Derive the expression for \( C_p - C_v \)

\[
C_p - C_v = \alpha^2 VT / \kappa T
\]

\[
\alpha = (1/V)(dV/dT)_p
\]

\[
\kappa_T = (1/V)(dV/dP)_T
\]

\( C_v = (dU/dT)_v \)

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

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

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 \( C_p \): \( C_p / T = (dS/dT)_p = C_v / T (dT/dT)_p + (\alpha/\kappa_T)(dV/dT)_p = C_v / T + (V \alpha^2 / \kappa_T) \)

\( C_p - C_v = \alpha^2 VT / \kappa T \)
Heat Capacity

Internal Energy of a gas

\[ U = \sum_{i=1}^{N} \frac{1}{2} m_i c_i^2 + \Phi(r_1, r_2, r_3, \ldots, r_N) \]

For an ideal gas the potential is 0

\[ \frac{1}{2} m \langle c^2 \rangle = \frac{3 k_B T}{2} \]

3 degrees of freedom each with \( \frac{1}{2} kT \) energy

\[ U_m = L \frac{3}{2} k_B T = \frac{3}{2} R T \]

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

Linear molecule, CO₂, can rotate in two axes, \( C_{V,m} = 5/2 \ R \)

Non-Linear, H₂O, 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 calometric measurements are made at atmospheric pressure.

From $C_v$ for an ideal gas you add $R$ to obtain $C_p$.

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

$$C_{p,m} - C_{v,m} = \frac{\alpha^2 TV}{K_T}$$
Heat Capacity

\[ U_m = L \frac{3}{2} k_B T = \frac{3}{2} RT \quad \quad \quad \quad \quad C_{V,m} = \left( \frac{\partial U_m}{\partial T} \right)_V = \frac{3}{2} R \]

Linear molecule, CO\(_2\), can rotate in two axes, \( C_{V,m} = \frac{5}{2} R \)
Non-Linear, H\(_2\)O, can rotate in three axes, \( C_{V,m} = \frac{6}{2} R \)

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

\[ C_{p,m} - C_{V,m} = \frac{\alpha^2 TV}{\kappa T} = R \]

\[ PV = RT \]
\[ \frac{dV}{dT} = \frac{R}{P} \]
\[ \frac{dV}{dP} = -\frac{RT}{P^2} \]

\( \alpha = \frac{1}{V} \left( \frac{dV}{dT} \right) = \frac{R}{PV} = \frac{1}{T} \)
\( \kappa = \frac{-1}{V} \left( \frac{dV}{dP} \right) = \frac{RT}{VP^2} = \frac{1}{P} \)

\[ \alpha^2 TV/\kappa T = VP/T = R \]
<table>
<thead>
<tr>
<th></th>
<th>Number of modes</th>
<th></th>
<th>Classical</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Translational</td>
<td>Rotational</td>
<td>Vibrational</td>
<td>$C_{V,m}/R$</td>
</tr>
<tr>
<td>A(g)</td>
<td>3</td>
<td></td>
<td>1</td>
<td>3/2</td>
</tr>
<tr>
<td>AB(g)</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>7/2</td>
</tr>
<tr>
<td>AB$_2$(g)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>non-linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB$_2$(g)</td>
<td>3</td>
<td>2</td>
<td>4</td>
<td>13/2</td>
</tr>
<tr>
<td>linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB$_{n-1}$(g)</td>
<td>3</td>
<td>3</td>
<td>(3n − 6)</td>
<td>3 + (3n − 6)</td>
</tr>
<tr>
<td>non-linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB$_{n-1}$(g)</td>
<td>3</td>
<td>2</td>
<td>(3n − 5)</td>
<td>7/2 + (3n − 6)</td>
</tr>
<tr>
<td>linear</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
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), H2(g) and H2O(g). The open symbols at 5000 K represent the limiting classical heat capacity.
Monoatomic H(g) with only translational degrees of freedom is already fully excited at low temperatures. The vibrational frequencies \((n)\) of H\(_2\)(g) and H\(_2\)O(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 \(\sim 10\) K.

