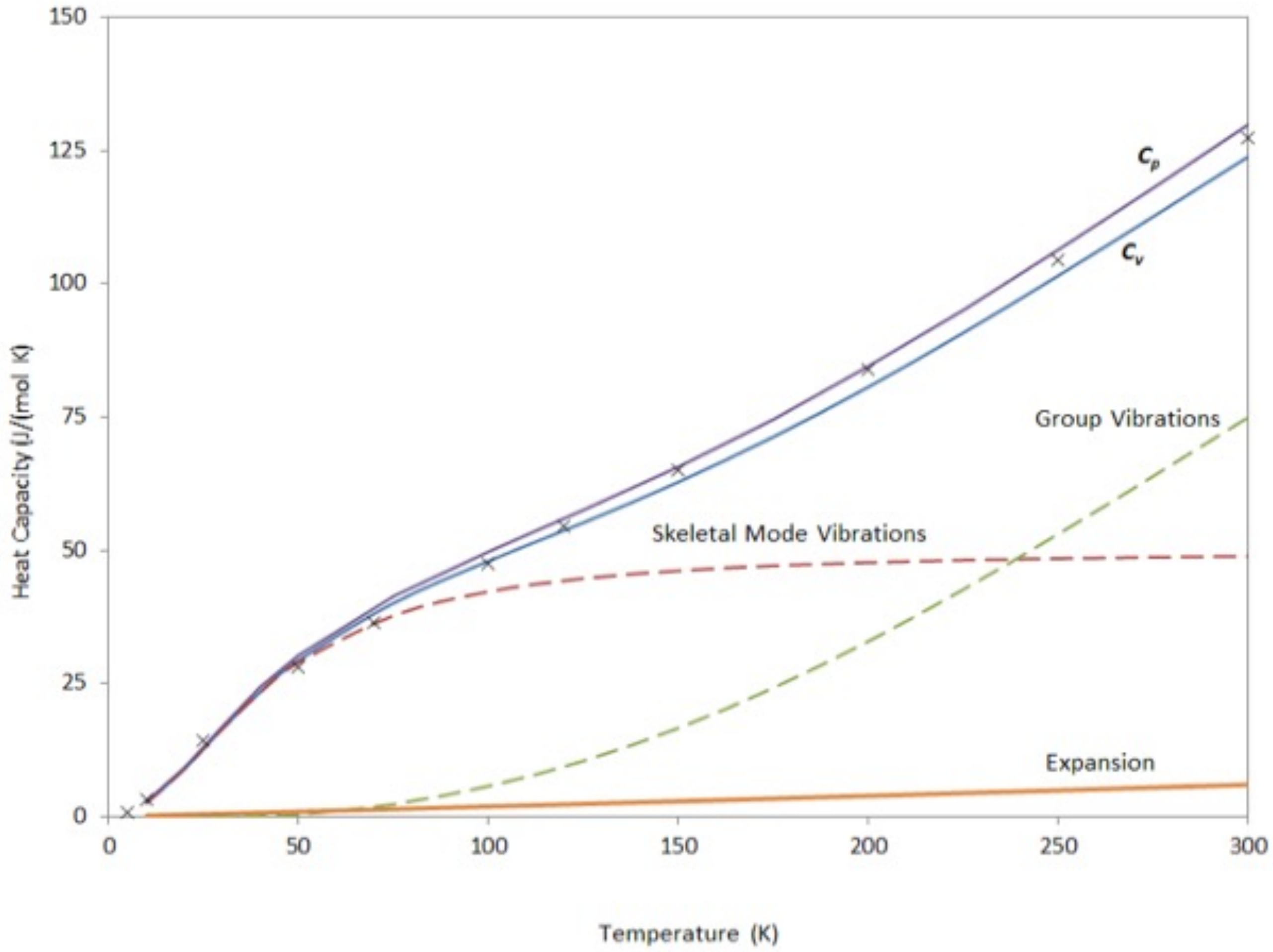
$V_m = 92.8 - 99.6\ \mathrm{cm}^3/\mathrm{mol}\ (0 - 300\mathrm{K})$

