

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

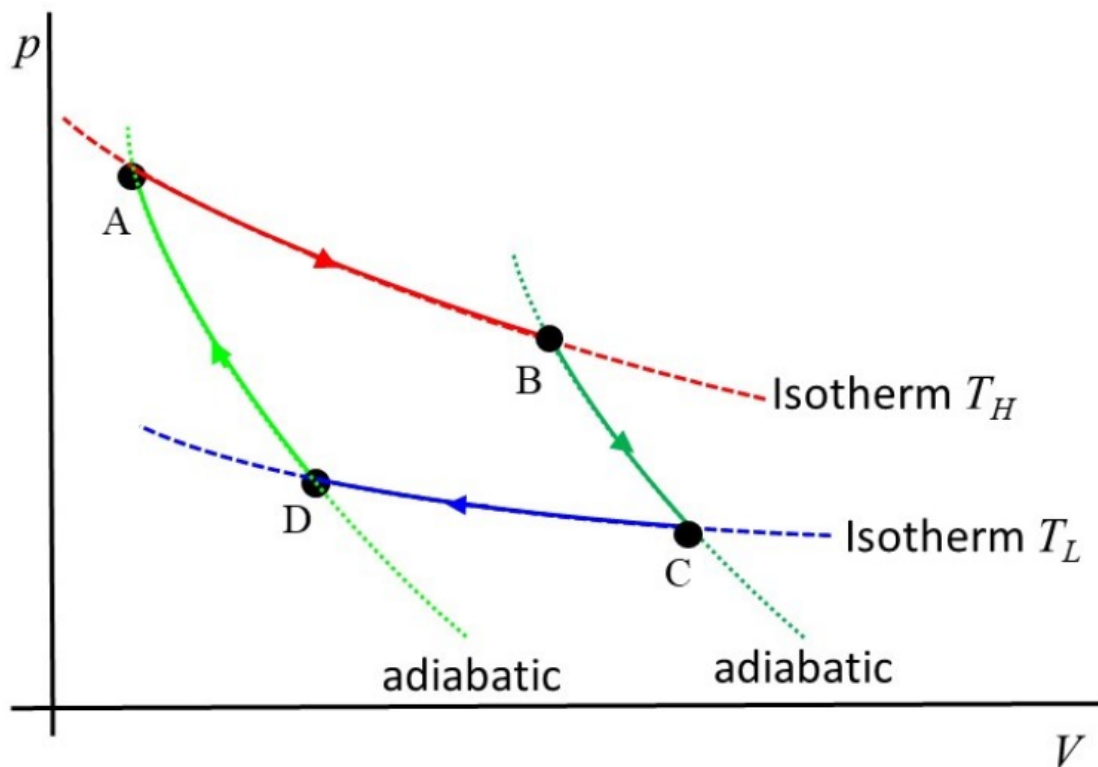


Figure 9: pV diagram for a Carnot Cycle.

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:

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

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

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

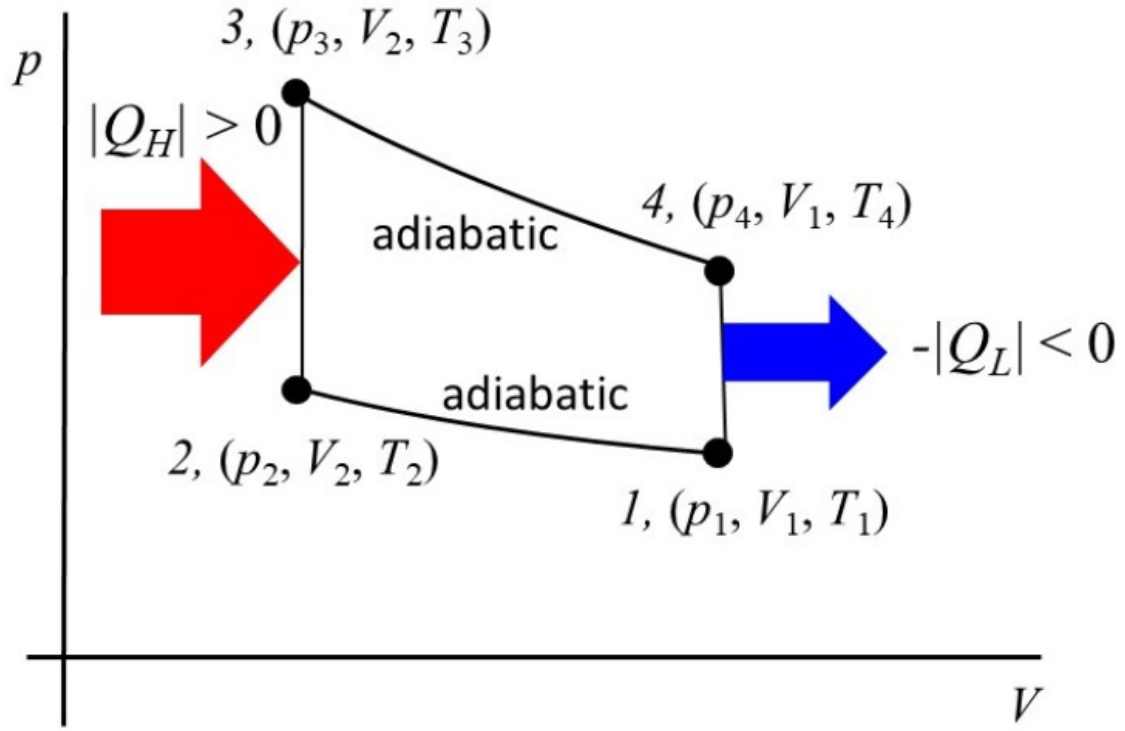


Figure 14: pV diagram of ideal Otto cycle.

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

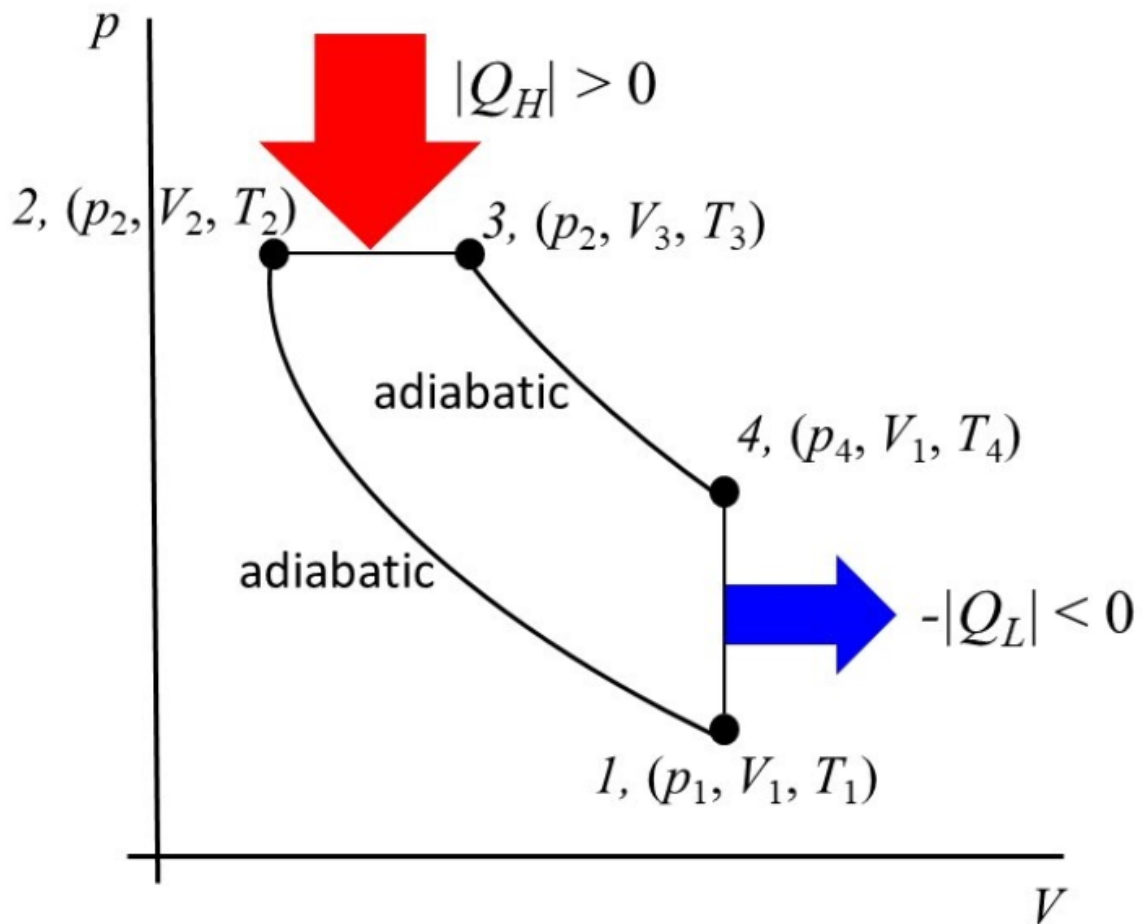


Figure 16: pV diagram of ideal Diesel Cycle.

