

Foundations of Physics 2B - Summary

Thermodynamics

Heat Capacity

The heat capacity is defined by:

$$\delta Q = C dT$$

Where δQ is the heat energy required to raise the temperature of a body by dT .

The heat capacity at constant volume is:

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = m c_V$$

Where m is the mass and c_V is the specific heat capacity at constant volume.

The same applies to constant pressure, C_P .

Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other.

Partial Derivatives

The total differential of a function $z = f(x, y)$ is defined by:

$$dz = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy = M(x, y)dx + N(x, y)dy$$

If $f(x, y, z) = 0$ we know that $x = x(y, z)$ and $y = y(x, z)$. We then have two theorems:

Reciprocal theorem:

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z = 1$$

Reciprocity theorem or cyclic relation:

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

Exact and Inexact Differentials

The total differential dz is exact if:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Which is true only if x and y are independent and so

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}$$

This is equivalent to saying that:

$$I = \int_1^2 dz(x, y) = \int_1^2 M(x, y)dx + \int_1^2 N(x, y)dy = z_2 - z_1$$

i.e. the integral of dz is *path independent*. All thermodynamic system properties (e.g. p , V , T , U , S) are such functions.

Note: Inexact differentials are denoted by δz .

First Law of Thermodynamics

If a system moves from an initial state, i , to a final state, f , via adiabatic paths, the work done is the same for all adiabatic paths.

Mathematically this can be stated as:

$$dU = \delta Q + \delta W$$

Heat Capacity

Using the 1st Law, we find that:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Proof:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - \left(\frac{\partial W}{\partial T}\right)_V$$

However, at constant volume W is constant, so we get:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

We also find that:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p \right] \left(\frac{\partial V}{\partial T}\right)_p$$

Proof:

Using $\delta W = -pdV$ we get:

$$\delta Q = dU + pdV$$

We can also find that for $U = U(T, V)$:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Combining the two gives:

$$\delta Q = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] dV$$

Using the definition of C_P :

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p$$

Now, using the expression for C_V :

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p$$

And so:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p$$

For an ideal gas:

$$C_P - C_V = R$$

We can also define the adiabatic index as:

$$\gamma = \frac{C_P}{C_V}$$

Reversible and Irreversible Processes

A process is reversible if:

- No frictional or dissipative forces exist
- No heat conduction is present due to finite temperature differences
- The process is quasi-static

Adiabatic and Diathermal Walls

An adiabatic wall means no heat can be exchanged through it whilst a diathermal wall does allow the passage of heat.

The equation of state for an ideal gas under adiabatic conditions is:

$$pV^\gamma = \text{constant}$$

Heat Engines

Heat engines are machines that produce work using a temperature difference between two heat reservoirs, known as a heat source and a heat sink.

Efficiency of a Heat Engine

In general:

$$\text{Efficiency} = \eta = \frac{\text{Product}}{\text{Expense}}$$

For a heat engine:

$$\eta = \frac{|\text{Work Done}|}{\text{Heat Input}} = \frac{Q_H - Q_L}{Q_H}$$

For a fridge:

$$\text{COP}_L = \frac{\text{Heat from Cold Reservoir}}{\text{Work Supplied}} = \frac{Q_L}{W}$$

For a heat pump:

$$\text{COP}_H = \frac{\text{Heat to Hot Reservoir}}{\text{Work Supplied}} = \frac{|Q_H|}{W}$$

Second Law of Thermodynamics

Clausius Statement:

It is impossible to devise a process whose sole result is the transfer of heat from a cold to a hot reservoir.

Kelvin-Planck Statement:

It is impossible to construct a device that operates in a cycle producing positive work that only interacts with one heat reservoir.

These two laws are logically equivalent.

More on Reversibility

- To show a process is reversible it is sufficient to show a reversible process exists
- To show a process is irreversible, it is sufficient to show that it violates the second law

Carnot Engines

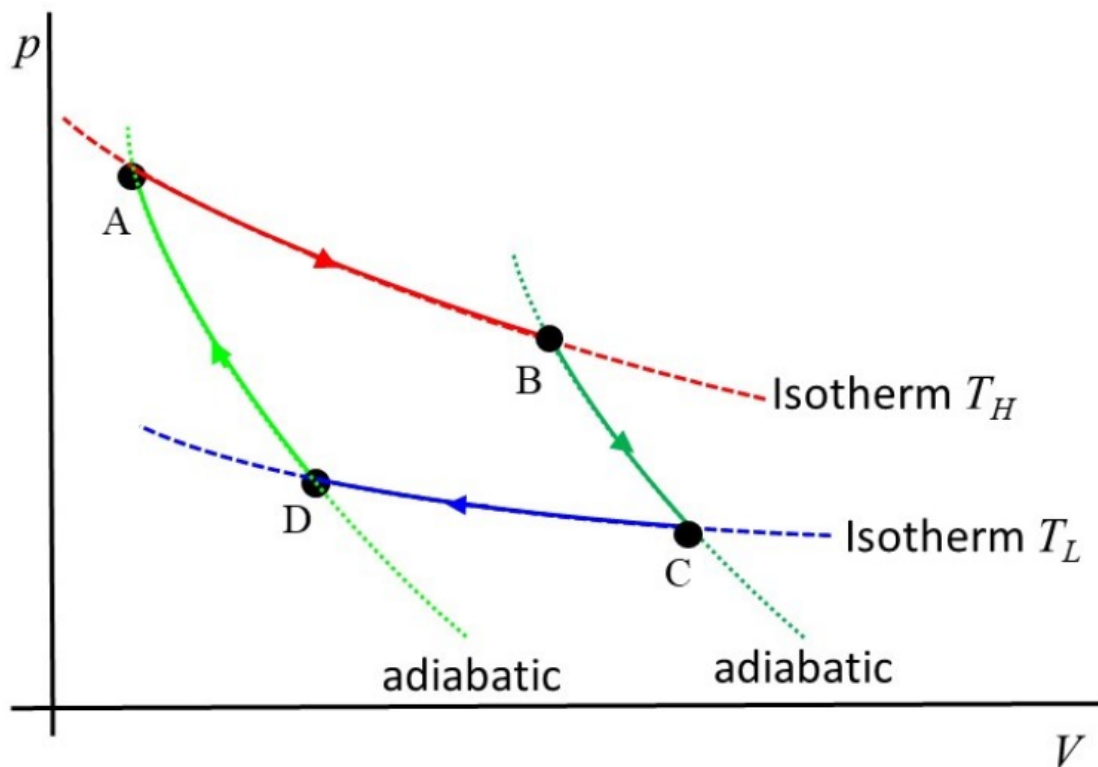


Figure 9: pV diagram for a Carnot Cycle.

The Carnot cycle is reversible.

We find the following relationship from the cycle:

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L}$$

This allows us to write the following as:

$$\eta = 1 - \frac{T_L}{T_H}; \quad \text{COP}_L = \frac{T_L}{T_H - T_L}; \quad \text{COP}_H = \frac{T_H}{T_H - T_L}$$

Proof of the Carnot Relation:

Work done on the isotherms at temperatures T_H ($-\delta W_{AB} = \delta Q_{AB}$) and T_C respectively are:

$$Q_H = - \int_A^B -pdV = \int_{V_A}^{V_B} \frac{RT_H}{V} dV = RT_H \ln\left(\frac{V_B}{V_A}\right)$$

$$Q_L = - \int_C^D -pdV = RT_L \ln\left(\frac{V_D}{V_C}\right) = -RT_L \ln\left(\frac{V_C}{V_D}\right)$$

The ratio of the heats is therefore given by:

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L} \frac{\ln(V_B/V_A)}{\ln(V_C/V_D)} \quad (*)$$

Using the equation of state for an ideal gas under adiabatic conditions:

$$p_A V_A^\gamma = p_D V_D^\gamma; \quad p_B V_B^\gamma = p_C V_C^\gamma$$

Since $pV = RT$, we can eliminate the pressures in terms of temperature:

$$p_A V_A = RT_H = p_B V_B; \quad p_C V_C = RT_L = p_D V_D$$

Hence

$$RT_H V_B^{\gamma-1} = RT_L V_C^{\gamma-1}; \quad RT_H V_A^{\gamma-1} = RT_L V_D^{\gamma-1}$$

And so:

$$\frac{T_H}{T_L} = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \equiv \left(\frac{V_D}{V_A}\right)^{\gamma-1}$$

Which gives:

$$\frac{V_C}{V_D} = \frac{V_B}{V_A}$$

Substituting this into (*) gives us the Carnot Relation:

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L}$$

Carnot Principles

There are two Carnot Principles:

- *Of all the heat engines working between two temperatures, none is more efficient than a Carnot engine.*
- *All reversible heat engines operating between two heat reservoirs have the same efficiency.*