$B = 3.58$ GPa

$\alpha_g = 2.37\ 10^{-4}$ and

$\alpha_r = 5.74\ 10^{-4}$ and

MOLAR HEAT CAPACITY OF PS VS TEMPERATURE



1. U. Gaur and B. Wunderlich, *J. Phys. Ref. Data*, Vol. 11, No. 2, (1982)

Average Energy and the Partition Function

Consider a set of N independent (No Enthalpy) molecules at different energy states, N_i molecules at E_i

The average energy is $E = \sum_i \ N_i E_i$

The Boltzmann Probability gives $N_i = \sum_i \ \frac{Ne^{-E_i/kT}}{Z}$ and $Z = \sum_i \ e^{-E_i/kT}$ is the partition function

Then $E = \frac{N}{Z} \sum_i \ E_i e^{-E_i/kT}$

Consider $\frac{d}{dT} e^{-E_i/kT} = +\frac{E_i}{kT^2} e^{-E_i/kT}$ so $E_i e^{-E_i/kT} = kT^2 \frac{d}{dT} e^{-E_i/kT}$

$$E = \frac{NkT^2}{Z} \sum_i \frac{d}{dT} e^{-E_i/kT}$$

$$EdT = \frac{NkT^2}{Z} dZ$$

$$E = -NkT \ lnZ$$

For ground state $E = 0$, Z at $T = 0$ is 1; for $T = \infty$, Z is the number of states (degeneracy)

For molecular vibrations $E = h\omega$

1907 Einstein Solid Model for Dulong Petit Law at high kT

Energy is quantized, quantum number is “n” goes from 1 to positive integer values for the principal quantum number

Smallest quantum of energy is $\varepsilon = h\nu$

Energy for quantum number ”n” is

$E_n = h\nu(n+1/2) = \varepsilon(n+1/2)$

Total number of quantum states N

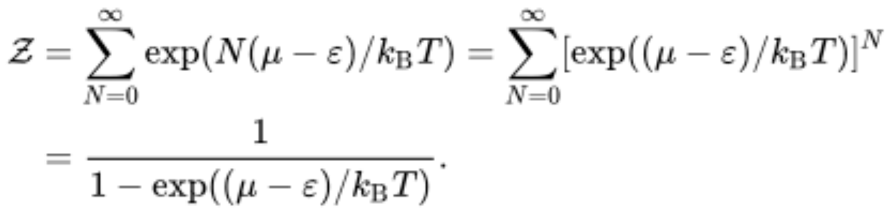
Total energy $N\varepsilon(n+1/2)$

Ground state energy μ

Geometric Series $\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r}$

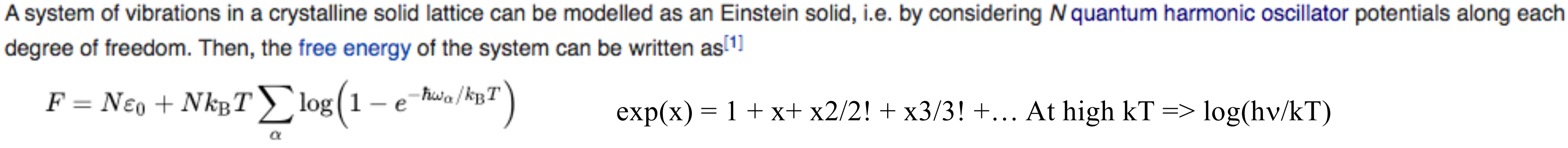
$$\begin{aligned}\mathcal{Z} &= \sum_{N=0}^{\infty} \exp(N(\mu-\varepsilon)/k_\mathrm{B}T) = \sum_{N=0}^{\infty} [\exp((\mu-\varepsilon)/k_\mathrm{B}T)]^N \\ &= \frac{1}{1-\exp((\mu-\varepsilon)/k_\mathrm{B}T)}.\end{aligned}$$

1907 Einstein Solid Model for Dulong Petit Law at high kT



$$\mathcal{Z} = \sum_{N=0}^{\infty} \exp(N(\mu - \varepsilon)/k_{\mathrm{B}}T) = \sum_{N=0}^{\infty} [\exp((\mu - \varepsilon)/k_{\mathrm{B}}T)]^N$$
$$= \frac{1}{1 - \exp((\mu - \varepsilon)/k_{\mathrm{B}}T)}.$$