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

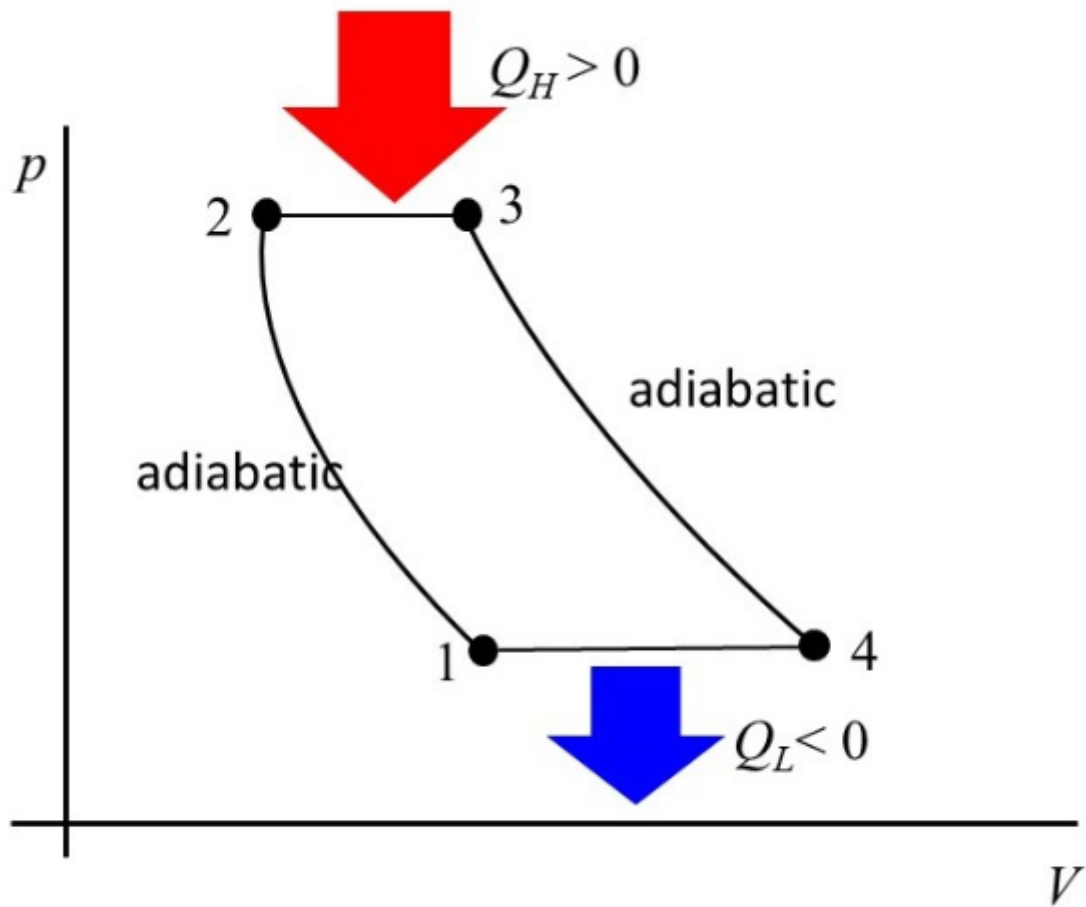


Figure 20: Brayton cycle pV diagram.

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:

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

Statistical Mechanics

Macro and Microstates

Macrostates

A **macrostate** of a system provides a description of how the system is behaving on average.

Microstates

A **microstate** of a system is the most detailed description of a system or assembly of particles we could possibly imagine.

In any system the number of microstates is finite and related to the ways we can arrange the individual particles within the system.

The number of microstates in a macrostate is denoted by Ω .

A system appears to choose a macroscopic configuration that maximises the number of associated microstates.

Counting Particles

Distinguishable Particles

In a solid, atoms can be distinguished by their type and position on the lattice where each particle will be in some energy state, ϵ_j .

We distribute the total number of particles, N , by states and this tells us the number of particles, n_j with energy ϵ_j . The number of microstates of the system is then:

$$\Omega = \frac{N!}{\prod_j n_j!}$$

Stirling Approximation

For large X , the Stirling approximation is:

$$\ln X! \cong X \ln X - X$$

Statistical Definitions of Temperature and Entropy

Temperature

The statistical definition of temperature is:

$$\beta = \frac{1}{k_B T} = \frac{d(\ln \Omega)}{dE}$$

Entropy

The entropy of a system in a particular macrostate is given by:

$$S = k_B \ln \Omega$$

If a macrostate is made up from a large number of microstates that are hard to measure, it is possible to show that the entropy is given by:

$$S = -k_b \sum_j P_j \ln P_j$$

Where P_j is the probability that the particle is in the j th macrostate.

The Boltzmann Distribution

Ensembles

An ensemble is where we (mentally) make lots of copies of a system to allow us to describe things probabilistically.

Two concern us: the **micro-canonical ensemble**, an ensemble of systems each having the same fixed energy and the **canonical ensemble**, an ensemble of systems each of which can exchange energy with a heat reservoir that fixes and defines the system's temperature.

The canonical ensemble is described by:

$$P(\epsilon) \propto \exp\left(-\frac{\epsilon}{k_B T}\right) = \exp(-\beta T)$$

Which is known as the Boltzmann distribution and describes how a small system behaves when it is coupled to a heat reservoir.

The distribution must be normalised, giving the probability that a given particle will have energy, ϵ_j , at temperature, T :

$$P(\text{state } j) = \frac{\exp\left(-\frac{\epsilon_j}{k_B T}\right)}{\sum_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)}$$

Where the sum on the bottom is known as the **partition function**.

This can be used for determining the number of particles n_j having ϵ_j . As we are dealing with large numbers, the Stirling approximation can be used and the most probable macrostate is found by maximising $\ln \Omega$.

Various conditions exist on the particle number and energy:

$$\sum_j (\ln n_j) dn_j = 0, \quad \sum_j dn_j = 0, \quad \sum_j \epsilon_j dn_j = 0$$

Lagrange multipliers can then be used to solve this problem so that:

$$\sum_j (\ln n_j + \alpha + \beta \epsilon_j) dn_j = 0$$

For this to be true, the term in brackets must be identically zero and this gives the Boltzmann distribution:

$$n_j = \exp(-\alpha - \beta \epsilon_j)$$

Here, α is the normalisation factor which is related to the partition function whilst $\beta = 1/(k_B T)$ is related to the temperature. This gives the final Boltzmann distribution:

$$n_j = \frac{N}{Z} \exp\left(-\frac{\epsilon_j}{k_B T}\right)$$

Boltzmann Distribution Derivation

To obtain the distribution, we maximise the number of macrostates. This is obtained from the way of arranging N particles into j states with n_j particles in the j th state. Because the system contains a finite number of particles, the minimisation takes place under the following conditions:

- The total particle number is fixed so $N = \sum_j n_j$
- The total energy of the system, its internal energy, is also fixed, $E = \sum_j \epsilon_j n_j$

Since we are dealing with a large number of particles, we maximise $\ln \Omega$ and use the Stirling approximation to make things easier.

The total differential of $\ln \Omega$ is given by:

$$d(\ln \Omega) = \left[\frac{\partial(\ln \Omega)}{\partial n_1} \right] dn_1 + \left[\frac{\partial(\ln \Omega)}{\partial n_2} \right] dn_2 + \cdots + \left[\frac{\partial(\ln \Omega)}{\partial n_i} \right] dn_i$$

Which tells us how we can vary the number of particles in each energy level by making small changes dn_j to the number in each level, n_j , individually. When we are at a maximum this differential will equal zero and it gives a condition on the most probable state.

Taking the natural logarithm of $\Omega = N! / (\prod_j n_j!)$ and applying the Stirling approximation gives:

$$\ln \Omega = N \ln N - N - \sum_j (n_j \ln n_j - n_j) = N \ln N - \sum_j n_j \ln n_j$$

Where $N = \sum_j n_j$.

Differentiating the last expression gives:

$$\begin{aligned} d(\ln \Omega) &= \left[\frac{\partial}{\partial n_j} \left(N \ln N - \sum_j n_j \ln n_j \right) \right] dn_j \\ &= \left[\frac{\partial N}{\partial n_j} \ln N + N \frac{1}{N} \frac{\partial N}{\partial n_j} - \sum_j \left\{ \ln n_j + \frac{1}{n_j} \times n_j \right\} \right] dn_j \end{aligned}$$

N is a constant, so $\partial N / \partial n_j = 0$ and this simplifies to $d(\ln \Omega) = - \sum_j \{ \ln n_j + 1 \} dn_j$.