**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 \(\frac{1}{2}\); 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.

**Figure 8.2** Molar h symbols at 5000 K.
Atoms in a crystal (Dulong and Petit Model)

*Works at high temperature*

Three Harmonic oscillators, x, y, z

Spring (Potential Energy)

\[ \frac{dU}{dx} = F = -kx \text{ where } x \text{ is 0 at the rest position} \]

\[ U = -\frac{1}{2} kx^2 \]

Kinetic Energy

\[ U = \frac{1}{2} mc^2 \]

Three oscillator per atom so \( U_m = 3RT \)

\[ x = A \sin \omega t \quad \omega = 2\pi v = \sqrt{\frac{K}{m}} \]

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

\[ C_{V,m} = 3R = 24.94 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ dU = -pdV + TdS \]

\[ d(U/dT)_V = T(dS/dT)_V = C_V \]

-SUV
-H A
-pGT
For a system with quantized energy and two states $\varepsilon_1$ and $\varepsilon_2$, the ratio of the probabilities of the two states is given by the Boltzmann potentials, ($\tau$ is the temperature $k_B T$)

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

If state $\varepsilon_2$ 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,

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

$Z$ normalizes the probability for a state “s”

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

The average energy for the system is

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

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

$$C_V = \frac{d}{d\tau} \left( \frac{\ln Z}{Z} \right).$$
From Kittel and Kroemer Thermal Physics Chapter 2

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

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

Two size scales, a and \( \lambda \).

If \( \lambda \geq a \) you are within a Brillouin Zone

Wavevector \( k = \frac{2\pi}{\lambda} \)

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

Two size scales, $a$ and $\lambda$

If $\lambda \geq a$, you are within a Brillouin Zone

Wavevector $k = 2\pi/\lambda$

$k$-vector is like the inverse-space vectors for the lattice

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 \( \lambda \).

If \( \lambda \geq a \) you are within a Brillouin Zone.

Wavevector \( k = 2\pi/\lambda \).

The density of states is defined by

\[
D(E) = \frac{1}{V} \cdot \frac{dZ_m(E)}{dE}
\]

The partition function can be defined in terms of \( E \) or in terms of \( k \).

\( E \) and \( k \) are related by the dispersion relationship which differs for different systems.

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

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

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.
Phonons

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

\[ n(\omega_{k,s}) = \frac{1}{\exp\left(\frac{\hbar \omega_{k,s}}{k_B T}\right) - 1} \]
Phonons

Dispersion relation for phonons

\[ \omega^2_{\pm} = K \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \pm K \sqrt{\left( \frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4 \sin^2 \frac{ka}{2}}{m_1 m_2}} \]

Plus optical
Minus Acoustic
Phonons From Dove

Phonons have energy $\hbar \omega / 2\pi$

The energy at 0K is not 0 it is $\frac{1}{2} \hbar \omega / 2\pi$

This is a consequence of energy quantization (lattice calculations are done at 0K)

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

$n$ is the number of photons at wavelength $\omega$ 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”
Phonons From Dove

Bose-Einstein Relationship

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

\[ \langle n \rangle = \frac{1}{Z} \sum_n n \exp(-\beta n\epsilon) \]
\[ = -\frac{1}{\beta Z} \frac{\partial Z}{\partial \epsilon} \]

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

\[ Z = \sum_n \exp(-\beta n\epsilon) \]
\[ = \frac{1}{1 - x} \sum_n x^n \]

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

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

Bose-Einstein Relationship

At high T

\[
\frac{1}{2} + n(\omega, T) = \frac{1}{2} + \frac{1}{\exp(\beta \epsilon) - 1} = \frac{\exp(\beta \epsilon) + 1}{2[\exp(\beta \epsilon) - 1]}
= \frac{(1 + \beta \epsilon + \cdots) + 1}{2[(1 + \beta \epsilon + \beta^2 \epsilon^2/2 + \cdots) - 1]}
= \frac{2 + \beta \epsilon + \cdots}{\beta \epsilon(2 + \beta \epsilon + \cdots)}
\approx \frac{1}{\beta \epsilon} = \frac{k_B T}{\hbar \omega}
\]

(9.10)

3 vibrations for each atom

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

E = 3RT
Phonons  From Dove

\[ c_V = \left( \frac{\partial E}{\partial T} \right)_V \]
\[ = \sum \hbar \omega \frac{\partial n}{\partial T} \]
\[ = \sum k_B \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{\exp(\hbar \omega / k_B T)}{[\exp(\hbar \omega / k_B T) - 1]^2} \]
Fig. 9.2 Comparison of calculated (line) and experimental (points) heat capacity of the mineral andalusite, Al$_2$SiO$_5$. 