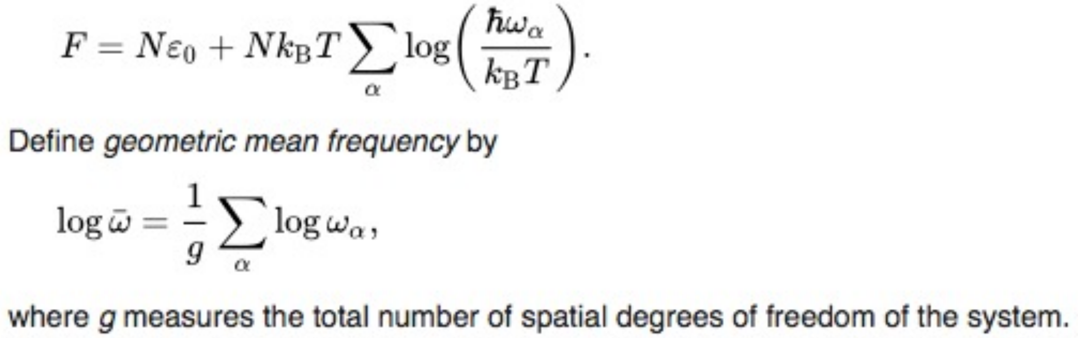
Energy = -kT log (Z); log(1/Z) = -log(Z)



A system of vibrations in a crystalline solid lattice can be modelled as an Einstein solid, i.e. by considering *N* quantum harmonic oscillator potentials along each degree of freedom. Then, the free energy of the system can be written as[1]

$$F = N\varepsilon_0 + Nk_{\mathrm{B}}T \sum_{\alpha} \log\left(1 - e^{-\hbar\omega_\alpha/k_{\mathrm{B}}T}\right)$$

exp(x) = 1 + x+ x2/2! + x3/3! +… At high kT => log(hν/kT)



$$F = N\varepsilon_0 + Nk_{\mathrm{B}}T \sum_{\alpha} \log\left(\frac{\hbar\omega_\alpha}{k_{\mathrm{B}}T}\right).$$

Define *geometric mean frequency* by

$$\log \bar{\omega} = \frac{1}{g} \sum_{\alpha} \log \omega_\alpha,$$

where *g* measures the total number of spatial degrees of freedom of the system.

F is A; E is U

1907 Einstein Solid Model for Dulong Petit Law at high kT

$$F = N\varepsilon_0 + Nk_{\mathrm{B}}T\sum_{\alpha}\log\left(\frac{\hbar\omega_\alpha}{k_{\mathrm{B}}T}\right).$$

F is A; E is U

$$F = N\varepsilon_0 - gNk_{\mathrm{B}}T\log k_{\mathrm{B}}T + gNk_{\mathrm{B}}T\log\hbar\bar{\omega}.$$

Using energy

$$E = F - T\left(\frac{\partial F}{\partial T}\right)_V,$$

we have

$$E = N\varepsilon_0 + gNk_{\mathrm{B}}T.$$

This gives heat capacity at constant volume

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = gNk_{\mathrm{B}},$$

Molar $C_v/N = gk$ or $C_v = 3R$ in 3d

Phonons From Dove

$$E = \hbar\omega\left[\frac{1}{2} + n(\omega, T)\right]$$

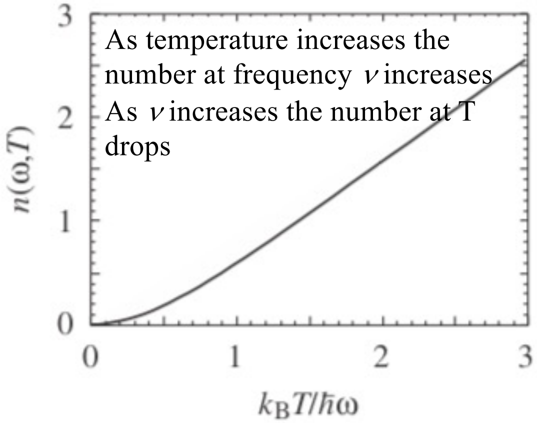
Bose-Einstein Relationship

$$\langle n \rangle = \frac{1}{Z}\sum_n n\exp(-\beta n\epsilon) \qquad Z = \sum_n \exp(-\beta n\epsilon)$$