Because we are dealing with large numbers, $n_j \gg 1$, we can approximate this as:

$$d(\ln \Omega) \approx - \sum_j \ln(n_j) dn_j$$

When this is equal to zero, it will determine the most probable macrostate.

We therefore have three conditions for the most probable macrostate:

- Because the **particle number is constant**, $\sum_j dn_j = 0$
- Because the **particle energy is constant**, $\sum_j \epsilon_j dn_j = 0$
- The condition on the **most probable macrostate**, $\sum_j \ln(n_j) dn_j = 0$

Using Lagrange multipliers to solve the problem, we write:

$$\sum_j (\ln n_j + \alpha + \beta \epsilon_j) dn_j = 0$$

This has to hold for all states of the system, so each term in the bracket must equal zero. Therefore

$$\ln n_j + \alpha + \beta \epsilon_j = 0$$

Which solves as:

$$n_j = A \exp(\beta \epsilon_j)$$

Where $A = \exp(-\alpha)$.

This gives us the distribution of particles in state j having energy ϵ_j . The number of particles with energy, ϵ_j , decreases as the energy increases. Thermodynamics can then be used to find the constants.

We know that:

$$N = \sum_j n_j = \exp(\alpha) \sum_j \exp(\beta \epsilon_j)$$

This gives us $A = \exp(\alpha)$ as our normalisation factor, such that

$$A = \frac{N}{\sum_j \exp(\beta \epsilon_j)} \equiv \frac{N}{Z}$$

Where Z is the partition function.

The First Law of thermodynamics tells us:

$$dU = \delta Q + \delta W = TdS - pdV$$

Now, for our distribution of particles with total energy, $E = U$, the total differential is given by

$$dE = d\left(\sum_j \epsilon_j n_j\right) = \sum_j \epsilon_j dn_j + \sum_j n_j d\epsilon_j (= dU)$$

Comparing with the First Law, it can be stated that:

$$TdS = \sum_j \epsilon_j dn_j$$

This is because the energy levels of the system can only depend on the volume, in other words $-pdV$ can only be addressed by the second term, whilst from the Boltzmann formalism of entropy, we know that the occupation number is related to the state entropy.

Using the Boltzmann formulation of entropy we can write:

$$TdS = Td(k_B \ln \Omega) = Tk_B d(\ln \Omega)$$

Using the differential form for the number of microstates, this becomes:

$$TdS \approx -Tk_B \sum_j \ln(n_j) dn_j = \sum_j \epsilon_j dn_j$$

Using the formalism for the Lagrange multipliers, and multiplying it by $k_B T$, we see:

$$k_B T \sum_j \ln(n_j) dn_j + k_B T \alpha \sum_j dn_j + k_B T \beta \sum_j \epsilon_j dn_j = 0$$

Using the condition we had on the initial distribution and substituting in for the TdS bit from above, this gives:

$$-\sum_j \epsilon_j dn_j + k_B T \beta \sum_j \epsilon_j dn_j = 0$$

Which tells us that $\beta = 1/(k_B T)$.

The Partition Function

Partition Function

This function acts as a normalisation factor to ensure correct counting, and contains the relevant information required to find many thermodynamic properties.

It is defined as:

$$Z = \sum_j \exp\left(-\frac{\epsilon_j}{k_B T}\right)$$

It is related to entropy via:

$$S = k_B \ln Z + \frac{U}{T}$$

And internal energy via:

$$U \equiv E = -\frac{d \ln Z}{d\beta} = -\frac{dT}{d\beta} \times \frac{d}{dT}(\ln Z) = -\frac{1}{d\beta/dT} \frac{d}{dT}(\ln Z) = k_B T^2 \frac{d}{dT}(\ln Z)$$

These two definitions can be used to determine the Helmholtz function:

$$F = -k_B T \ln(Z)$$

Chemical Potential

This concept arises in systems that can exchange energy with their surroundings. If the chemical potential is different between two places, particles can flow, rather like heat flows between temperature differences.

If a particle is added to a system, the internal energy changes according to:

$$dU = TdS - pdV + \mu dN$$

Where μ is the chemical potential and N is the number of particles. Furthermore, the chemical potential can be related to both the Gibbs and Helmholtz functions as

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$

Quantum Particles

Quantum Particles

Particles of a gas are intrinsically indistinguishable. Indistinguishable particles cannot be labelled.

Quantum mechanics gives two types of indistinguishable particles, bosons and fermions. Look at the wavefunction whereby swapping particles either leaves the wavefunction unchanged or introduces an overall minus sign. In both cases, the probability of state occupation doesn't change.

Distribution Functions

A distribution function, $f(\epsilon)$, tells us the occupancy of a given energy state. It is probabilistic, telling us the probability that the state of energy ϵ_j is occupied.

The density of states on the other hand, provides a measure of how many energy states exist in a given energy range, $d\epsilon$ or equivalently momentum range, and is given by $g(\epsilon)d\epsilon$. Its form depends on the particle type and geometry.

The number of states in a system having energy ϵ is then given by:

$$n(\epsilon) = f(\epsilon)g(\epsilon)$$

Maxwell-Boltzmann Distribution

This gives the classical gas distribution, with the number of ways of arranging the particles being:

$$\Omega_{MB} = \prod_i \frac{(n_i + g_i + 1)!}{n_i! (g_i + 1)!} \sim \prod_i \frac{(g_i)^{n_i}}{n_i!}$$

Since we have a large number of particles, and many more energy levels than particles meaning that $g_i \gg n_i$ the approximation follows.

The distribution function is continuous and hence written as:

$$f_{\text{MB}} = A \exp\left(-\frac{\epsilon}{k_B T}\right)$$

Bose-Einstein Distribution

To derive this distribution we count the number of microstates in which n_i bosons can be arranged in g_i states, with any number of particles allowed in each states. The total number of arrangements is:

$$\Omega_{\text{BE}} = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \sim \prod_i \frac{(n_i + g_i)!}{n_i! g_i!}$$

Writing the distribution in terms of a function, obtained by imagining that the energy levels become smeared out:

$$f_{\text{BE}} = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) - 1}$$

Bose-Einstein Condensation

As the term in the exponent tends towards one, the distribution "blows up". All particles end up migrating to the lowest energy state and quantum effects become apparent on a macroscopic scale. **Bose-Einstein condensation** is a universal phenomenon which was first observed by Cornell and Weimann in 1995, when 2000 Rubidium atoms were seen to behave as one for 10 seconds.

Fermi-Dirac Distribution

The number of ways of counting the available microstates is:

$$\Omega_{\text{FD}} = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!}$$

Since we know how many levels will be filled.

For a continuous range of energies, the distribution function is:

$$f_{\text{FD}}(\epsilon) = \frac{1}{\exp\left(\frac{\epsilon - \epsilon_F}{k_B T}\right) + 1}$$

The chemical potential is defined as the energy where the occupation probability of a state is half. It reaches its maximum value, the **Fermi Energy**, ϵ_F , as the temperature tends towards zero. At $T = 0$ K, all the states up to and including the Fermi energy are occupied by particles, and all states above this energy are empty. Adding one more particle increases the overall energy by $\mu = \epsilon_F$.

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 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