Phonons From Dove
Phonons From Dove

Phonon Free Energy

Including ground state energy

At high $T$

\[
F = -\frac{1}{\beta} \ln Z
\]

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

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

\[
F = \frac{1}{\beta} \ln(\beta \epsilon) \quad S = -\frac{\partial F}{\partial T}
\]

\[
S = k_B [1 - \ln(\beta \epsilon)]
\]
Phonons  From Dove

For a crystal sum over all vibrations

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

*Fig. 9.2* Comparison of calculated (line) and experimental (points) heat capacity of the mineral andalusite, Al₂SiO₅.
For quantized phonons

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

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

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

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

\[ \langle s \rangle = \frac{\exp(-y)}{1 - \exp(-y)} \]

\[ \langle s \rangle = \frac{1}{\exp(h\omega/\tau) - 1}. \]

Planck Distribution

\[ \langle \varepsilon \rangle = \langle s \rangle \hbar\omega = \frac{\hbar\omega}{\exp(h\omega/\tau) - 1}. \]
**Einstein Model**
*Works at low and high temperature*
*Lower at low temperature*

**Quantized energy levels**

\[ \varepsilon_n = (n + \frac{1}{2}) \hbar \omega \]

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

\[ \bar{U} = 3N(\frac{1}{2} + \bar{n})\hbar \omega_E = 3N\left( \frac{\hbar \omega_E}{2} + \frac{\hbar \omega_E}{\exp(\hbar \omega_E / k_B T) - 1} \right) \]
Einstein Model
Works at low and high temperature
Lower at low temperature

Average energy for a crystal with three identical oscillators

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

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

Einstein temperature:

$$\Theta_E = \frac{\hbar\omega_E}{k_B}$$
Einstein Model

Works at low and high temperature

Lower at low temperature

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

Figure 8.3 Experimental heat capacity of Cu at constant pressure compared with \( C_{V,m} \) calculated by the Einstein model using \( \Theta_E = 244 \) K. The vibrational frequency used in the Einstein model is shown in the insert.
**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.
Debye Model

Works

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.

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

Before we had $F = -Ku$
Propose a solution:

\[ u_n = u_0 \cos(\omega t - qna) \]

**Phase angle \( \delta \)**

**Wave vector** \( q = 2\pi/\lambda \)

Atomic spacing is “a”

Use in the equation of motion and solve for frequency

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

**Angular frequency of vibrations as a function of wavevector, \( q \)**

\[ \omega(q) = \sqrt{\frac{4K}{m}} \sin\left(\frac{qa}{2}\right) \]
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, \( q \)

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

For small wave vectors \( \sin(\theta) \Rightarrow \theta \)

**Acoustic or Ultrasonic range**

\[ \omega \approx a \sqrt{\frac{K}{m}} |q| \]

Long wavelengths

Group Velocity = \( \frac{d\omega}{dq} = a\sqrt{\frac{K}{m}} \)

Speed of sound in the solid

Material is a continuum at these large distances

Acoustic or Ultrasonic range
Dispersion Curve

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

Angular frequency of vibrations as a function of wavevector, \( q \)

For large wave vectors (short wavelengths)

Dispersion region

\( \omega \) 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.
Diatonic Chain Model

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

**Acoustic and Optical modes**

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

\[
\omega_o^2 = K \left[ \left( \frac{m_1 + m_2}{m_1 m_2} \right) + \frac{\sqrt{(m_1 - m_2)^2 + 4 m_1 m_2 \cos^2 qa}}{m_1 m_2} \right] 
\]
Figure 8.9 The dispersion curve for a one-dimensional diatomic chain of atoms, \( m_2 < m_1 \).