$$= -\frac{1}{\beta Z}\frac{\partial Z}{\partial \epsilon} \qquad \sum_n x^n = \frac{1}{1-x}$$

$$\langle n \rangle = Z\exp(-\beta\epsilon) = \frac{1}{\exp(\beta\epsilon) - 1} \qquad Z = \frac{1}{1 - \exp(-\beta\epsilon)}$$

$$n(\omega, T) = \frac{1}{\exp(\hbar\omega/k_B T) - 1}$$



As temperature increases the number at frequency ν increases
As ν increases the number at T drops

Fig. 9.1 The Bose–Einstein distribution $n(\omega, T)$ as a function of $k_B T/\hbar\omega$.

Phonons From Dove

Einstein Model for Heat Capacity

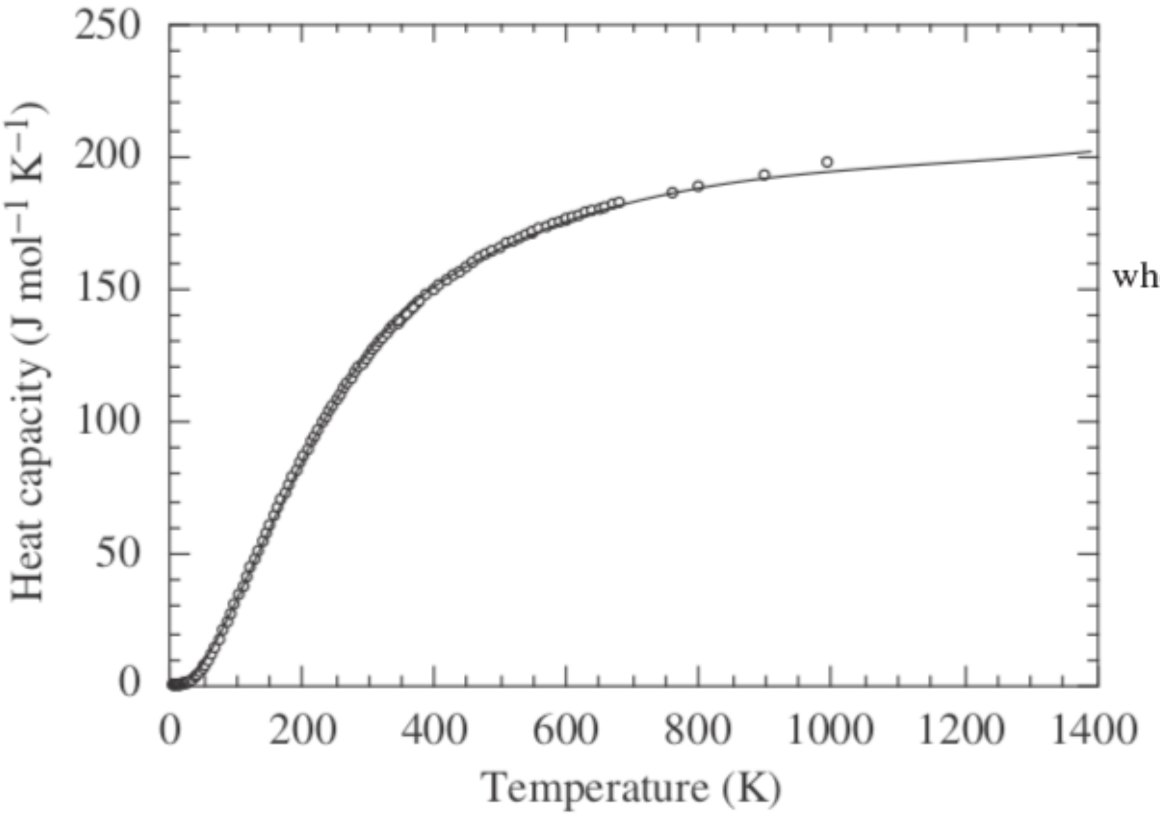
$$E = \hbar\omega\left[\frac{1}{2} + n\right]$$