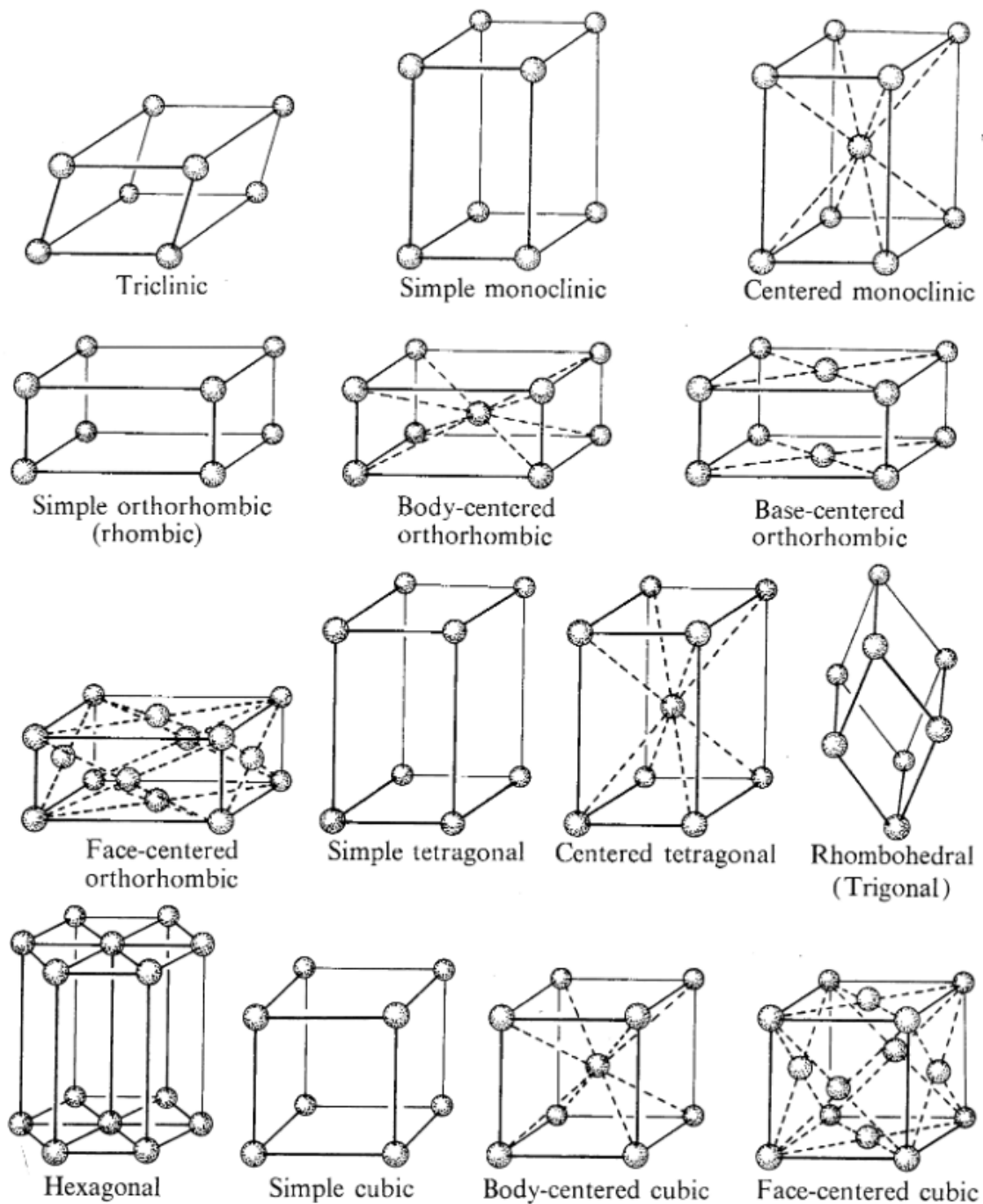


Fig. The fourteen three-dimensional Bravais lattices.

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 ($00\bar{1}$).

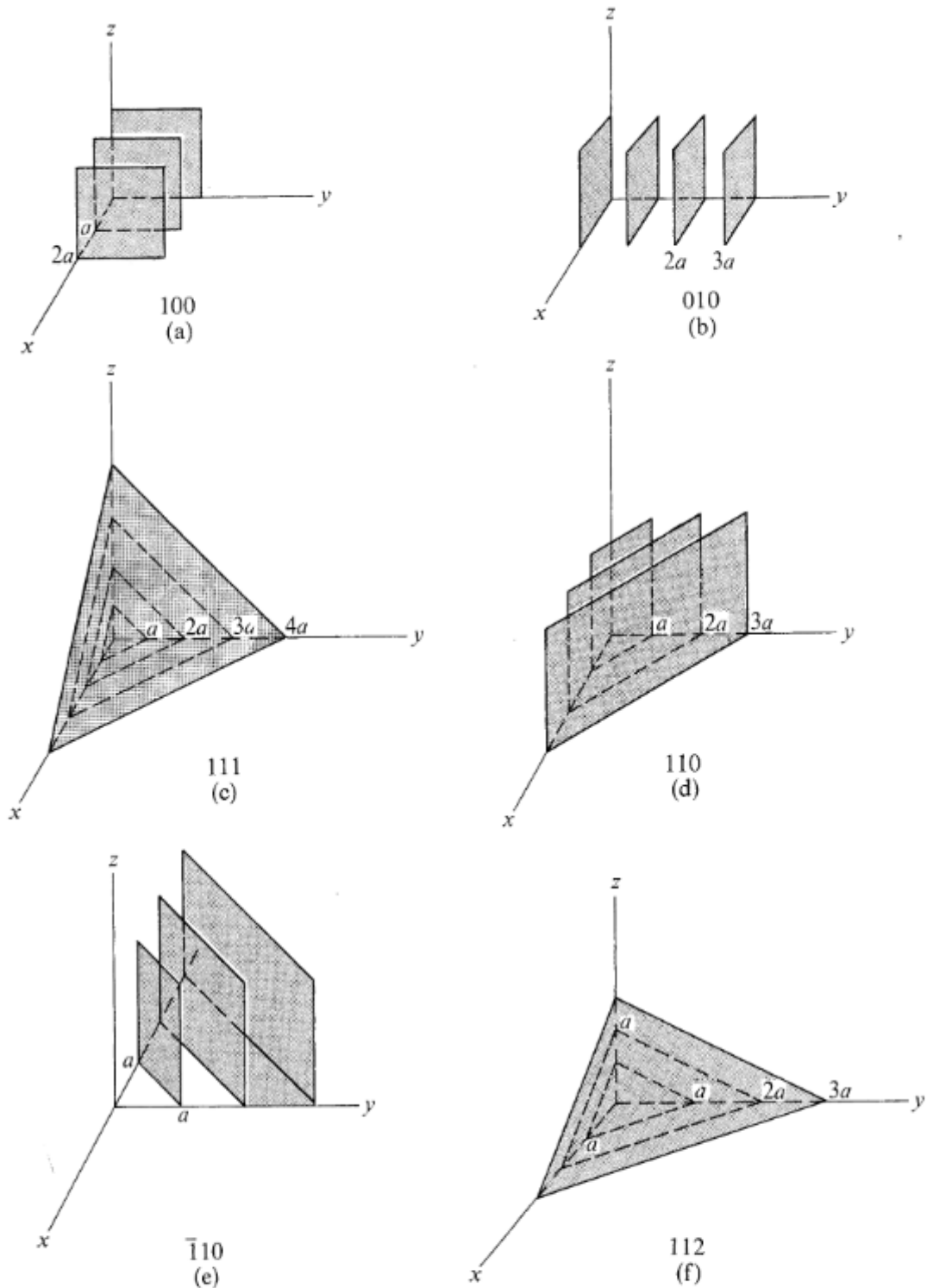


Fig. Examples of important cubic crystal planes. (a) 100 planes; (b) 010 planes; (c) 111 planes; (d) 110 planes; (e) $\bar{1}10$ planes; (f) 112 planes. (After C. A. Wert and R. M. Thomson, *Physics of Solids*. New York: McGraw-Hill, 1964.)

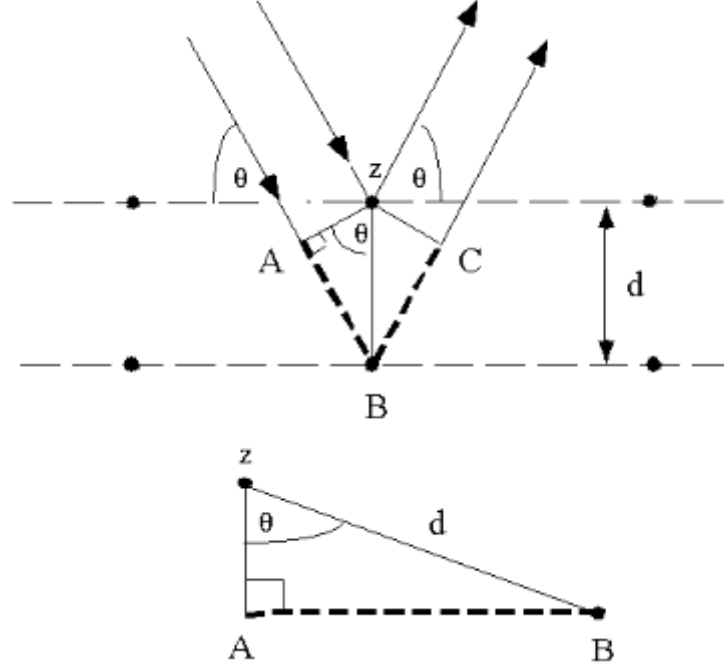
Wave Diffraction and the Reciprocal Lattice

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 **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 **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}' .