Otto Cycle

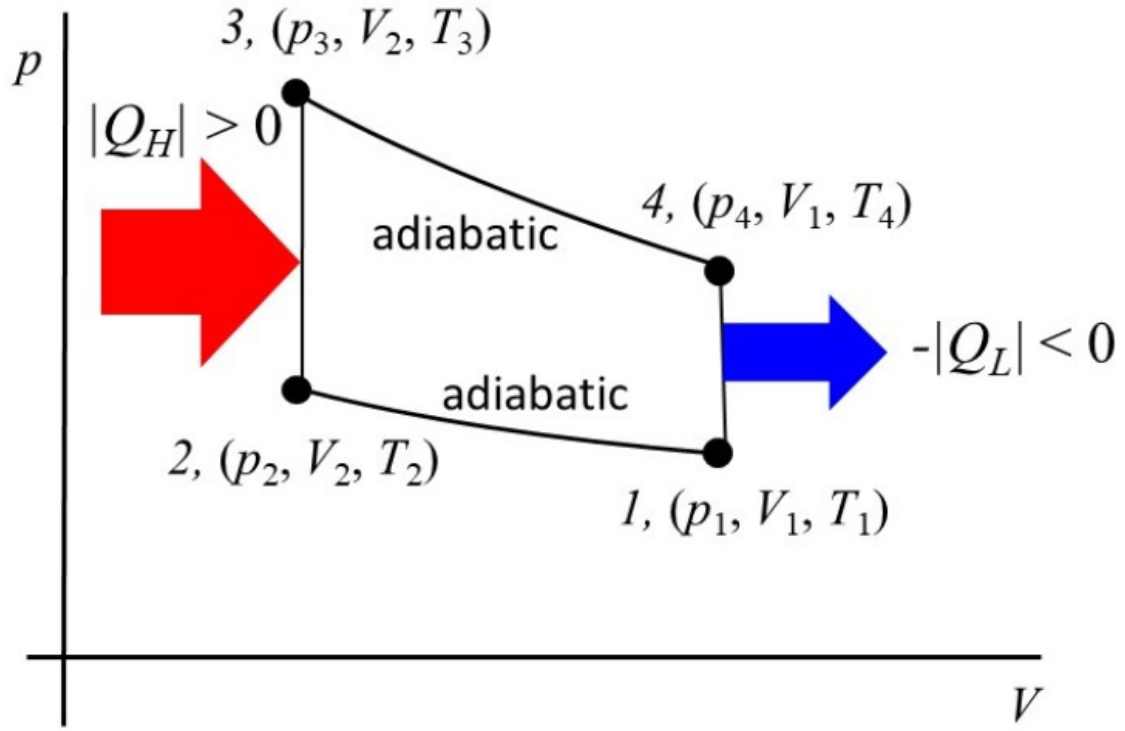


Figure 14: pV diagram of ideal Otto cycle.

The efficiency of an Otto cycle (for petrol engines) is given by:

$$\eta_{\text{Otto}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \left(\frac{V_1}{V_2} \right)^{1-\gamma} = 1 - r^{1-\gamma}$$

Where r is the compression ratio which is typically between 7 and 10.

Proof:

Considering each process for the Otto cycle in turn:

1 to 2: An adiabatic compression with

$$p_1 V_1^\gamma = p_2 V_2^\gamma \Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

2 to 3: Isothermal heating with

$$Q_H = \int_{T_2}^{T_3} C_V dT = C_V (T_3 - T_2) > 0$$

3 to 4: Adiabatic expansion with

$$p_3 V_3^\gamma = p_4 V_4^\gamma \Rightarrow T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1} \Rightarrow T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

4 to 1: Isothermal cooling with:

$$Q_L = \int_{T_4}^{T_1} C_V dT = C_V (T_1 - T_4) < 0$$

The efficiency is hence:

$$\eta = 1 - \frac{|Q_L|}{Q_H} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

Considering the adiabatic parts, we can write:

$$T_1 = \frac{T_2 V_2^{\gamma-1}}{V_1^{\gamma-1}}$$

And:

$$\frac{T_3 V_2^{\gamma-1}}{T_4^{\gamma-1}} = V_1^{\gamma-1}$$

Which gives:

$$\frac{T_1}{T_4} = \frac{T_2}{T_3}$$

Rearranging the efficiency gives:

$$\eta = 1 - \frac{T_1 \left[\left(\frac{T_4}{T_1} \right) - 1 \right]}{T_2 \left[\left(\frac{T_3}{T_2} \right) - 1 \right]}$$

Since the two terms in brackets are equal, we can write the efficiency as:

$$\eta_{\text{Otto}} = 1 - \left(\frac{V_1}{V_2} \right)^{1-\gamma} = 1 - r^{1-\gamma}$$

Diesel Cycle

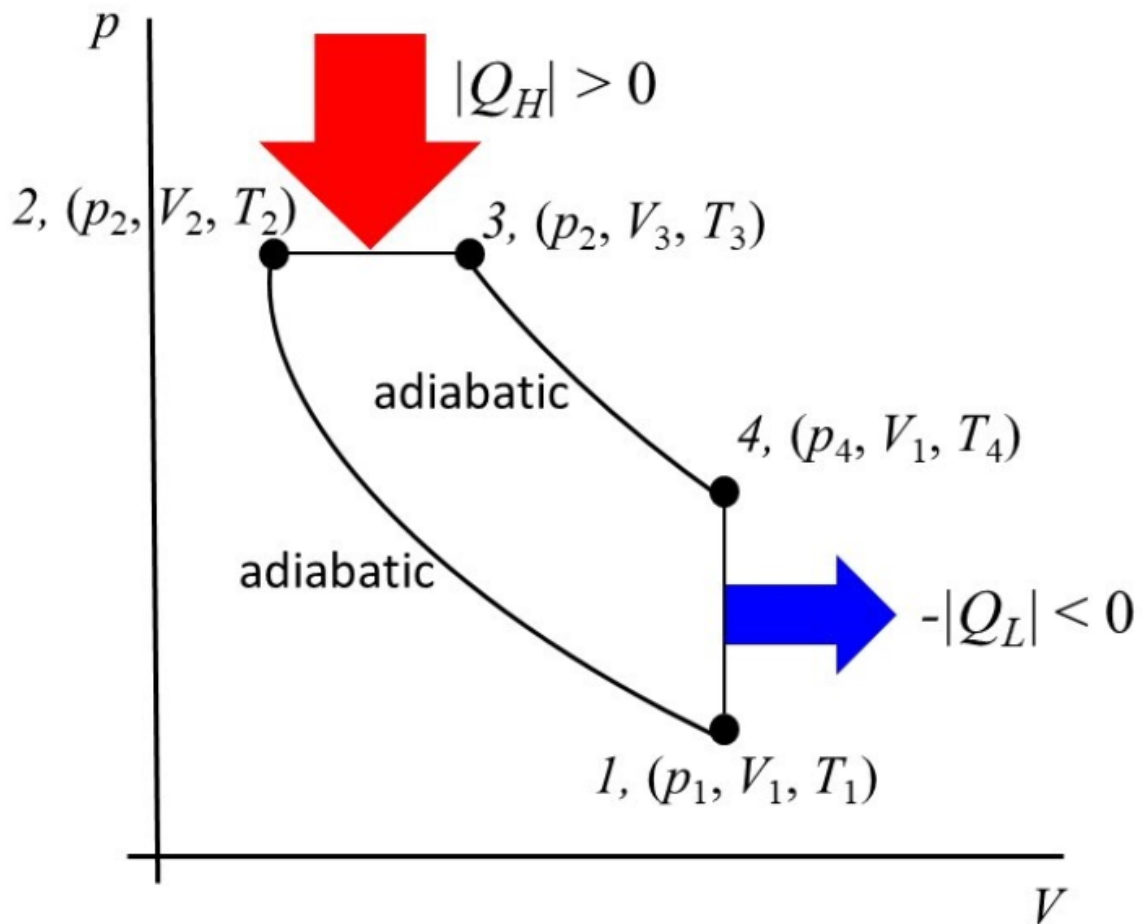


Figure 16: pV diagram of ideal Diesel Cycle.

The efficiency of the Diesel cycle (for diesel engines) is given by:

$$\eta_{\text{Diesel}} = 1 - \frac{1}{r^{\gamma-1}} \left[\frac{(r_c^\gamma - 1)}{\gamma(r_c - 1)} \right]$$

Where $r_c = V_3/V_2$ is the cut-off ratio. In the limit that $r_c \rightarrow 1$ the efficiency becomes the same as the Otto cycle.

Brayton Cycle

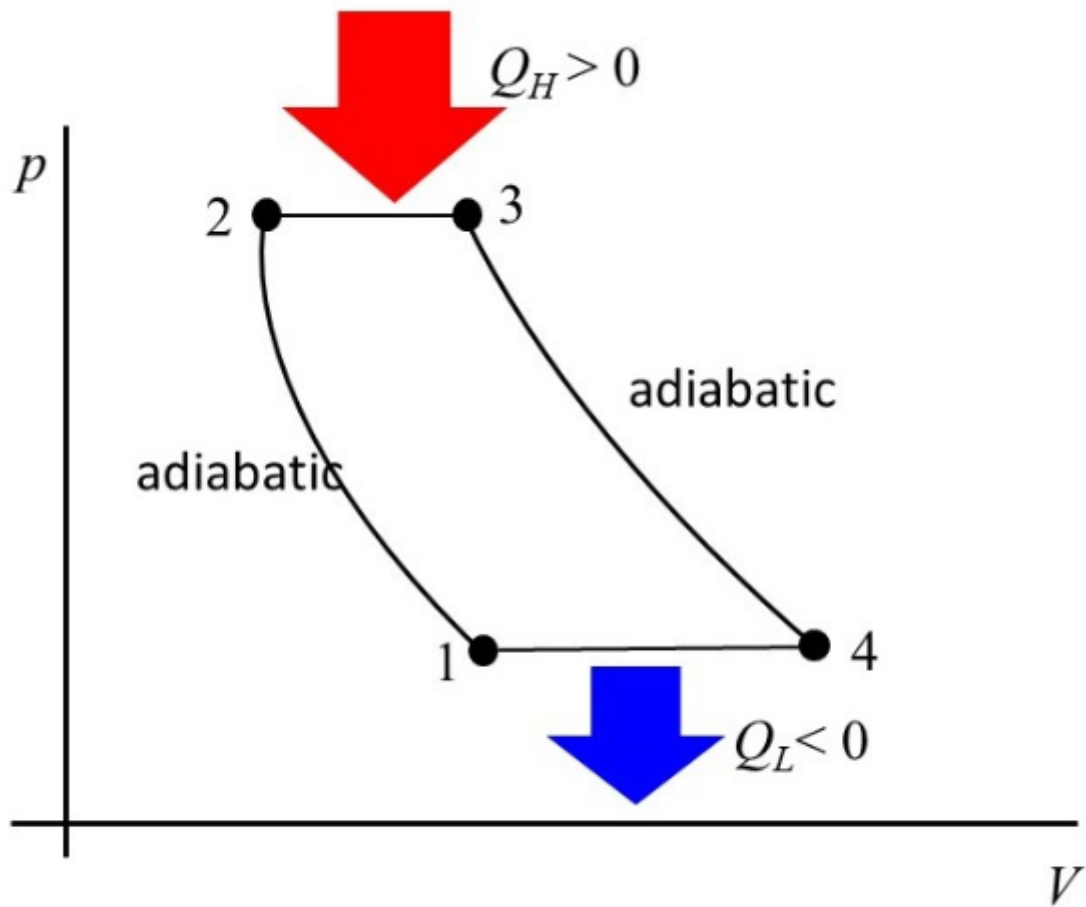


Figure 20: Brayton cycle pV diagram.