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V$$
$$= \sum \hbar\omega \frac{\partial n}{\partial T}$$
$$= \sum k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2}$$

E is U

$$n(\omega, T) = \frac{1}{\exp(\hbar\omega/k_B T) - 1}$$

Phonons From Dove



$$C_{V,\mathrm{m}} = \left(\frac{\mathrm{d}\overline{U}}{\mathrm{d}T}\right)_V = 3R\left(\frac{\Theta_\mathrm{E}}{T}\right)^2 \frac{\exp(\Theta_\mathrm{E}/T)}{[\exp(\Theta_\mathrm{E}/T)-1]^2}$$

where Θ_E, the **Einstein temperature**, is defined by

$$\Theta_\mathrm{E} = \frac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}}$$

Fig. 9.2 Comparison of calculated (line) and experimental (points) heat capacity of the mineral andalusite, Al_2SiO_5.

Phonons From Dove

Phonon Free Energy

$$Z = \frac{1}{1 - \exp(-\beta\epsilon)}$$

$$F = -\frac{1}{\beta}\ln Z$$

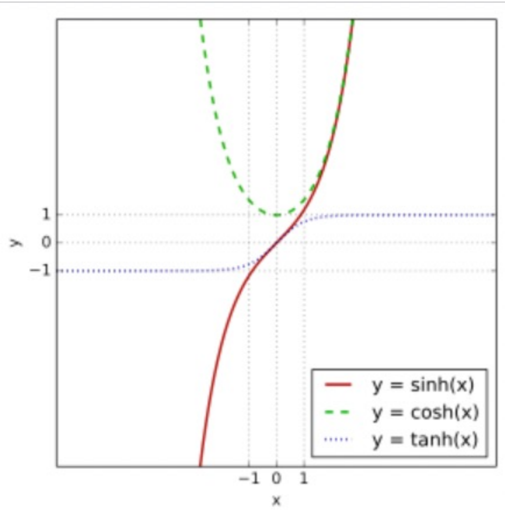
F is A Helmholz Free Energy

$$F = \frac{1}{2}\epsilon + \frac{1}{\beta}\ln[1 - \exp(-\beta\epsilon)]$$

Including ground state energy

$$= \frac{1}{\beta}\ln[2\sinh(\beta\epsilon/2)]$$

$$\sinh x = \frac{e^x - e^{-x}}{2} = \frac{e^{2x} - 1}{2e^x} = \frac{1 - e^{-2x}}{2e^{-x}}$$



At high T

$$F = \frac{1}{\beta}\ln(\beta\epsilon)$$

$$S = -\partial F/\partial T$$

$$S = k_B[1 - \ln(\beta\varepsilon)]$$

Phonons From Dove

For a crystal sum over all vibrations

$$F = \frac{1}{\beta} \sum_{\mathbf{k},\nu} \ln\{2\sinh[\beta\hbar\omega(\mathbf{k},\nu)/2]\}$$

F is A Helmholz Free Energy

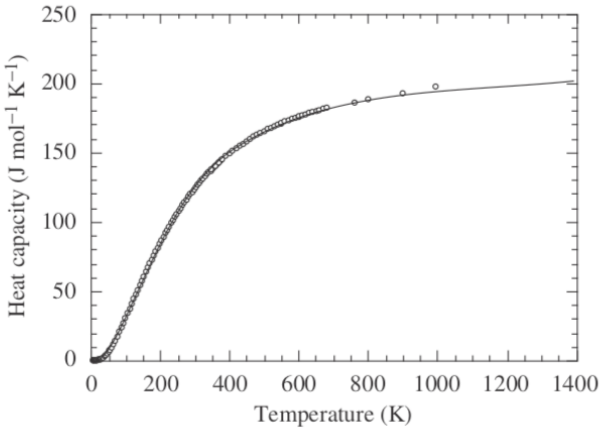


Fig. 9.2 Comparison of calculated (line) and experimental (points) heat capacity of the mineral andalusite, Al_2SiO_5.