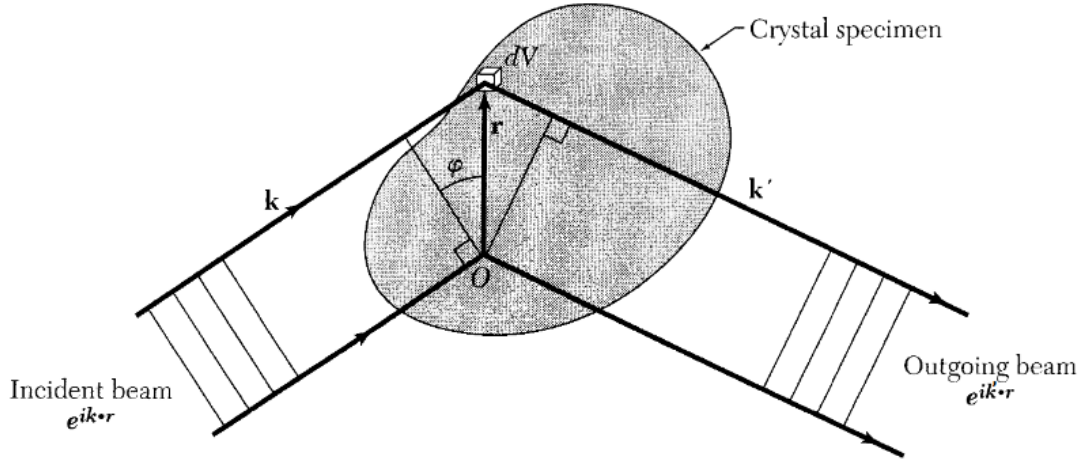


Figure 6 The difference in path length of the incident wave \mathbf{k} at the points O , \mathbf{r} is $r \sin \phi$, and the difference in phase angle is $(2\pi r \sin \phi)/\lambda$, which is equal to $\mathbf{k} \cdot \mathbf{r}$. For the diffracted wave the difference in phase angle is $-\mathbf{k}' \cdot \mathbf{r}$. 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.

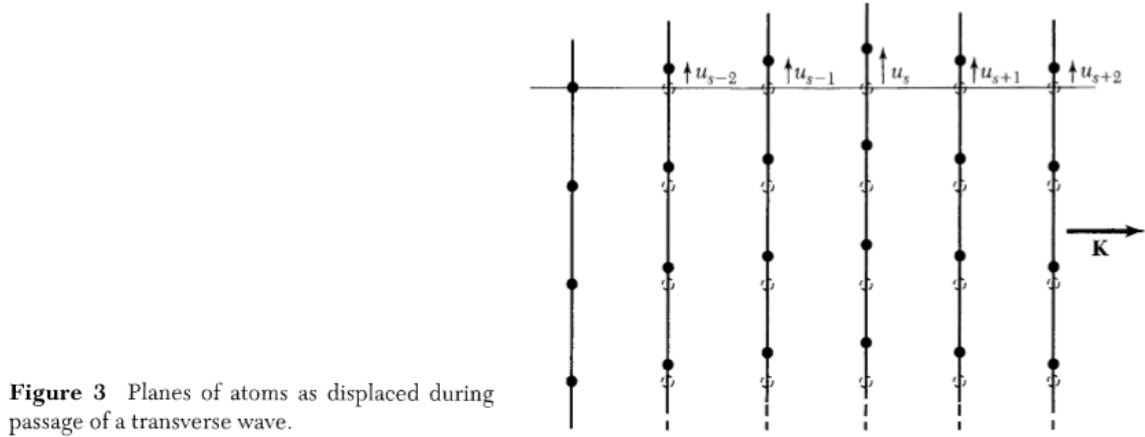
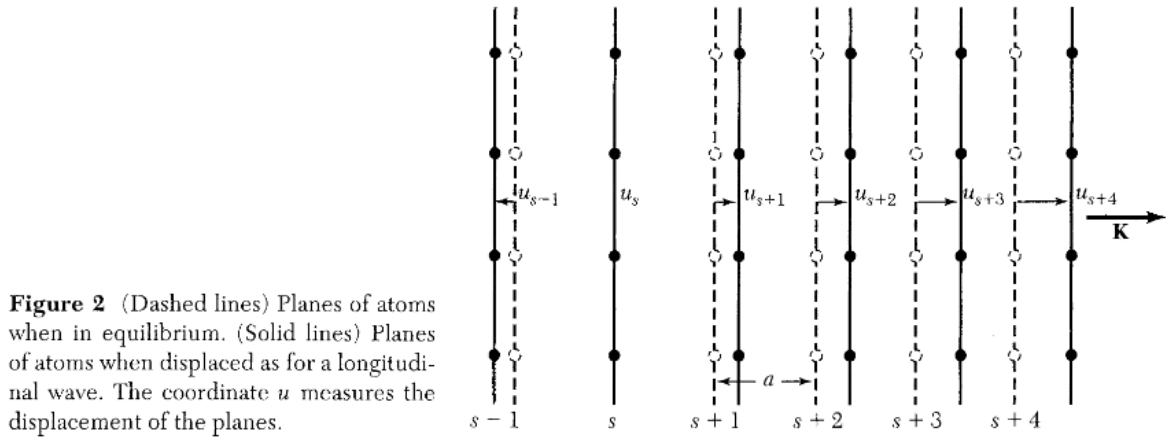
The vibrations in crystals will be quantised. The quanta of vibration are called **phonons**.

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:

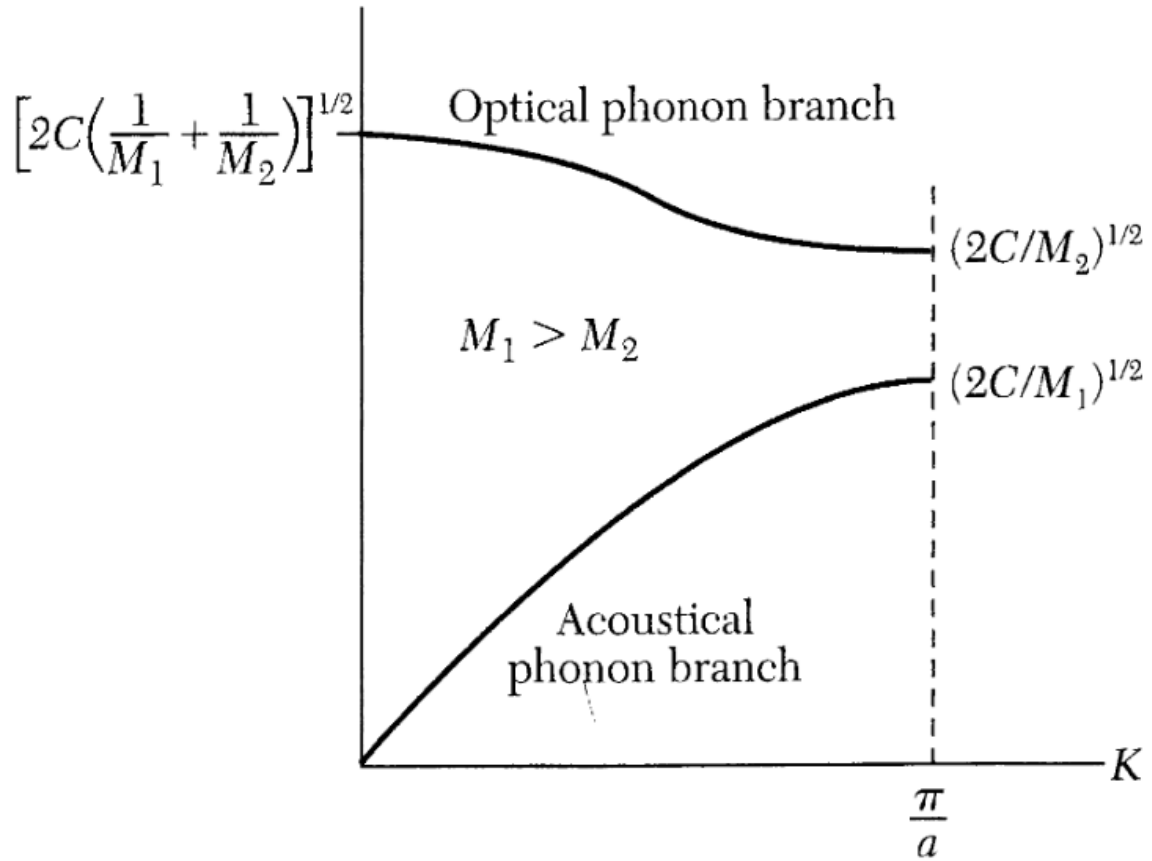
$$\omega^2 \cong \frac{C}{2(M_1 + M_2)} K^2 a^2$$

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 $\exp(-\hbar \omega_E / k_B T)$.