\[
\omega_a \approx a \sqrt{\frac{2K}{m_1 + m_2}} |q|
\]

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

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

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

\[ \text{n atoms in unit cell} \]
\[ 3N_A \cdot n \text{ vibrational modes} \]
\[ 3N_A \text{ acoustic modes (Unit cell vibrates as an entity)} \]
\[ 3N_A(n-1) \text{ optical modes (deformation of unit cell)} \]

At high T each mode has \( k_B T \)
So heat capacity is \( 3R \)

Number of vibrational modes

\[ 3N_A g(v)dv \quad \text{where} \quad \int_0^\infty g(v)dv = 1 \]

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

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
Debye Model

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, $g(\omega)$, above a cutoff frequency, $\omega_D$

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

\[
g(\omega) = 0 \quad \text{for} \quad \omega > \omega_D
\]
Debye Model

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, \( \theta_D \)

\[ \Theta_D = \frac{\hbar \omega_D}{k_B} = 2\pi \frac{h v_D}{k_B} \]
Debye Model

\[ \Theta_D = \frac{h \omega_D}{k_B} = 2\pi \frac{h v_D}{k_B} \]

Heat Capacity is given by,

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

Einstein temperature:

\[ \Theta_E = \frac{h \omega_E}{k_B} \]

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 $\Theta_E = 244 \text{ K}$ and $\Theta_D = 314 \text{ K}$. The vibrational density of states according to the two models is shown in the insert.
Figure 8.13 Lattice heat capacity of three different polymorphs of carbon; $C_{60}$ [5], graphite and diamond.

Higher Characteristic $T$ represents stronger bonds.
Table 8.2. Debye temperature ($\Theta_D$ in K) and electronic heat capacity coefficient (see Section 8.4) ($\gamma$ in mJ K$^{-1}$ mol$^{-1}$) of the elements.

|   | Li  | Be  | Na  | Mg  | K   | Ca  | Sc  | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  | Ga  | Ge  | As  | Se  | Br  | Kr  |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|   | 344 | 1440| 158 | 400 | 91  | 230 | 360 | 420 | 380 | 630 | 410 | 470 | 445 | 450 | 315 | 327 | 320 | 374 | 282 | 90  | 72  |
|   | 18  | 2   | 14  | 14  | 21  | 77  | 88  | 92  | 16  | 180 | 50  | 48  | 73  | 7  | 6   | 6   | 14  | 14  | 22  | 37  | 24  | 56  |
|   |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
|   | Rb | Sr  | Y   | Zr  | Nb  | Mo  | Tc  | Ru  | Rh  | Pd  | Ag  | Cd  | In  | Sn  | Sb  | Te  | I   | Xe  |     |     |     |     |
|   | 56 | 147 | 280 | 291 | 275 | 450 | 21  | 600 | 480 | 274 | 225 | 209 | 108 | 200 | 211 | 153 | 64  |     |     |     |     |     |
|   | 24 | 37  | 30  | 88  | 21  | 34  | 49  | 34  | 49  | 100 | 6  | 7 |     |     |     |     |     |     |     |     |     |     |
| Cs| 33 | 110 | 142 | 252 | 240 | 400 | 12  | 25  | 240 | 66  | 165 | 72  | 79  | 105 | 119 | 159 | 64  |     |     |     |     |     |

Higher Characteristic T represents stronger bonds
Higher Characteristic $T$ represents stronger bonds

**Figure 8.14** Debye temperature of the alkali halides.
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 \( \omega_D \) from E

For Cu, \( \Theta_D = 344K \)

\[ \Theta_D = \frac{h\omega_D}{k_B} = 2\pi \frac{hV_D}{k_B} \]

\( \omega_D = 32 \) THz

\( K = 13.4 \) N/m
\( \omega_D = 18 \) THz
Table 8.3 Comparison of Debye temperatures derived from heat capacity data and from elastic properties.