From Kittel and Kroemer Thermal Physics Chapter 3

$$Z = \sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau).$$

For quantized phonons

$$\langle s \rangle = \frac{\exp(-y)}{1-\exp(-y)}.$$

This is of the form $\sum x^i$ with x <<1 equals 1/(1-x)

$$Z = \frac{1}{1-\exp(-\hbar\omega/\tau)}.$$

$$P(s) = \frac{\exp(-s\hbar\omega/\tau)}{Z}.$$

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

$$\langle s \rangle = \sum_{s=0}^{\infty} sP(s) = Z^{-1}\sum s\exp(-s\hbar\omega/\tau).$$

Planck Distribution

$$\sum s\exp(-sy) = -\frac{d}{dy}\sum \exp(-sy)$$

$$= -\frac{d}{dy}\left(\frac{1}{1-\exp(-y)}\right) = \frac{\exp(-y)}{[1-\exp(-y)]^2}.$$

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

Einstein Model
Works at low and high temperature
Lower at low temperature

Quantized energy levels

$$\varepsilon_n = (n + \tfrac{1}{2})\hbar\omega$$

Bose-Einstein statistics determines the distribution of energies

The mean “n” at T is given by

$$\bar{n} = \frac{1}{\exp(\hbar\omega/k_B T) - 1}$$

Average energy for a crystal with three identical oscillators

$$\bar{U} = 3N(\tfrac{1}{2} + \bar{n})\hbar\omega_E = 3N\left(\frac{\hbar\omega_E}{2} + \frac{\hbar\omega_E}{\exp(\hbar\omega_E\ /\ k_B T) - 1}\right)$$

Einstein Model

Works at low and high temperature

Lower at low temperature

Average energy for a crystal with three identical oscillators

$$\overline{U} = 3N(\tfrac{1}{2} + \overline{n})\hbar\omega_{\mathrm{E}} = 3N\left(\frac{\hbar\omega_{\mathrm{E}}}{2} + \frac{\hbar\omega_{\mathrm{E}}}{\exp(\hbar\omega_{\mathrm{E}} / k_{\mathrm{B}}T) - 1}\right)$$

$$C_{V,\mathrm{m}} = \left(\frac{\mathrm{d}\overline{U}}{\mathrm{d}T}\right)_V = 3R\left(\frac{\Theta_{\mathrm{E}}}{T}\right)^2 \frac{\exp(\Theta_{\mathrm{E}}/T)}{[\exp(\Theta_{\mathrm{E}}/T) - 1]^2}$$

Einstein temperature: $\Theta_{\mathrm{E}} = \dfrac{\hbar\omega_{\mathrm{E}}}{k_{\mathrm{B}}}$

Einstein Model

Works at low and high temperature

Lower at low temperature

$$C_{V,\mathrm{m}} = 3R = 24.94\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$C_{V,\mathrm{m}} = \left(\frac{\mathrm{d}\overline{U}}{\mathrm{d}T}\right)_V = 3R\left(\frac{\Theta_\mathrm{E}}{T}\right)^2 \frac{\exp(\Theta_\mathrm{E}/T)}{[\exp(\Theta_\mathrm{E}/T)-1]^2}$$