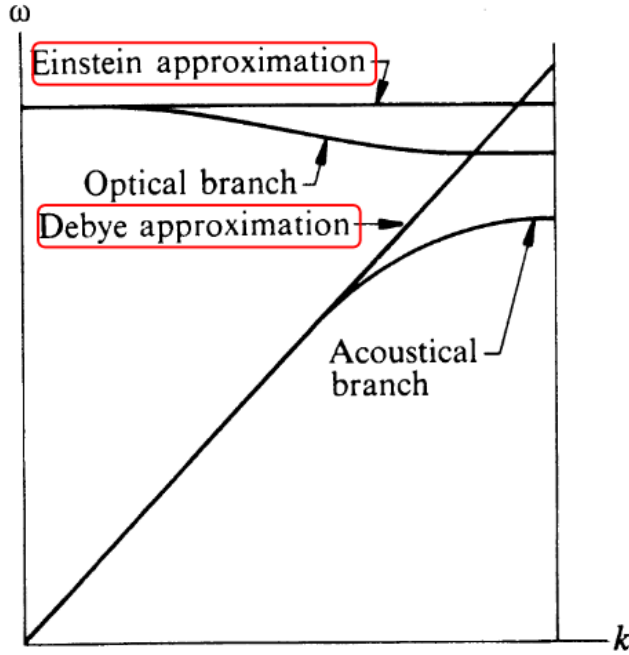


Fig. 4.5 Comparison of Einstein and Debye approximations for the dispersion relation of lattice waves, referred to a linear diatomic lattice.

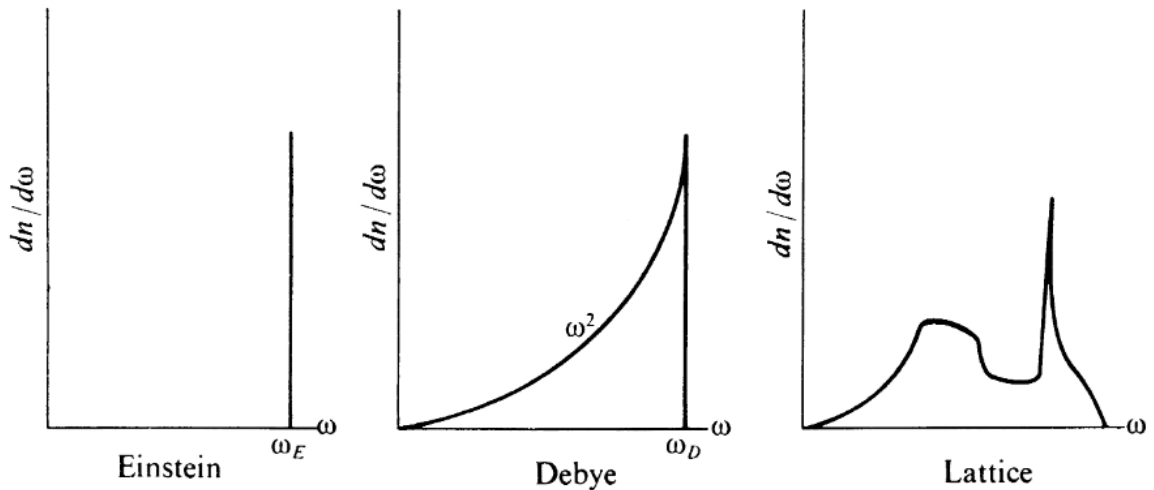


Fig. 4.11 Mode spectra for the Einstein and Debye approximations and a lattice. A combination of Einstein and Debye frequencies (acoustic and optical) can result in a good estimate of the mode spectrum for real crystals.

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.

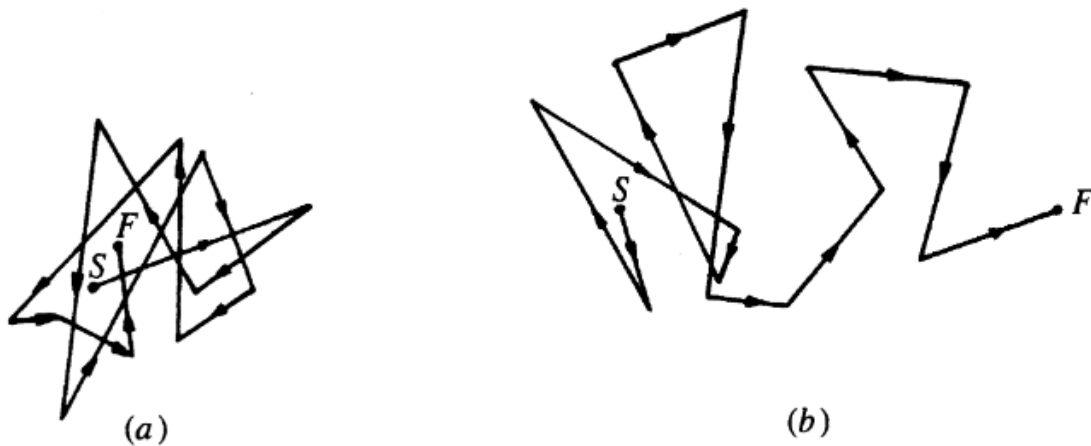


Figure illustrating drift velocity. (a) zero electric field, (b) finite electric field. In an electric field the start and finish positions differ – leading to a net flow of current.

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

The Fermi energy, E_F , is defined as the energy of the highest occupied energy level in the ground state of an n electron system.

We can determine the Fermi energy at 0 Kelvin:

All the points in k -space have a value of energy since we know that:

$$E = \frac{\hbar^2 k^2}{2m_e}$$

These points lie on a sphere in k -space with a radius k ,

At 0 Kelvin all the energy states up to the surface of the sphere are occupied, all those outside the sphere are empty. The effect of temperature is to spread out the surface of the sphere in k -space. This spherical surface represents a surface of constant energy and is called a **Fermi-sphere** or **Fermi-surface**.

The radius k_F is determined by multiplying the volume of the sphere in k -space by the number of electron energy states per unit volume and setting that equal to the total number of electrons N .

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

Rearranging:

$$k_F = \left(\frac{3N\pi^2}{L^3}\right)^{\frac{1}{3}} = (3\pi^2 n)^{1/3}$$

Where k_F is the **Fermi wavevector** and n is the free electron density.

The Fermi Energy is hence:

$$E_F = \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3}$$

The velocity of an electron at the Fermi surface is the **Fermi velocity**:

$$v_F = \frac{\hbar k_F}{m_e}$$

The Density of States

The volume of k -space between k and $k + \delta k$ is $4\pi k^2 \delta k$ where $4\pi k^2$ is the surface area of the sphere of radius k .

The total number of k states between k and $k + \delta k$ is:

$$\begin{aligned} n(k)\delta k &= \frac{L^3}{4\pi^3} 4\pi k^2 \delta k \\ &= \frac{L^3}{\pi^2} k^2 \delta k \end{aligned}$$

To calculate the density of states as a function of energy $n(E)$ we express the density of states in terms of unit energy range. By definition:

$$n(k)\delta k = n(E)\delta E$$

And so:

$$n(E)\delta E = \frac{L^3}{\pi^2} k^2 \delta k$$

Using:

$$k^2 = \frac{2m_e E}{\hbar^2}$$

We have:

$$\frac{dk}{dE} = \frac{m_e^{1/2}}{\sqrt{2}\hbar} E^{-1/2}$$

We can then set $\delta k/\delta E = dk/dE$ and get:

$$n(E) = \sqrt{2} \frac{L^3}{\pi^2} \frac{m_e^{3/2}}{\hbar^3} E^{1/2}$$

This is the bulk 3D density of states for the free electron model.

Note that the energy density of states function depends on the dimensions of the system (volume, $V = L^3$, in the cubic system).

Nearly Free Electron Model

Failures of the Free Electron Model

- Hall coefficients
- Temperature dependence on conductivity
- Specific heat

Bloch's Theorem

Considering a 1D crystal system, suppose that a wavefunction $\psi(x)$ satisfies a 1D time independent Schrodinger equation with a periodic potential $V(x)$ at an energy eigenvalue of E .

Consider a function $\phi(x) = \psi(x + R)$ where R is a lattice vector. The Schrodinger equation evaluated at $x + R$ must give the same solution when evaluated at x and so $\psi(x)$ also satisfied the same Schrodinger equation with an energy eigenvalue of E .

We can then write:

$$\psi(x + R) = c(R)\psi(x)$$

Where $c(R)$ is a constant.

From the situation above we can say $c(R) = 1$.

If we perform a series of lattice transformations:

$$\begin{aligned}\psi(x + R_1 + R_2) &= \psi((x + R_1) + R_2) = \psi(x + (R_1 + R_2)) \\ c(R_2)\psi(x + R_1) &= c(R_1 + R_2)\psi(x) \\ c(R_1)c(R_2)\psi(x) &= c(R_1 + R_2)\psi(x)\end{aligned}$$

So we can say:

$$c(R_1 + R_2) = c(R_1)c(R_2)$$

And so:

$$c(nR) = [c(R)]^n, \quad n = 0, 1, 2, \dots$$

The wavefunction has to then satisfy periodic boundary conditions over M lattice translations where $Ma = L$.