The efficiency of the Brayton cycle (for gas turbines) is:

$$\eta_{\text{Brayton}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = \frac{1}{r_p^{(\gamma-1)/\gamma}}$$

Where $r_p = p_2/p_1$ is the pressure ratio.

Clausius Inequality

The Clausius inequality tells us that:

$$\oint \frac{\delta Q}{T} \leq 0$$

Heat is thus not conserved in a thermodynamic process, unless it is reversible and places a direction on some processes.

Entropy

The entropy change between two thermodynamic states, A and B , is

$$dS = \frac{\delta Q_{\text{rev}}}{T}$$

So

$$S(B) - S(A) = \int dS = \int_A^B \frac{\delta Q}{T}$$

An adiabatic process has no heat change ($\delta Q = 0$) and so known as an *isentropic process*.

Entropy Change for any Process

The entropy change for an irreversible process is:

$$\Delta S = \int_A^B \frac{\delta Q_{\text{rev}}}{T} \geq \int_A^B \frac{\delta Q}{T}$$

Where δQ_{rev} is the reversible heat energy change.

Hence we find that:

$$\delta Q \leq T dS$$

And since $\delta Q = 0$ in thermally isolated systems:

$$dS \geq 0$$

Entropic Statement of the Second Law

In every process taking place in an ideal system, the entropy change of the system either increases or remains constant.

First Law in Terms of Entropy

The first law of thermodynamics can be written as:

$$dU = T dS - p dV$$

Internal Energy

The function of state U has natural variables of S and V , so we can write $U = U(S, V)$. Since dU is an exact differential, we can always write $dU = U_f - U_i$.

We can also write for a reversible isochoric process:

$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

Enthalpy

A similar relationship at constant pressure is enthalpy which is defined as:

$$H = U + pV$$

Hence:

$$dH = T dS + V dp$$

Enthalpy as natural variables S and p , with $H = H(S, p)$ and represents the heat absorbed by the system at constant pressure:

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

Helmholtz Function

The Helmholtz function is termed a free energy and is defined as:

$$F = U - TS$$

And hence:

$$dF = -pdV - SdT$$

It has natural variables V and T , with $F = F(V, T)$. For a reversible, isothermal process $dF = -pdV$.

Gibbs Function

Another free energy, it is defined as:

$$G = H - TS = F + pV = U + pV - TS$$

Hence:

$$dG = Vdp - SdT$$

With natural variables p and T , so $G = G(p, T)$. G represents the maximum mechanical work that can be done between equilibrium states and is conserved in isothermal, isobaric process (e.g. at a phase transition).

Maxwell Relations

The four relationships are:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_p$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$T = -\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$

These can then be manipulated to find the Maxwell Relations:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (\text{M1})$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (\text{M2})$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (\text{M3})$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \quad (\text{M4})$$

Generalised Quantities

The general form of the heat capacity at some constant property, α , is:

$$C_\alpha = \left(\frac{\partial Q}{\partial T}\right)_\alpha = T\left(\frac{\partial S}{\partial T}\right)_\alpha$$

Generalised susceptibilities quantify how much something changes when a generalised force is applied. Common ones are the isobaric and adiabatic expansivities:

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p; \quad \beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$$

Similarly the isothermal and adiabatic compressibilities give the fractional volume changes when pressure is applied and are defined by:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T; \quad \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$$

TdS and Energy Equations

The TdS equations are:

$$TdS = C_V dT + T \left(\frac{\partial p}{\partial T} \right)_V dV \quad (\text{TS1})$$

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp \quad (\text{TS2})$$

The energy equations are:

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p \quad (\text{E1})$$

$$\left(\frac{\partial U}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p - p \left(\frac{\partial V}{\partial p} \right)_T \quad (\text{E2})$$

Effectiveness of a Process

The effectiveness of a process is defined as:

$$\text{Effectiveness} = \eta_{\text{rev}} = \frac{|\text{Best Possible Work}|}{\text{Heat In}}$$

The Second Law Efficiency is then:

$$\eta_{2\text{nd}} = \frac{\text{Actual Efficiency}}{\text{Effectiveness}}$$

Availability and Available Energy

The available energy of a device (also known as the device's exergy) tells us the maximum work that could be obtained from a system in a particular state, operating in a specific environment.

The available work and availability are defined via the following, where p_0 and T_0 are the pressure and temperature of the environment:

$$A = U + p_0 V - T_0 S$$

$$dA = dU + p_0 (V_2 - V_1) - T_0 (S_2 - S_1)$$

Relationship to Thermodynamic Potentials

If the Helmholtz function is considered, we can find that:

$$\delta W \geq dF$$

With the equality holding in reversible processes.

At thermal equilibrium, the Helmholtz function takes a minimum value.

Useful Work and Irreversibility

The useful work is defined as the difference between the actual work done during the thermodynamic process (total work produced by the device) and the surroundings work (which would be done against the atmosphere, or is dissipated as heat etc.):

$$W_{\text{use}} = W_{\text{act}} - W_{\text{surr}}; \quad W_{\text{surr}} = p_0(V_2 - V_1)$$

The reversible work, W_{rev} is defined as the maximum amount of useful work that can be produced by a device, or minimum work that must be supplied to a system, as it undergoes a change between two states, when operating on a reversible cycle.

The irreversibility of a process is defined as:

$$I = W_{\text{rev}} - W_{\text{use}} = T_0 \Delta S_{\text{Universe}}$$

Where T_0 is the Universe temperature (normally that of the external environment) and $\Delta S_{\text{Universe}}$ is the change of the entropy of the universe.

Latent Heats

The latent heat of a phase change is:

$$L = \Delta Q_{\text{rev}} = T_0 \Delta S$$

In other words, at a phase change the entropy changes from $S_1 \rightarrow S_2$ at constant temperature T_0 .

Clausius-Clapeyron Equation

This equation describes how pressure changes with temperature for a system having two phases which are in equilibrium:

$$\left(\frac{\partial p}{\partial T} \right)_{i \rightarrow f} = \frac{L_{i \rightarrow f}}{T(V_f - V_i)}$$

Where $L_{i \rightarrow f}$ is the specific heat of transformation on going from phase i to phase f .

Joule-Kelvin Effect

For a gas expanding through a porous plug at constant enthalpy, we can define the Joule-Kelvin coefficient, a measure of how the temperature changes with respect to the pressure, as:

$$\mu_{\text{JK}} = \left(\frac{\partial T}{\partial p} \right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right]$$

Third Law of Thermodynamics

Nernst's statement:

The entropy change of any reaction in a system in internal equilibrium is zero near absolute zero.

Planck's statement:

The entropy change of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.

Third Law Consequences

The contribution to the entropy of a system by each aspect of the system which is in thermodynamic internal equilibrium tends to zero as $T \rightarrow 0$.

It is impossible to reach $T = 0$ in a finite number of steps.

Thermodynamics of Real Gases

The van der Waals equation is given by:

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Condensed Matter Physics

Crystal Lattices and Miller Indices

Lattice Structure

The set of mathematical points from which the crystal is constructed is called the lattice.

The group of atoms at each lattice point is called the basis.

In three dimensions the lattice is defined using the three translational unit vectors:

$$\mathbf{a}_1, \mathbf{a}_2 \text{ and } \mathbf{a}_3$$

The repeating nature of the lattice means that the arrangement of atoms in the crystal is the same when viewed from the points \mathbf{r}' and \mathbf{r} where they are related by:

$$\mathbf{r}' = \mathbf{r} + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

Where n_1 , n_2 and n_3 are arbitrary integers.

The set of points defined by \mathbf{r}' above for all values of n_1 , n_2 and n_3 defines the lattice.

The lattice is called a **primitive lattice** if any two points always satisfy the equation for all possible values of integer n_1 , n_2 and n_3 .

The volume defined by \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 describes the volume of the smallest unit used to build up the crystal:

$$V = (\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3$$

The primitive lattice vectors define the crystal axes.

There is always a minimum of one atom per unit cell.

The primitive unit cell is called the **Wigner-Seitz cell**.