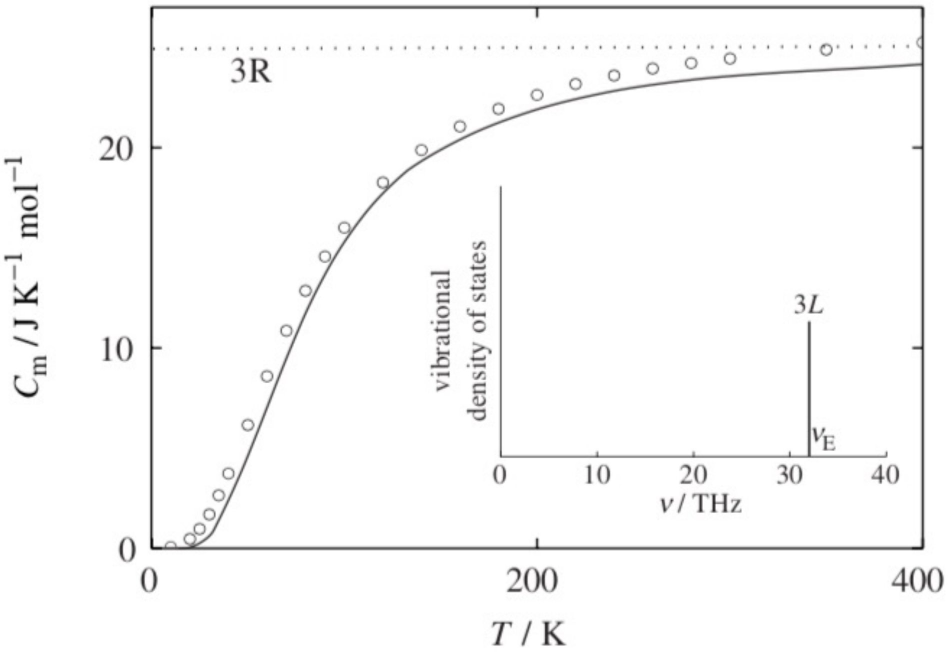
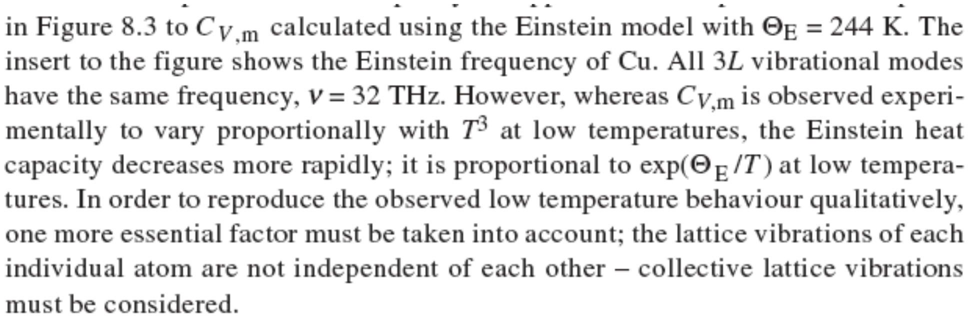


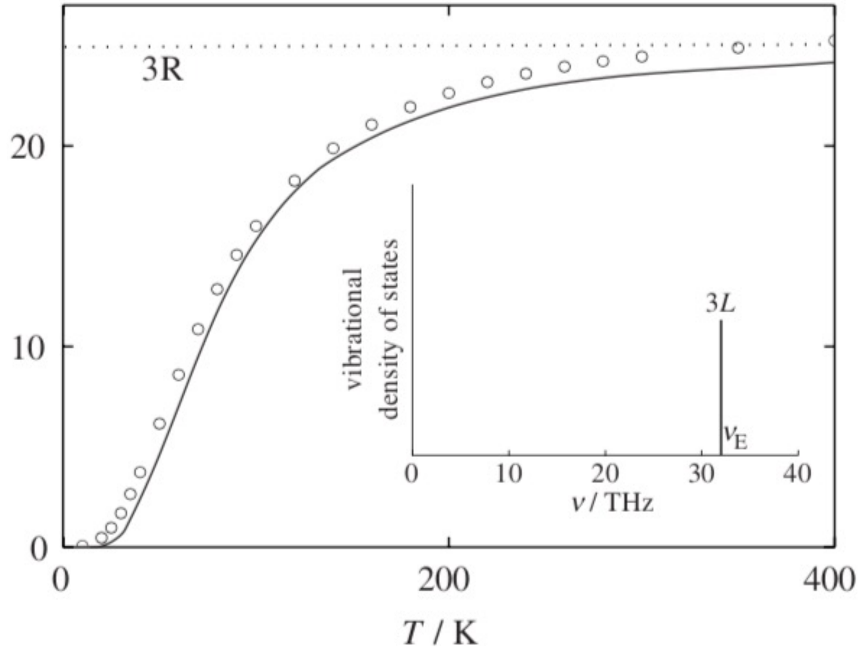
Figure 8.3 Experimental heat capacity of Cu at constant pressure compared with $C_{V,\mathrm{m}}$ calculated by the Einstein model using $\Theta_\mathrm{E} = 244$ K. The vibrational frequency used in the Einstein model is shown in the insert.