From this we have:

$$\psi(x + Ma) = \psi(x) \implies [c(a)]^M = 1$$

Which allows us to write:

$$c(a) = \exp ika$$

Where

$$ka = \frac{2\pi l}{M}, \quad l = 0, \pm 1, \pm 2, \dots$$

M is the total number of atoms and a is the lattice constant.

Hence for any lattice translation $\mathbf{R} = m\mathbf{a}$ we have:

$$c(R) = [c(a)]^M = \exp iMka = \exp ikR$$

Where:

$$k = \frac{2\pi l}{L}, \quad l = 0, \pm 1, \pm 2, \dots$$

L is the total dimension of our 1D system.

Free electron model:

$$\psi(x) = C \exp ikx$$

A plane wave with constant energy

Nearly Free electron model:

$$\psi(x + R) = C \exp ik(x + R) = C \exp ikR \quad \psi(x) = C \exp ikR \exp ikx = C u_k(R) \exp ikx$$

This is true for any value of R .

The Bloch theorem tells us that **the wavefunctions of electrons in a periodic potential are comprised of two parts:**

- A plane wave $\exp i(\mathbf{k} \cdot \mathbf{r})$
- A Bloch function $u_k(R)$ which has the periodicity of the lattice and modulates the intensity of the plane wave

A consequence of the Bloch Theorem is that only k values in a range $-\pi/a < k < +\pi/a$ (chosen by convention) are physically distinct. This region corresponds to the first Brillouin zone (in a simple cubic lattice).

Energy Band Diagrams

We can plot out the different possibilities of the energy dependence on wavevector k . These are called energy bands.

In the free electron model:

$$E(k) = \frac{\hbar^2 k^2}{2m_e}$$

The free electron behaviour follows the $E \propto k^2$ curve. This is consistent with a free electron and we can determine the momentum $\hbar k$ and the group velocity $\partial\omega/\partial k$ from this relationship.

Free Electron Model

$$E = \hbar^2 k^2 / 2m_e$$

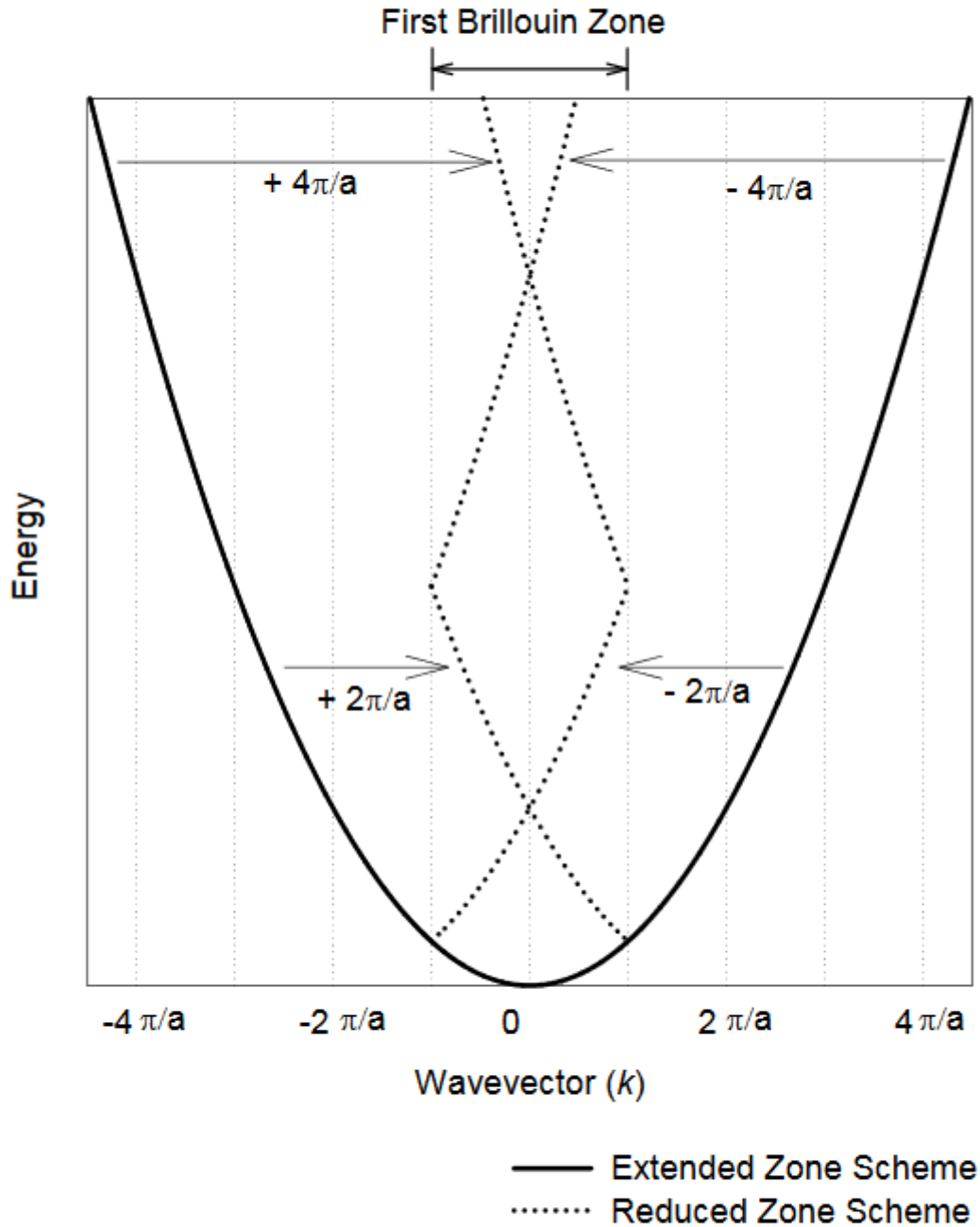


Diagram showing energy bands produced by Bloch state in the first Brillouin zone for the free electron model.

The lines represent the start of the energy bands with the number of states increasing according to the density of states.

If there are M unit cells in the length L of the 1D solid then each band can accommodate

$$\frac{2\pi}{a} \frac{L}{\pi} = 2M$$

electrons.

Electrons states in energy bands subject to a periodic potential are described as **Bloch states**. This implies the motion of the electron is modified by the periodic potential.

Properties of Energy Bands

Energy Gaps

There are two alternative ways of describing the origin of the energy gap: Bragg reflection and interference between wavefunctions.

Bragg Reflection

Bragg proposed that we can assume that a small fraction of an incident EM wave is reflected from parallel planes of atoms in a crystal.

An alternative form of the Bragg condition ($2d \sin \theta = n\lambda$) is:

$$k = \frac{n\pi}{d \sin \theta}$$

If $\sin \theta = 1$ this gives us corresponding k values at which energy gaps appear: $k = n\pi/a$ where a is the lattice constant.

Interference

If we consider the electron states which propagate through the crystal as waves, there will be an interaction between the electron wavefunctions and the periodic potential. At certain special wavelengths, related to the crystal period, interference will occur which gives rise to energy gaps, or regions where there are no valid solutions to the Schrödinger equation.

Energy Bands

We know for travelling waves the group velocity is given by:

$$v_{\text{group}} = \frac{d\omega}{dk}$$

This can be considered the velocity of the electron wavepacket.

Since $E = \hbar\omega$:

$$v_{\text{group}} = \frac{1}{\hbar} \frac{dE(k)}{dk}$$

Velocity of Bloch Electrons

We can calculate that:

$$v_{\text{group}} = \frac{1}{\hbar} \frac{d}{dk} \left[\frac{\hbar^2 k^2}{2m_e} \right] = \frac{\hbar k}{m_e} = \frac{p}{m_e} = v$$

Where $p = \hbar k$ is called the **crystal momentum**. *It is not the same as the electron momentum.*

It is considered the momentum an electron appears to have whilst moving through a crystal in a Bloch state or energy band, and is due to the interaction between the electron and the periodic potential of the crystal.

Current Carried by Energy Bands

The current density is given by:

$$j = ne\langle v \rangle$$

Where n is the electron density and $\langle v \rangle$ is the average velocity of electrons in a band.

Suppose we have M energy states in an energy band occupied by $2M$ electrons, we have:

$$\begin{aligned}\langle v \rangle &= \frac{1}{\hbar} \int_{-\pi/a}^{\pi/a} \frac{dE}{dk} \frac{a}{2\pi} dk \\ &= \frac{a}{2\pi\hbar} \left[E\left(\frac{\pi}{a}\right) - E\left(-\frac{\pi}{a}\right) \right]\end{aligned}$$

We know that $k = \pm\pi/a$ are physically equivalent values of the Bloch wavevector and so $E(\pi/a) = E(-\pi/a)$ and thus $\langle v \rangle = 0$ so $j = 0$.