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Cu</th>
<th>Al</th>
<th>NaCl</th>
<th>KBr</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_D$(Elastic)</td>
<td>226.4</td>
<td>344.4</td>
<td>428.2</td>
<td>321.9</td>
<td>182.8</td>
<td>834.1</td>
</tr>
<tr>
<td>$\Theta_D$(CV)</td>
<td>226.2</td>
<td>345.1</td>
<td>426</td>
<td>320</td>
<td>184</td>
<td>838</td>
</tr>
</tbody>
</table>
How to obtain $C_p$ from calculated $C_V$?

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

At low $T$ $C_V = C_p$

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
Figure 8.15  $C_{p,m} - C_{V,m}$ and $C_{V,m} - C_{V,m,\text{fix}}$ for Mo and W [6]
Approximate relationships for $C_p - C_V$

Nernst–Lindeman relationship

\[ C_{p,m} - C_{V,m} = \frac{V \alpha^2}{\kappa T C_{p,m}^2} C_{p,m}^2 T = AC_{p,m}^2 T \]

If you know the thermal expansion coefficient,

\[ C_{p,m} - C_{V,m} = \gamma_G \alpha C_{V,m} T \]

\[ \gamma_G = \left[ \frac{\partial p}{\partial (U/V)} \right]_V = \frac{\alpha V}{\kappa T C_{V,m}} \]

Grüneisen parameter.
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

\[ 3N_A g(v)dv \quad \text{where} \quad \int_0^\infty g(v)dv = 1 \]

Figure 8.16 (a) IR and (b) Raman spectra for the mineral calcite, CaCO₃. 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).
-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

\[ S_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E / T)}{[\exp(\Theta_E / T) - 1]^2} \]

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

\[ \theta_E = \hbar \omega_E / k_B \]

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

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

\[ \theta_D = \hbar \omega_D / k_B \]
Figure 8.17 Entropy of a monoatomic solid for different values of the Debye temperature, $\Theta_D$. 

\[ S / J K^{-1} \text{ mol}^{-1} \]

- $\Theta_D = 300 \text{ K}$
- $\Theta_D = 400 \text{ K}$
- $\Theta_D = 500 \text{ K}$
Calorimetrically determine $S$ at high temperature then find the Debye temperature that makes the calculation of $S$ match

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

Large $\Theta_D$ means more stable

Figure 8.18 Entropy Debye temperature, $\Theta_S$, for (a) alkali earth dihalides [10] and (b) first series transition metal carbides [11].
Group Contribution Method for Entropy and Heat Capacity

Sum the component entropy and heat capacities

Estimation of thermodynamic data for metallurgical applications

P.J. Spencer*

Lehrstuhl für Theoretische Hüttenkunde, RWTH Aachen, D-52056 Aachen, Germany

Received 10 October 1997; accepted 24 November 1997
Entropy correlates with molar volume

\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{\alpha}{\kappa_T} \quad \text{or} \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial \Theta}{\partial V} \right)_T \left( \frac{\partial S}{\partial \Theta} \right)_T
\]

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

TIMOTHY J. B. HOLLAND
Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, England
\[ dG = -SdT + Vdp \]

For a transition \( \Delta G = 0 \)
And
\[ \frac{dp}{dT} = \frac{\Delta S}{\Delta V} \]
\( \Delta S \) and \( \Delta V \) have the same sign

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

**pyroxene > perovskite > garnet > ilmenite**

**pyroxene < garnet < ilmenite < perovskite**

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.

**Entropy**

**Density = mass/volume**
Electronic Heat Capacity

Electrons have three degrees of freedom so contribute $\frac{3}{2}R$ to the heat capacity. Dulong Petit $3R$ plus $\frac{3}{2} R$ for a monovalent metal like Cu, 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.
Heat from 0K to $T$ 

$\Delta U = N_1 k_B T$

$N_1 = n(\varepsilon_F) k_B T$

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

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

$C_E = \gamma T$

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

$\gamma$ is the electronic heat capacity coefficient
Table 8.2. Debye temperature ($\Theta_D$ in K) and electronic heat capacity coefficient (see Section 8.4) ($\gamma$ in mJ K$^{-1}$ mol$^{-1}$) of the elements.