Three Dimensional Crystals

TABLE
The Fourteen Bravais Lattices and Conventional Unit
Cells in Three Dimensions*

SYSTEM	NUMBER OF LATTICES IN SYSTEM	LATTICE SYMBOLS	NATURE OF UNIT-CELL AXES AND ANGLES	LENGTHS AND ANGLES TO BE SPECIFIED
Triclinic	1	<i>P</i>	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	a, b, c α, β, γ
Monoclinic	2	<i>P</i> <i>C</i>	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	a, b, c β
Orthorhombic	4	<i>P</i> <i>C</i> <i>I</i> <i>F</i>	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	a, b, c
Tetragonal	2	<i>P</i> <i>I</i>	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	a, c
Rhombohedral (Trigonal)	1	<i>R</i>	$a = b = c$ $\alpha = \beta = \gamma$ $< 120^\circ, \neq 90^\circ$	a α
Hexagonal	1	<i>P</i>	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	a, c
Cubic	3	<i>P</i> <i>I</i> <i>F</i>	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	a

For each crystal system there are four possible variants:

1. Primitive (or simple lattice)
2. Innenzentriert (or body centred)
3. Face centred
4. Base Centred

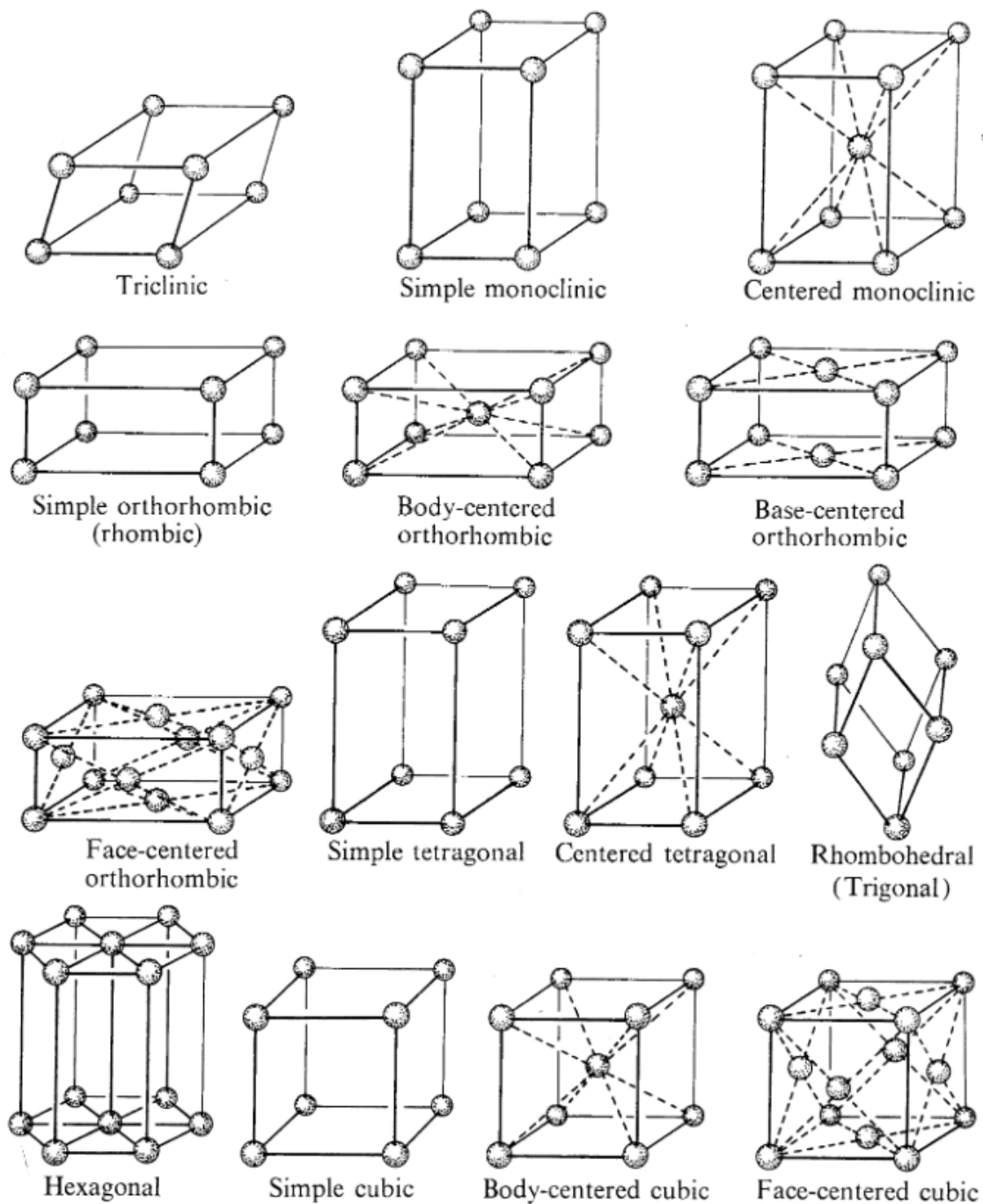


Fig. The fourteen three-dimensional Bravais lattices.

Miller Indices

Miller indices describe a particular crystallographic plane or direction within the crystal.

To determine the crystal plane:

1. Find the intercepts on the axes in terms of the lattice constants a_1 , a_2 and a_3
2. Take the reciprocal of these numbers
3. Reduce to three integers having the same ratio, normally the smallest three integers
4. This result will give the index of the plane normally denoted by (hkl)
5. If one of the indices is negative this is denoted by a bar above the index

This plane will intersect the unit cell at a_1/h , a_2/k and a_3/l

The separation between planes is given by:

$$f = \frac{1}{\sqrt{\frac{h^2}{a_1^2} + \frac{k^2}{a_2^2} + \frac{l^2}{a_3^2}}}$$

Or for a cube where $a_1 = a_2 = a_3 = a$:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{N}}$$

For example, the six faces of the simple cubic lattice are denoted by the six planes: (100), (010), (001), ($\bar{1}00$), ($0\bar{1}0$) and ($00\bar{1}$).

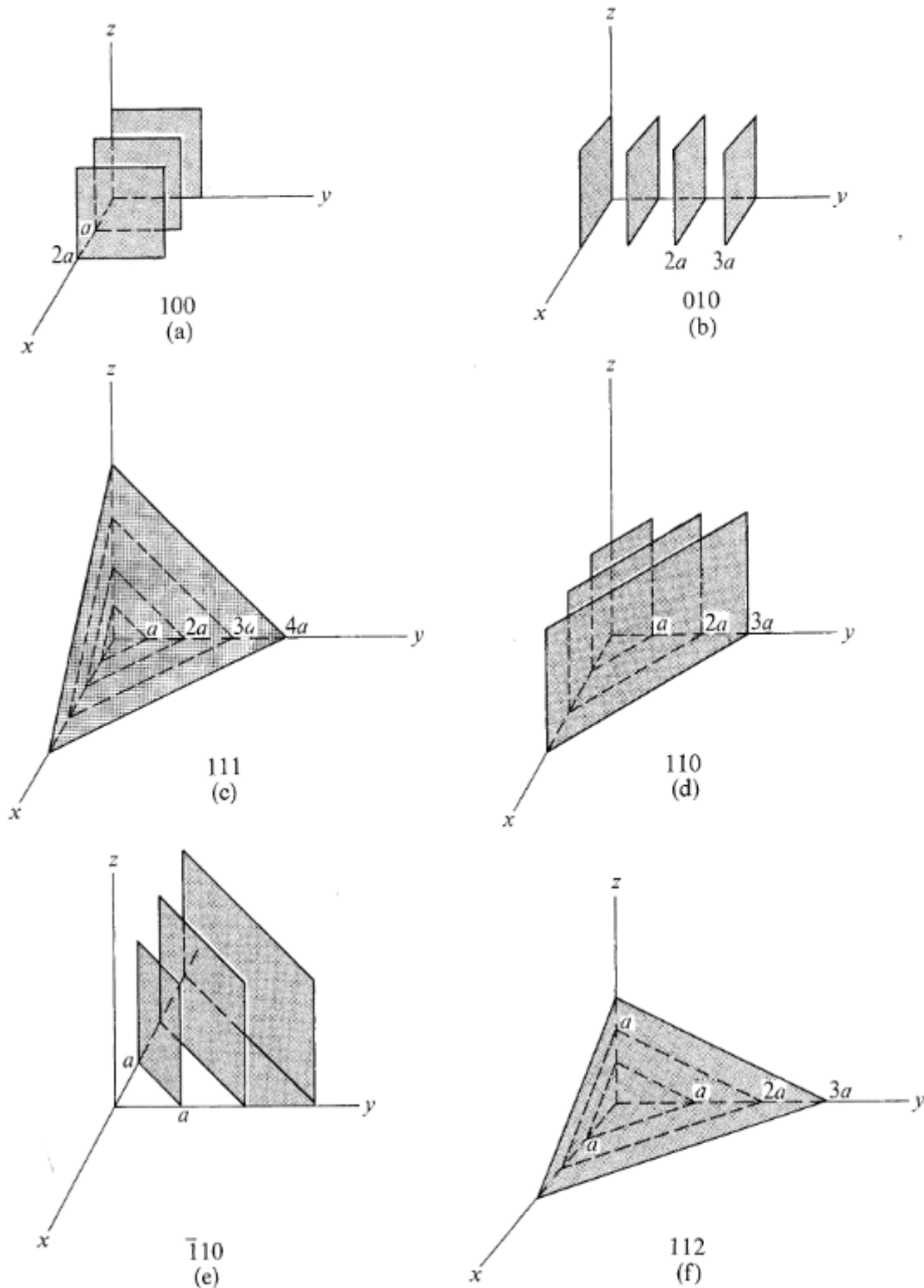


Fig. Examples of important cubic crystal planes. (a) 100 planes; (b) 010 planes; (c) 111 planes; (d) 110 planes; (e) $\bar{1}10$ planes; (f) 112 planes. (After C. A. Wert and R. M. Thomson, *Physics of Solids*. New York: McGraw-Hill, 1964.)

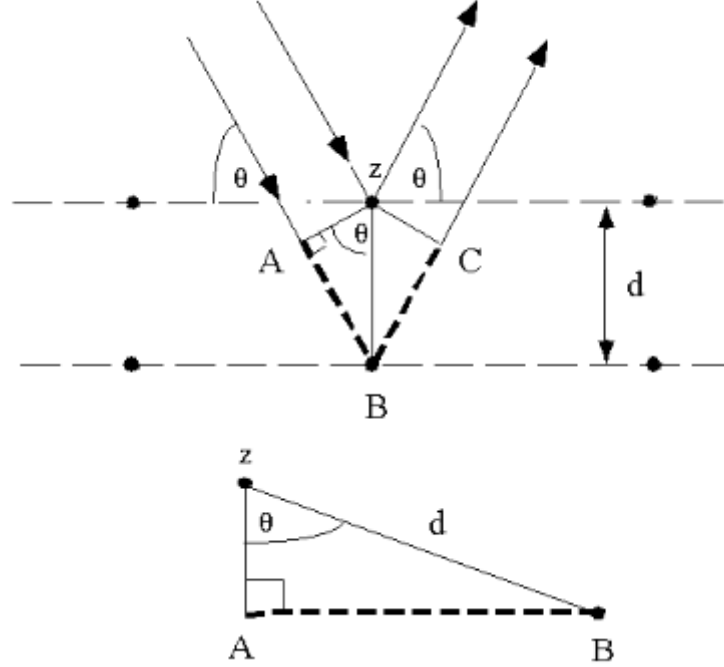
Wave Diffraction and the Reciprocal Lattice

Diffraction of Waves by Crystals

Bragg's Law for Diffraction is:

$$2d \sin \theta = n\lambda$$

The geometry of the derivation is shown below:



Bragg's law is a direct consequence of the periodic nature of a crystal lattice. A more detailed analysis of periodic structures can be undertaken using **Fourier Analysis**.