Einstein Model
Works at low and high temperature
Lower at low temperature

$$C_{V,\mathrm{m}} = 3R = 24.94\ \mathrm{J\ K^{-1}\ mol^{-1}}$$



in Figure 8.3 to $C_{V,\mathrm{m}}$ calculated using the Einstein model with $\Theta_E = 244$ K. The insert to the figure shows the Einstein frequency of Cu. All $3L$ vibrational modes have the same frequency, $\nu = 32$ THz. However, whereas $C_{V,\mathrm{m}}$ is observed experimentally to vary proportionally with T^3 at low temperatures, the Einstein heat capacity decreases more rapidly; it is proportional to $\exp(\Theta_E/T)$ at low temperatures. In order to reproduce the observed low temperature behaviour qualitatively, one more essential factor must be taken into account; the lattice vibrations of each individual atom are not independent of each other – collective lattice vibrations must be considered.



Single vibrational mode for all three DOF
Low T behavior $\exp(\Theta_E/T)$ doesn't work
C_v follows T^3
Lattice vibrations are coupled to each other
Collective Lattice Vibrations

Figure 8.3 Experimental heat capacity of Cu at constant pressure compared with $C_{V,\mathrm{m}}$ c
culated by the Einstein model using $\Theta_E = 244$ K. The vibrational frequency used in the Ei
stein model is shown in the insert

Debye Model

Works

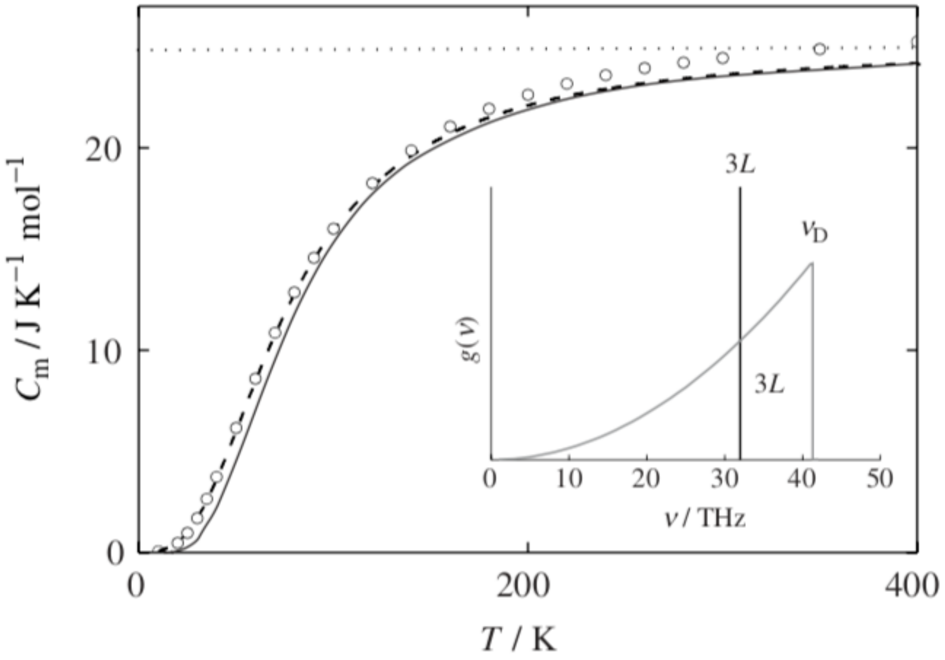


Figure 8.12 Experimental heat capacity of Cu at constant pressure compared with the Debye and Einstein $C_{V,m}$ calculated by using $\Theta_E = 244$ K and $\Theta_D = 314$ K. The vibrational density of states according to the two models is shown in the insert.