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
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<td>Re</td>
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</table>
For $T < 10K$

\[ C_V = \beta T^3 + \gamma T \]

\[ C_{p,m}/T = \gamma + \beta T^2 \]

\[ \gamma = 7 \text{ mJ K}^{-2} \text{ mol}^{-1} \]

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

Magnetic excitation
Magnon
Spin waves

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

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

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

Transition can occur on doping of an oxide like Fe$_2$O$_3$
Temperature or Pressure Changes
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, $\Delta S$

$N_{un}$ unpaired electrons

Total spin quantum number $\mathcal{S} = \sum \frac{1}{2} N_{un}$

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

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

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

Figure 8.23 Heat capacity of Fe$_2$O$_3$ [18]. The heat capacity is deconvoluted to show the relative magnitude of the main contributions. $C_{dil} = C_{p,m} - C_{V,m} = \alpha^2 TV/k_T$. 
Co$_3$O$_4$ Transitions

The normal spinel contains Co$^{2+}$ at tetrahedral sites and low-spin Co$^{3+}$ at octahedral sites. The heat capacity effect observed at $T \beta 900$K 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$3O4$ at around 30 K.

Figure 8.24 Heat capacity of Co$_3$O$_4$ [23–25]. The insert shows the magnetic order–disorder transition at around 30 K [24] in detail.
The **spinel structure** is formulated $\text{MM'}_2\text{X}_4$, where $\text{M}$ and $\text{M'}$ are tetrahedrally and octahedrally coordinated cations, respectively, and $\text{X}$ is an anion (typically $\text{O}$ or $\text{F}$). The structure is named after the mineral $\text{MgAl}_2\text{O}_4$, and oxide spinels have the general formula $\text{AB}_2\text{O}_4$. 
### Schottky Defect

Schottky defect occurs in those ionic crystals where difference in size between cation and anion is small.

In Schottky defect, both cation and anion leave the solid crystal.

The atoms permanently leave the crystal.

One Schottky defect leads to the formation of two vacancies.

Due to vacancy formation, Schottky defect reduces density of 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 (CeO₂)
- Thorium Dioxide (ThO₂)

### Frenkel Defect

Frenkel defect usually occurs in those ionic crystals where size of anion is quite large as compared to that of the cation.

In Frenkel defect, only the smaller ion (cation) leaves its original lattice site; whereas, the anion remains in original lattice sites.

Here, atoms leave the original lattice site and occupy interstitial position. So atoms reside within the solid crystal.

One Frenkel defect creates one vacancy and one self-interstitial defect.

The number of atoms present in the crystal before and after Frenkel defect remains same.

Density of the solid crystal before and after Frenkel defect remains same as no atom leaves the solid.

Common materials where Frenkel defect can be found are:
- Zinc Sulfide (ZnS)
- Silver Chloride (AgCl)
- Silver Bromide (AgBr)
Two levels with energy spacing $\varepsilon/k_B$

$T > \varepsilon/k_B$ both levels occupied equally

$T < \varepsilon/k_B$ only lower level occupied

Boltzmann statistics yields

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

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

Figure 8.25  The Schottky-type heat capacity of Nd$_2$S$_3$ [28]. The insert shows the total heat capacity of ErFeO$_3$ [29].
Schottky Defects

Endothermic formation enthalpy
Entropy associated with disorder of defect location

\[ C_{V,m} = \frac{1}{RT^2} \left[ \Delta_{\text{vac}} H_m^2 \exp \left( \frac{\Delta_{\text{vac}} S_m}{R} \right) \right] \exp \left( -\frac{\Delta_{\text{vac}} H_m}{RT} \right) \]
Fast Ion Conductors

Solid electrolytes for batteries and fuel cells

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

Also, Cu$_2$S, Ag$_2$S. NaS battery

Heat Capacity drops with temperature
Liquids and Glasses

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 lead to decrease in $C_p$

Later, $S$ increases with $T$

$$T(dS/dT)_p = C_p$$
Anomalous behavior of glasses near absolute 0

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

Behavior is due to anharmonic vibrations

Figure 8.26 Heat capacity of glassy and crystalline $B_2O_3$ [42–44] and glassy Se [41] plotted as $C_{p,m}T^{-3}$ versus $T$. 
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.
Pseudo-second order transition behavior of glasses