Fourier Analysis

We know that the crystal lattice is invariant under any translation \mathbf{T} of the form:

$$\mathbf{T} = u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3$$

Where u_i are integers.

Because of this, any local physical property is also invariant under \mathbf{T} .

We know for the electron density $n(\mathbf{r})$:

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$$

Using Fourier Analysis we can write the electron density n in one dimension, x , as:

$$n(x) = n_0 + \sum_{p>0} \left[C_p \cos\left(\frac{2\pi p x}{a}\right) + C_s \sin\left(\frac{2\pi p x}{a}\right) \right]$$

Where we have assumed that the periodicity in the x direction (the lattice constant) is a . Here p are positive integers and C_p and C_s are real constants called the Fourier coefficients of the expansion.

The equation above can be written as:

$$n(x) = \sum_p n_p \exp\left(\frac{2\pi i p x}{a}\right)$$

Where the sum is over all integers p positive, negative and zero. The coefficients n_p are now complex numbers,

The requirement that $n(x)$ is real puts a constraint on the coefficients n_p :

$$n_{-p}^* = n_p$$

The Fourier representation in 3 dimensions is:

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$$

Where \mathbf{G} is a set of vectors which mean that $n(\mathbf{r})$ is invariant under all crystal translations \mathbf{T} .

Reciprocal Lattice

The vectors of the axes of the reciprocal lattice are:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

As the vectors $\mathbf{a}_{1,2,3}$ are the primitive vectors of the crystal lattice, the vectors $\mathbf{b}_{1,2,3}$ are the vectors of the reciprocal lattice.

The vectors defined by the equations above are orthogonal to two axis vectors of the crystal lattice:

$$\mathbf{a}_j \cdot \mathbf{b}_i = 2\pi \delta_{ij}$$

The reciprocal lattice constructed as:

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

Where h, k, l are the Miller indices and \mathbf{G} is the reciprocal lattice vector.

If we have $\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$ then:

$$n(\mathbf{r} + \mathbf{T}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{T})$$

Where

$$\begin{aligned} \exp(i\mathbf{G} \cdot \mathbf{T}) &= \exp[i(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot (u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3)] \\ &= \exp[2\pi i(hu_1 + ku_2 + lu_3)] = 1 \end{aligned}$$

Demonstrating

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$$

X-Rays and Structure Factor

X-Ray Diffraction from Crystals

Consider an incident beam on a crystal with an *incident* wavevector \mathbf{k} which scatters the beam with an *outgoing* wavevector \mathbf{k}' .

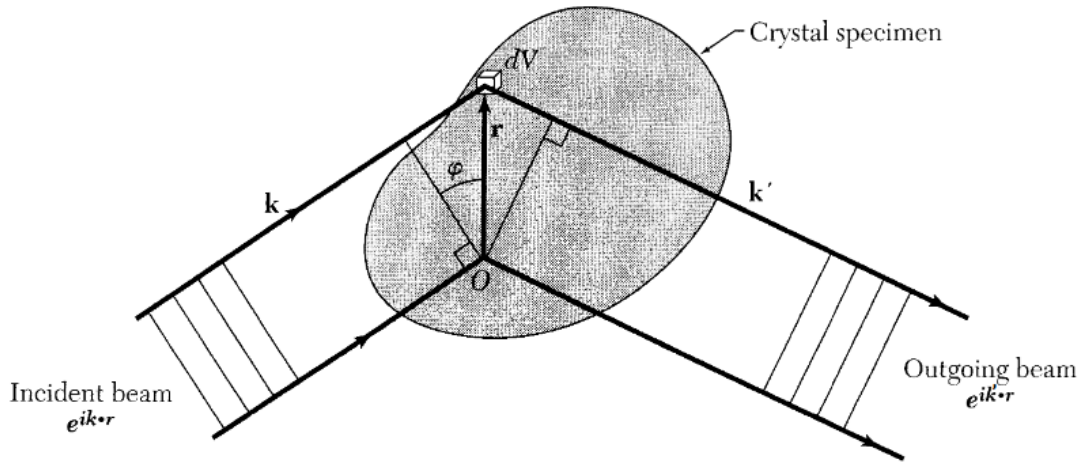


Figure 6 The difference in path length of the incident wave \mathbf{k} at the points O , \mathbf{r} is $r \sin \phi$, and the difference in phase angle is $(2\pi r \sin \phi)/\lambda$, which is equal to $\mathbf{k} \cdot \mathbf{r}$. For the diffracted wave the difference in phase angle is $-\mathbf{k}' \cdot \mathbf{r}$. The total difference in phase angle is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$, and the wave scattered from dV at \mathbf{r} has the phase factor $\exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$ relative to the wave scattered from a volume element at the origin O .

Assuming that the amplitude of the scattered wave is proportional to the local electron concentration, $n(\mathbf{r})$, the amplitude of the electric and magnetic field vectors in the scatter wave is proportional to the integral:

$$F = \int dV n(\mathbf{r}) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] = \int dV n(\mathbf{r}) \exp(-i\Delta\mathbf{k} \cdot \mathbf{r})$$

The integral is over the volume of the crystal dV . For elastic scattering, $|\mathbf{k}'| = |\mathbf{k}|$.

F is called the scattering amplitude and $\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$.

$\Delta\mathbf{k}$ is the change in wavevector and is called the scattering vector.

For Bragg scattering, the **Bragg Condition** must be satisfied:

$$\Delta\mathbf{k} = \mathbf{G}$$

Substituting for $n(\mathbf{r})$ into F gives:

$$F = \sum_{\mathbf{G}} \int dV n_{\mathbf{G}} \exp[i(\mathbf{G} - \Delta\mathbf{k}) \cdot \mathbf{r}]$$

When the Bragg condition is satisfied:

$$F = V n_{\mathbf{G}}$$

For a particular reciprocal lattice vector \mathbf{G} .

During an elastic scattering process:

$$k^2 = k'^2$$

And so when $\Delta\mathbf{k} = \mathbf{G}$ and hence $\mathbf{k} + \mathbf{G} = \mathbf{k}'$ then:

$$(\mathbf{k} + \mathbf{G})^2 = k^2$$

Rearranging:

$$2\mathbf{k} \cdot \mathbf{G} = G^2$$

This is an alternative statement of the Bragg scattering condition.

Brillouin Zones

A Brillouin Zone is a Wigner-Seitz primitive cell (primitive unit cell) in the reciprocal lattice.

Modifying the diffraction condition gives:

$$\mathbf{k} \cdot \left(\frac{1}{2} \mathbf{G} \right) = \left(\frac{1}{2} G \right)^2$$

To construct the Brillouin zone start at the origin of the reciprocal lattice. Select a reciprocal lattice vector \mathbf{G} , and draw a plane normal to the vector at its midpoint. This plane forms the boundary of the first Brillouin zone.

A x-ray will be diffracted if its wavevector \mathbf{k} has the magnitude and direction specified by the equation above.

Primitive Cubic - Reciprocal Lattice

The primitive lattice vectors of a primitive cubic lattice are:

$$\mathbf{a}_1 = a\hat{\mathbf{x}}; \mathbf{a}_2 = a\hat{\mathbf{y}}; \mathbf{a}_3 = a\hat{\mathbf{z}}$$

The vectors $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are unit vectors of unit length and orthogonal to each other.

The volume of the unit cell is:

$$\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = a^3$$

The primitive lattice vectors of the reciprocal lattice are given by:

$$\mathbf{b}_1 = \left(\frac{2\pi}{a} \right) \hat{\mathbf{x}}; \mathbf{b}_2 = \left(\frac{2\pi}{a} \right) \hat{\mathbf{y}}; \mathbf{b}_3 = \left(\frac{2\pi}{a} \right) \hat{\mathbf{z}}$$

The volume of the first Brillouin zone is $(2\pi/a)^3$.

BCC Lattice - Reciprocal Lattice

The primitive (unit) vectors for the bcc lattice are:

$$\mathbf{a}_1 = \frac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}); \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}); \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

The volume of the unit cell is:

$$\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \frac{1}{2}a^3$$

Here, the reciprocal lattice vectors are:

$$\mathbf{b}_1 = \left(\frac{2\pi}{a} \right) (\hat{\mathbf{y}} + \hat{\mathbf{z}}); \mathbf{b}_2 = \left(\frac{2\pi}{a} \right) (\hat{\mathbf{x}} + \hat{\mathbf{z}}); \mathbf{b}_3 = \left(\frac{2\pi}{a} \right) (\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

An fcc lattice is the reciprocal lattice of a bcc lattice

FCC Lattice - Reciprocal Lattice

The primitive unit vectors for the fcc lattice are:

$$\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}); \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{z}}); \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

The volume of the unit cell is:

$$\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \frac{1}{4}a^3$$

The reciprocal lattice vectors are:

$$\mathbf{b}_1 = \left(\frac{2\pi}{a} \right) (-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}); \mathbf{b}_2 = \left(\frac{2\pi}{a} \right) (\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}); \mathbf{b}_3 = \left(\frac{2\pi}{a} \right) (\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

A bcc lattice is the reciprocal lattice of an fcc lattice

Form Factor and the Structure Factor

The structure factor describes the intensity of a scattered X-ray wave.

The scattering amplitude of an incident wave for N unit cells is then given by:

$$F_{\mathbf{G}} = N \int_{\text{cell}} dV n(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) = NS_{\mathbf{G}}$$

Where the quantity $S_{\mathbf{G}}$ is the structure factor and is defined as an integral over a single unit cell with the origin at $\mathbf{r} = 0$.

The total electron concentration in the unit cell is:

$$n(\mathbf{r}) = \sum_{j=1}^s n_j(\mathbf{r} - \mathbf{r}_j)$$

Where there are s atoms in the unit cell.

The structure factor can now be written as integrals over s atoms in the unit cell:

$$\begin{aligned} S_{\mathbf{G}} &= \sum_j \int dV n_j(\mathbf{r} - \mathbf{r}_j) \exp(-i\mathbf{G} \cdot \mathbf{r}) \\ &= \sum_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j) \int dV n_j(\boldsymbol{\rho}) \exp(-i\mathbf{G} \cdot \boldsymbol{\rho}) \end{aligned}$$

Where $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}_j$.

The atomic form factor is defined as:

$$f_j = \int dV n_j(\boldsymbol{\rho}) \exp(-i\mathbf{G} \cdot \mathbf{r}_j)$$

Combing the two expressions gives the **structure factor of the crystal unit cell**:

$$S_{\mathbf{G}} = \sum_j f_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j)$$

Or in terms of the integer pre-factors xyz and hkl :

$$S_{\mathbf{G}}(hkl) = \sum_j f_j \exp[-2\pi i(hx_j + ky_j + lz_j)]$$

(x_j, y_j, z_j) position coordinates for \mathbf{r} and (h, k, l) coordinates of \mathbf{G} .

The intensity of the scattered radiation is $|S_{\mathbf{G}}^2|$.

Bonding

Repulsion

When two atoms are brought close together $r < 0.3 \text{ nm}$ they repel. This comes from the Pauli Exclusion Principle: *no two electrons in an atom can be in the same quantum state*.

Attraction

The attraction is due to electromagnetism.

The **cohesive energy** of a crystal is defined as the energy required to separate its constituent parts into neutral free atoms at rest with an infinite separation.

The **lattice energy** of an ionic crystal is the energy required to create free ions at infinite separation from the crystal.

Van der Waals Interaction

Van der Waals interaction occurs in three different types of systems:

1. Two permanent dipoles
2. One permanent dipole and one induced dipole
3. Two induced dipoles

The latter is also called the London force.

Considering a spherically symmetric atom with an amount of charge q moving a distance L , the dipole moment is then $p = qL$.

At an arbitrary point P the electric potential is given by:

$$V = \frac{Q}{4\pi\epsilon_0} \left(\frac{1}{r_b} - \frac{1}{r_a} \right)$$

The electric potential is then:

$$V(r) = \frac{\mathbf{p} \cdot \mathbf{r}_1}{4\pi\epsilon_0 r^2}$$

Where \mathbf{p} is the electric dipole vector and \mathbf{r}_1 is the unit vector along r .

The potential energy (derivation not necessary) is:

$$U(r) = \frac{A}{r^6}$$

And the force between atoms is then:

$$F(r) = -\frac{dU}{dr} = \frac{A}{r^7}$$

Which is much weaker than other forces.

Repulsive Interaction

The exact functional form of the repulsion due to the Pauli Exclusion Principle is difficult to determine. Experimental data on inert gas solids shows that an empirical function of the form B/r^{12} works well.

Considering an inert gas with both attractive and repulsive elements gives the expression:

$$U(r) = 4\epsilon \left[-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12} \right]$$

This is often called the Lennard-Jones 6-12 potential where constants $A = 4\epsilon\sigma^6$ and $B = 4\epsilon\sigma^{12}$ are used.

The potential can be used to model the interatomic behaviour and predict a range of phenomena.

Ionic Crystals

In considering the overall energy of an ionic bond there are two energies that must be considered:

1. The ionisation energy
2. The electron affinity

This energy is provided by the electrostatic attraction between the ions:

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

To calculate the energy more closely we introduce the Madelung Constant.

The coefficient of $1/R$ is called the Madelung Constant. It is generally denoted by the symbol α and its value depends on the lattice structure.

It is a correction factor which tells of the impact of only considering the influence of nearest neighbours in a lattice rather than considering all the atoms in a lattice.

For an fcc lattice, $\alpha = 1.7475$.

Covalent Crystals

The binding depends on the relative spin orientation. The Pauli Exclusion Principle modifies the distribution of charge according to the spin orientation. The spin dependent Coulomb energy is called the **exchange interaction**.

Because of the Pauli Exclusion Principle the total wavefunction must be antisymmetric when electrons are exchanged.

The total wavefunction is $\Psi_{\text{total}} = \psi_{\text{pos}} \phi_{\text{spin}}$

The covalent bond is $\Psi_{\text{anti}} = \psi_{\text{sym}} \phi_{\text{anti}}$ where $\phi_{\text{anti}} = \uparrow_1 \downarrow_2$ which has $S = 0$.

Static Lattice Failure and Phonons

Phonons

Consider a crystal in which the atoms vibrate elastically about a mean position.

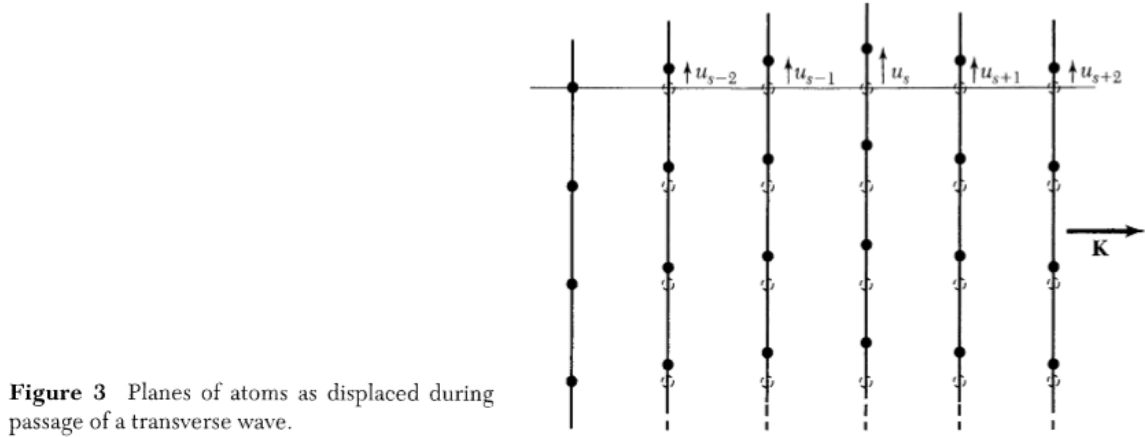
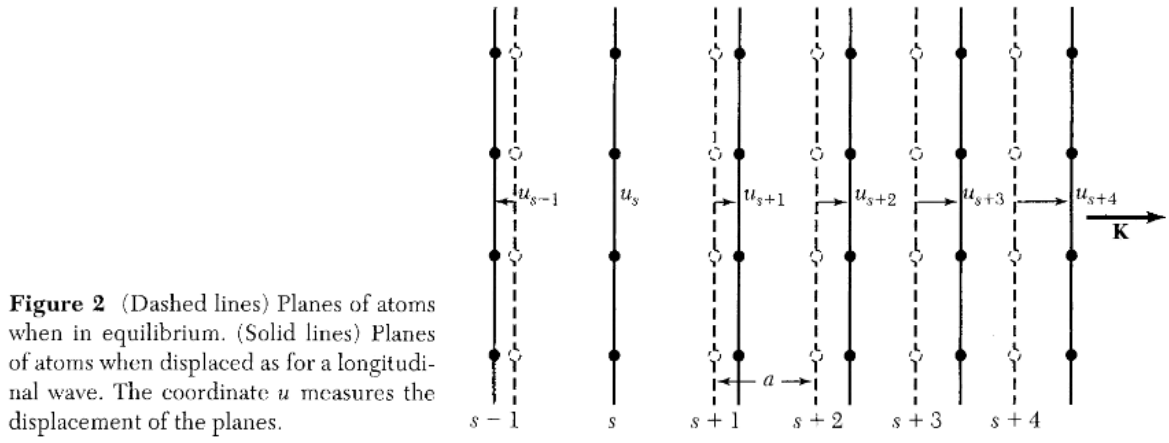
The vibrations in crystals will be quantised. The quanta of vibration are called **phonons**.

The displacement of the plane of atoms is described by a single coordinate u_s for plane s .

In the case where the displacement is parallel to the direction of propagation, this is described as a **longitudinal wave**.

Waves with displacements perpendicular to the direction of propagation are called **transverse waves**.

There is one longitudinal wave and two transverse waves for each wavevector.



We know that the energy of an oscillating system is given by:

$$E = \frac{1}{2} k A^2$$

Where k is the spring constant given by $k = m\omega^2$ and A is the maximum amplitude of vibration.

The total force on the plane from Hooke's Law is then:

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s)$$

C is the force constant between nearest neighbour planes.

The equation of motion for an atom in the plane s is then:

$$M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$$

We expect the solution to be of the form $\exp(-i\omega t)$ so we can say that:

$$\frac{d^2 u_s}{dt^2} = -\omega^2 u_s$$

And so:

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s)$$

This equation describes the motion of adjacent planes of atoms u_s , u_{s+1} and u_{s-1} .

The general form of the solution of this equation is:

$$u_{s\pm 1} = u \exp i(s \pm 1)ka = u \exp(isKa) \exp(\pm iKa)$$

Where a is the spacing between adjacent planes, K is the wavevector and u is the maximum amplitude. Note that a depends on the direction of propagation.

Substituting into the equation gives:

$$-\omega^2 M u \exp(isKa) = Cu\{\exp[i(s+1)Ka] + \exp[i(s-1)Ka] - 2\exp[isKa]\}$$

Which can be reduced to:

$$\omega^2 M = -C[\exp(iKa) + \exp(-iKa) - 2]$$

Using that $2 \cos Ka = \exp(iKa) + \exp(-iKa)$:

$$\omega^2 = \left(\frac{2C}{M}\right) (1 - \cos Ka)$$

Using trig identities we get:

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{Ka}{2} \right|$$

This is the **dispersion relation** describing the frequency dependence of propagation.