Figure 8.28 Heat capacity of glassy B$_2$O$_3$ at different heating rates [50].
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.
Thermodynamic and Kinetic Fragility

Fragile versus strong glass

Kinetics: Deviation from Arrhenius behavior

\[ \eta = \eta_0 \exp\left(-E_a/k_BT\right) \]

Scaled Exponential

\[ \eta = \eta_0 \exp\left(-E_a/k_BT\right)^m \]
Fig. 13: Correlation of glass and liquid fragilities for an ensemble of glass-formers.
Heat Capacity of Polymers

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

Einstein method works well above 100K

\[ E(\Theta/T) = \frac{((\Theta/T)^2 \exp(\Theta/T))}{[\exp(\Theta/T) - 1]^2} \]

\[ C_E = N k \sum N_E E(\Theta/T) \]

\[ N_E = 3N_{\text{Atoms}} - N \]

where \( N_{\text{Atoms}} \) is the number of atoms in a mer unit:
3 for \( \text{CH}_2 \)

\( N = \) number of skeletal modes of vibration:
2 for \( -(\text{CH}_2)_n - \)

Einstein temperature:
\[ \Theta_E = \frac{h \omega_E}{k_B} \]

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

\[ N_{\text{Atoms}} = \text{number of atoms in a mer unit} \]
3 for \( \text{CH}_2 \)

\( N = \text{number of skeletal modes of vibration} \)
2 for \( -(\text{CH}_2)_n - \)
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

\[ D_3(\theta/T_3) = \frac{3(\theta/T_3)^3}{\theta_3^3} \int_0^{\theta_3} \left\{ \left[ (\theta/T)^4 \exp(\theta/T) \right] / \left[ \exp(\theta/T) - 1 \right]^2 \right\} d(\theta/T) \]

\[ C_v / 3Nk = D_3(\theta/T_3) \]

\[ \theta_3 = \hbar v_3 / k \]

For skeletal modes normal to the chain

Strong covalent interactions along chains described by 1d Debye function

\[ D_1(\theta/T_1) = \frac{(\theta/T_1)^2}{\theta_1^2} \int_0^{\theta_1} \left\{ \left[ (\theta/T)^2 \exp(\theta/T) \right] / \left[ \exp(\theta/T) - 1 \right]^2 \right\} d(\theta/T) \]

\[ C_v / 3Nk = D_1(\theta/T_1) \]

\[ \theta/T = \hbar v_1 / k \]

For skeletal vibrations in the chain axis

Linear heat capacity increase from 0 to 200K
At low frequency 3D vibrations, at high frequency 1D vibrations

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

\[ C_T = \frac{Nk}{3} \left[ \frac{(6.7 T/\theta_1)^2}{1 + (6.7 T/\theta_1)^2} \right] \]
Polystyrene

\[ \text{Atoms} = 16 \text{ atoms per unit} \]

\[ N = 6 \text{ skeletal mode vibrations} \]

\[ NE = 42 \]

\[ \theta_1 = 285 \text{ K} \]

42 total atomic group modes of vibration

Or calculate with the Tasarov Equation

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

\[ C_E = Nk \sum_{NE} E(\theta/T) \]

\[ C_T = 6R \left( \frac{(T/42.5)^2}{1 + (T/42.5)^2} \right) \]
\[ C_P - C_V = -T \left( \frac{dV/dT}{dV/dP} \right)_P / \left( \frac{dV/dP}{dV/dT} \right)_T = V\alpha^2BT \]

\[ V_m = 92.8 - 99.6 \text{ cm}^3/\text{mol} (0 - 300 \text{K}) \]

\[ B = 3.58 \text{ GPa} \]

\[ \alpha_g = 2.37 \times 10^{-4} \text{ and} \]

\[ \alpha_f = 5.74 \times 10^{-4} \text{ and} \]