The boundary of the first Brillouin zone lies at $K = \pm\pi/a$.

Group Velocity

The group velocity is defined by

$$v_g = \frac{\partial \omega}{\partial k}$$

Or in vector notation:

$$\mathbf{v}_g = \nabla_{\mathbf{K}} \omega(\mathbf{K})$$

This gives the group velocity:

$$v_g = \sqrt{\frac{Ca^2}{M}} \cos \frac{Ka}{2}$$

Which zero at the edge of the first Brillouin zone and corresponds to a standing wave and we have zero net velocity.

Long Wavelength Limit

When $Ka \ll 1$ we expand $\cos Ka \equiv 1 - \frac{1}{2}(Ka)^2$ so the dispersion relation becomes:

$$\omega = \sqrt{\frac{C}{M}} Ka$$

Which shows that $\omega \propto K$ in the long wavelength limit. This is equivalent to stating that the velocity of sound is independent of frequency in this regime. Here $v = \omega/K$ as for elastic waves in a continuum.

Phonons and Thermal Properties

Two Atom Basis Per Lattice Point

The equations of motion assume that only nearest neighbour interactions are considered and that the force constants are identical between all nearest neighbour pairs of planes.

Hence the equations of motion of atoms M_1 and M_2 in planes u_s and v_s are:

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s)$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s)$$

The solution, as before, is in the form of a travelling wave which will have different amplitudes u, v on alternate planes:

$$u_s = u \exp(isKa) \exp(-i\omega t)$$

$$v_s = v \exp(isKa) \exp(-i\omega t)$$

Where a is the distance between identical planes.

Substituting the solutions into the equations and solving gives:

$$\omega^2 = \frac{C(M_1 + M_2)}{M_1 M_2} \pm \frac{C(M_1 + M_2)}{M_1 M_2} \sqrt{1 - \frac{2M_1 M_2 (1 - \cos Ka)}{(M_1 + M_2)^2}}$$

In the long wavelength limit, $Ka \ll 1$:

The two solutions are:

Optical Branch:

$$\omega^2 \cong 2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right)$$

Note that ω is independent of K .

Acoustic Branch:

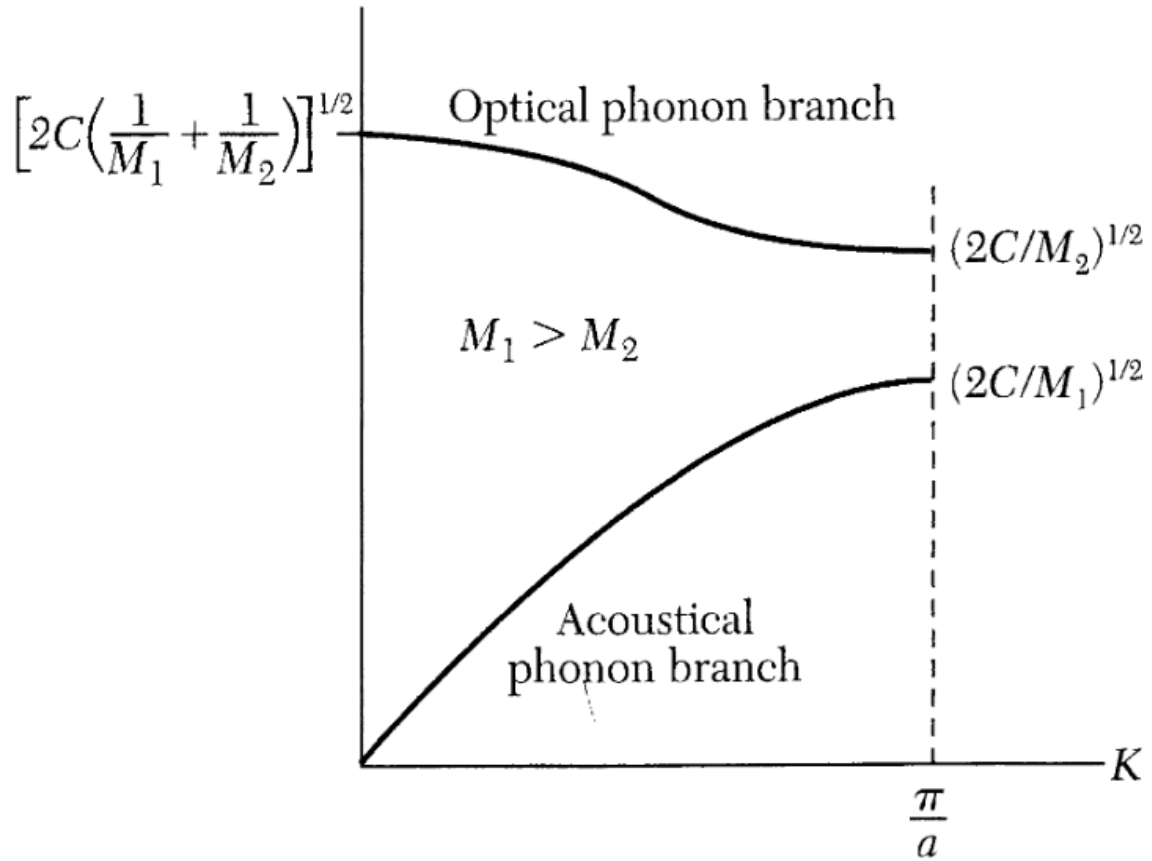
$$\omega^2 \cong \frac{C}{2(M_1 + M_2)} K^2 a^2$$

Note that $\omega \propto K$.

At the maximum value of K namely $K_{\max} = \pm\pi/a$:

The two solutions are:

$$\omega^2 = \frac{2C}{M_1}; \quad \omega^2 = \frac{2C}{M_2}$$



Considering the optical branch at $K = 0$ we find that:

$$\frac{u}{v} = -\frac{M_2}{M_1}$$

Which means that *the atoms vibrate out of phase but the centre of mass stays fixed*.

If the two atoms have different charge, the motion can be excited by electromagnetic waves.

There is a frequency gap between $(2C/M_1)^{1/2}$ and $(2C/M_2)^{1/2}$ at the boundary of the first Brillouin zone. These frequencies will be reflected by the material. [\[citation needed\]](#)

Thermal Properties

The Dulong-Petit Law states that

$$C_V = 3R$$

At low temperatures C_V falls off and observes a T^3 law.

Here, we define:

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V$$

Supplying more thermal energy to a lattice increases the internal energy U , in turn increasing the number of phonons. This contribution is called the lattice heat capacity C_{lat} .

The total energy of all phonons at a temperature T is given by the sum over all phonon modes (summing over wavevector K and longitudinal and transverse modes p):

$$U_{\text{lat}} = \sum_K \sum_p U_{K,p} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar \omega_{K,p}$$

Where $\langle n_{K,p} \rangle$ is the thermal equilibrium occupancy number of phonons with wavevector and polarisation K and p .

The functional form of $\langle n_{K,p} \rangle$ is given by the Planck distribution function:

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

At high temperatures the function is linear when $k_B T \ll \hbar\omega$.

Substituting these expressions gives:

$$U_{\text{lat}} = \sum_K \sum_p U_{K,p} = n = \frac{\hbar\omega_{K,p}}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

The number of modes of a given polarisation p in the frequency range from ω to $\omega + d\omega$ is written as $D(\omega)d\omega$ and is called the density of states.

The density of states for each polarisation is given by:

$$D(\omega) = \frac{dN}{d\omega} = \left(\frac{VK^2}{2\pi^2} \right) \left(\frac{dK}{d\omega} \right)$$

This describes the number of phonon modes in a given frequency or energy range.

Debye Model for Density of States

In the Debye model the dispersion relation is written:

$$\omega = vK$$

Where v is the velocity of sound.

The density of states then becomes:

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v^3}$$

So the number of phonons $D(\omega) \propto \omega^2$.

It is assumed that there are N acoustic phonon modes where N is the number of unit cells in the system.

The cut-off frequency (maximum frequency) is:

$$\omega_D^3 = \frac{6\pi^2 v^3 N}{V}$$

This corresponds to the Debye wavevector:

$$K_D = \frac{\omega_D}{v} = \left(6\pi^2 \frac{N}{V} \right)^{\frac{1}{3}}$$

The number of modes with $K \leq K_D$ is the same as the total number of degrees of freedom of a monatomic lattice.

Einstein Model of Density of States (hiss hiss)

The Einstein model treats the oscillators as having the same quantised energy. To develop this approach, consider N oscillators of the same frequency ω_E which for simplicity we assume to be in just one dimension.

The Einstein density of states is then given by the expression:

$$D(\omega) = N\delta(\omega - \omega_E)$$

The thermal energy of the system is:

$$U = N \langle n \rangle \hbar \omega_E = \frac{\hbar \omega_E}{\exp(\hbar \omega_E / k_B T) - 1}$$

The heat capacity is then:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = N k_B \left(\frac{\hbar \omega_E}{k_B T} \right)^2 \frac{\exp(\hbar \omega_E / k_B T)}{(\exp(\hbar \omega_E / k_B T) - 1)^2}$$

The high temperature limit becomes $3Nk_b = 3R$ which is the Dulong-Petit law.

At low temperatures, the Debye approximation confirms $C_V \propto T^3$ while the Einstein relation decreases as $\exp(-\hbar \omega_E / k_B T)$.

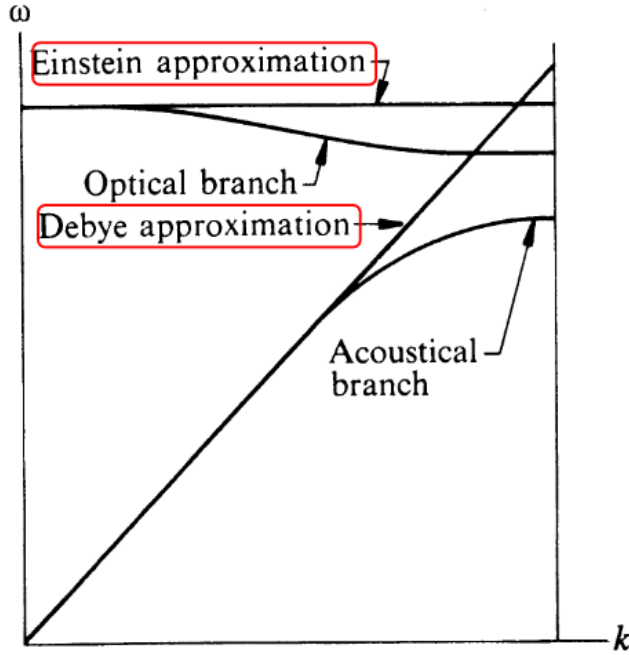


Fig. 4.5 Comparison of Einstein and Debye approximations for the dispersion relation of lattice waves, referred to a linear diatomic lattice.

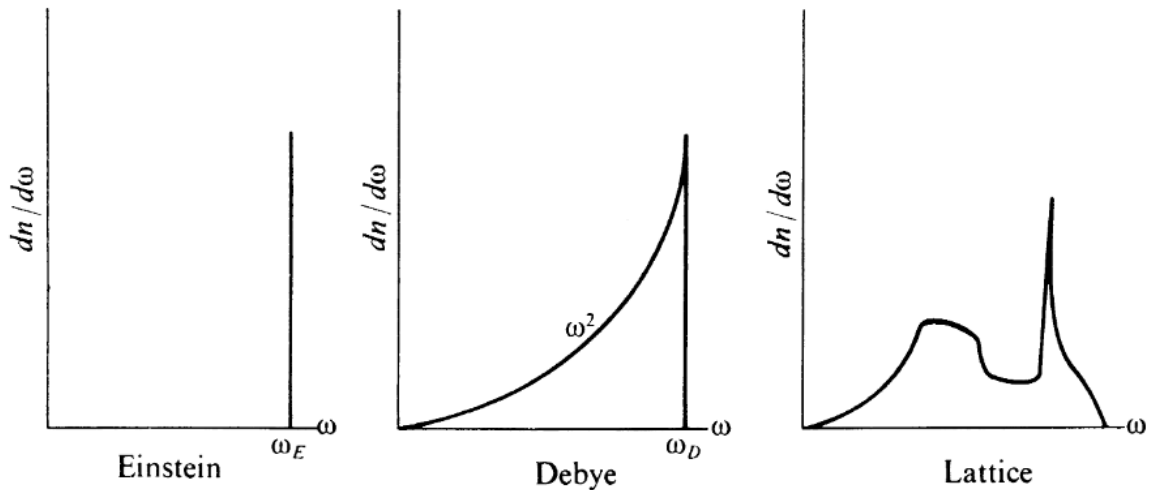


Fig. 4.11 Mode spectra for the Einstein and Debye approximations and a lattice. A combination of Einstein and Debye frequencies (acoustic and optical) can result in a good estimate of the mode spectrum for real crystals.

Drude Theory of Electrons in Metals

Drude Model

Drude constructed the model by applying the kinetic theory of gases to metals which he considered as a "gas of electrons". Drude assumed that this positive charge was in heavier, immobile particles.

Assumptions made:

- Outer valence electrons have become detached from atoms and move freely around the metal, behaving as a **classical gas**.
- Electric fields due to negative electrons and positive ions cancel on average and can be ignored.

Specific Heat Capacity of Electrons

The mean kinetic energy of a classical particle is:

$$E_{KE} = \frac{3}{2} k_B T$$

The specific heat capacity of each electron is given by:

$$C_V = \frac{dE_{KE}}{dT} = \frac{3}{2} k_B$$

This is independent of temperature.

Electrical Conductivity

Begin with Ohm's law:

$$E = \rho J$$

Where E is the electric field, ρ is the resistivity and J is the current density. Ohm's law can also be written as:

$$J = \sigma E$$

Where σ is the electrical conductivity.

An assumption in the Drude model is that collisions occur between electrons and electrons and other electrons or ions.

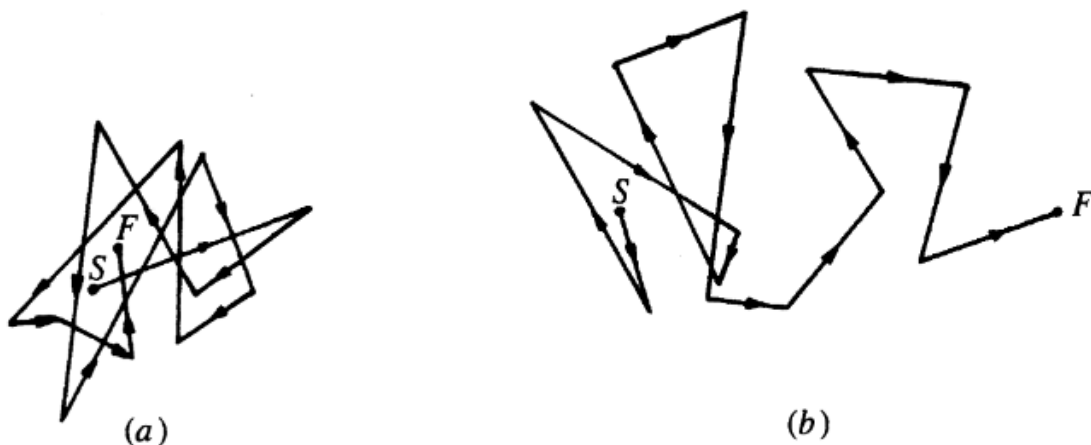


Figure illustrating drift velocity. (a) zero electric field, (b) finite electric field. In an electric field the start and finish positions differ – leading to a net flow of current.

The average time between collision events is the relaxation time, τ .

When an electric field, \mathbf{E} , is present there is a mean electronic velocity in the opposite direction to the field called the drift velocity.

Considering an electron a time t after a collision, if the velocity immediately after the collision was \mathbf{v}_0 , the velocity at time t will be:

$$\mathbf{v} = \mathbf{v}_0 - \frac{|e|\hbar}{m_e} \mathbf{E}$$

Assuming that the direction is random following a collision, there will be no contribution from \mathbf{v}_0 to the average electronic velocity:

$$\mathbf{v}_{\text{avg}} = -\frac{|e|\hbar}{m_e} \mathbf{E}$$

Current flow is given by:

$$\mathbf{J} = -n|e|\mathbf{v} = \frac{n|e|^2\hbar}{m_e} \mathbf{E}$$

And so:

$$\sigma = \frac{n|e|^2\hbar}{m_e}$$

Where n is the valence electron density per unit volume.

Thermal Conductivity of Electrons

Considering a temperature gradient dT/dz then thermal energy will be transported along the gradient in the opposite direction.

The rate at which electrons carry excess heat per unit area past a point in the metal is given by:

$$Q = -nv_z C_V v_z \tau \frac{dT}{dz}$$

The negative sign signifies that the hottest electrons will move in the direction of decreasing temperature.

The thermal average of $v_z^2 = k_B T / m_e$ so that:

$$Q = -n \frac{k_B}{m_e} T C_V \tau \frac{dT}{dz}$$

The thermal conductivity, κ , is defined by:

$$Q = -\kappa \frac{dT}{dz}$$

Substituting the earlier value for $C_V = 3/2 k_B$ we get:

$$\kappa = \frac{3}{2} n \frac{k_B^2 T}{m_e} \tau$$

Wiedemann-Franz Law

Using the Drude Model we get:

$$\frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T$$

Where $\frac{\kappa}{\sigma T} = 1.11 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$.

This is about half the value observed in experiment. **This is due to two factors which roughly cancel.**

Quantum Free Electron Model (Sommerfeld Model)

Free Electron Model

Assumptions made:

- Valence electrons of each atom are assumed to move freely throughout the metal

- The effect of the ions and other electrons cancel on average and can be ignored

The free electron model describes the crystalline metal as an empty box of the same dimension as the crystal. It is described by one parameter, the dimensions of the system:

$$\mathbf{L} = (L_x, L_y, L_z)$$

The potential is defined as:

$$V(\mathbf{r}) = \begin{cases} 0 & \text{if in box} \\ \infty & \text{if not in box} \end{cases}$$

Periodic Boundary Conditions

In 3D the periodic boundary conditions are written as:

$$\psi(x, y, z) = \psi(x + L_x, y, z) = \psi(x, y + L_y, z) = \psi(x, y, z + L_z)$$

For all values of x, y, z .

In a cubic system $|L| = |L_x| = |L_y| = |L_z|$.

Free Electron Wavefunction

Beginning with the time-independent Schrodinger Equation:

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The solution of the Schrodinger equation in the solid is:

$$\psi(x, y, z) = A \exp i(k_x x + k_y y + k_z z) = A \exp i(\mathbf{k} \cdot \mathbf{r})$$

Where:

$$k_x = \frac{2\pi l}{L}, \quad k_y = \frac{2\pi m}{L}, \quad k_z = \frac{2\pi n}{L}, \quad l, m, n = 0, \pm 1, \pm 2, \dots$$

The allowed values of wavevector come from the periodic boundary conditions which are specified simply by the dimensions of the system L_x, L_y, L_z .

The energy of the solution is:

$$E = \frac{\hbar^2}{m_e} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{m_e}$$

The solution ψ_{lmn} is the free electron wavefunction.

k -space

Each allowed quantum state which can be occupied by an electron is labelled by the quantum numbers k_x, k_y, k_z . This can be thought of a point in k -space with coordinates (k_x, k_y, k_z) .

The allowed points form a regular mesh in this space with a separation of $2\pi/L$ between the points in each direction.

Each point in k -space is surrounded by a volume of $(2\pi/L)^3$ where there are no other k -states.

Allowing for spin up and spin down electrons, we have:

$$2 \left(\frac{L}{2\pi} \right)^3 = \frac{L^3}{4\pi^3}$$

Electron energy states per unit volume of k -space.

Fermi Energy and Fermi Surface