This tells us that **a completely filled energy band makes no contribution to the current carried by a crystal.**

Equation of Motion for Bloch Electrons

Consider a force F applied to an electron in a crystal. We know the rate at which the energy changes must be the rate at which the force does work:

$$Fv_{\text{group}} = \frac{dE}{dt} = \frac{dE}{dk} \times \frac{dk}{dt}$$

We know that:

$$v_{\text{group}} = \frac{1}{\hbar} \frac{dE}{dk}$$

So:

$$\hbar \frac{dk}{dt} = F$$

The rate of change of **crystal momentum** is equal to the applied force.

Effective Mass

Consider the $E(k)$ relation near a band extremum at $k = k_0$ where $\frac{dE}{dk} = 0$ and hence the group velocity is zero. It will be of a general form (Taylor expansion):

$$E = E(k_0) + \frac{1}{2}A(k - k_0)^2$$

The group velocity as a function of k is then

$$v_{\text{group}}(k) = \frac{A(k - k_0)}{\hbar}$$

Comparing this with free particles we have:

$$v_{\text{free}} = \frac{p}{m} = \frac{\hbar k}{m}$$

The electrons behave as though they had an effective mass:

$$m_{\text{eff}} = \frac{\hbar^2}{A}$$

From Taylor's theorem it can be shown that:

$$A = \left. \frac{d^2 E}{dk^2} \right|_{k=k_0}$$

From this, the **effective mass** is given by:

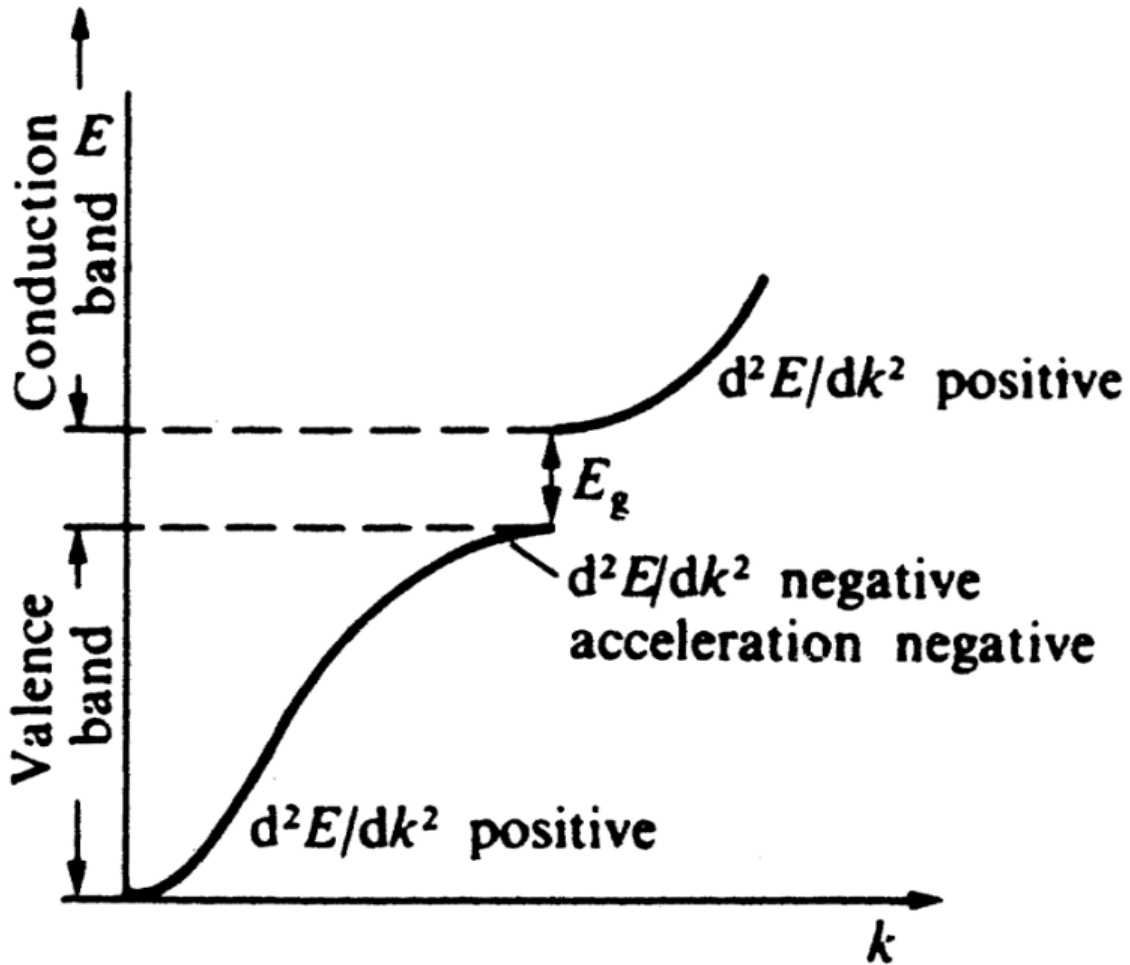
$$m_{\text{eff}} = \hbar^2 \left[\frac{d^2 E(k)}{dk^2} \right]^{-1}$$

The effective mass is therefore *proportional to the inverse curvature of the $E(k)$ band.*

At the centre of the Brillouin zone we can write:

$$E = \frac{\hbar^2 k^2}{2m_{\text{eff}}}$$

We have a constant curvature and therefore a constant effective mass. (This is often called the parabolic approximation).



Electrons and Holes

A hole is an empty or unoccupied electron state. The properties of holes are:

1. The charge on the hole is $+e$
2. The hole wavevector is $k_h = -k_e$ where k_e is the wavevector of the missing electron.
3. The hole energy is $E_h(k_h) = -E(k_e)$
4. The hole velocity is $v_h = v_e$
5. The hole effective mass is $m_{\text{eff}}(\text{hole}) = -m_{\text{eff}}(e)$ and is positive at the top of a band

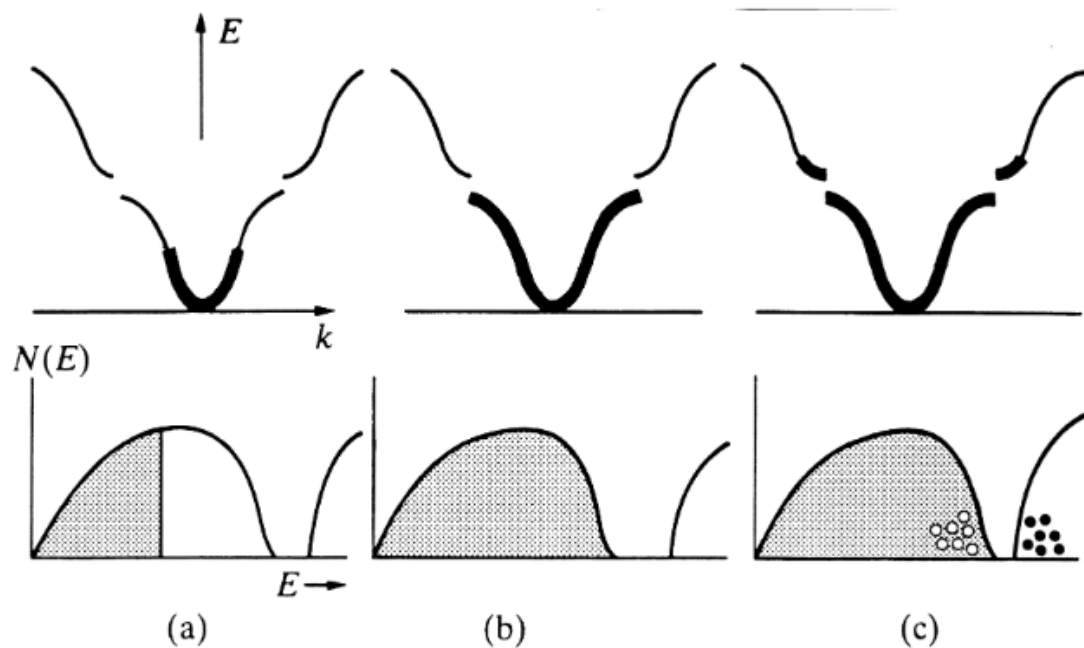
Metals Insulators and Semiconductors

We know that the number of k -states in each band is equal to N , the number of atoms in the crystal. Each k -state is populated by two electrons giving $2N$ electron energy states.

If a metal has only one conduction electron per atom the bottom half of the band will be occupied. This leaves large numbers of empty states for electrons to move into. The energy distribution in this system is that predicted by the free and nearly-free electron model.

The situation when there is an even number of electrons per atom is different. In this case the electrons would occupy all the energy states in the energy band. As there are no empty k -states to occupy when an electric field is applied this material will be an insulator. If the bandgap is sufficiently small a proportion of electrons may be excited across the bandgap. **In this case we have a semiconductor.**

In a metal the conductivity decreases with increasing temperature. In a semiconductor the conductivity increases with increasing temperature.



Optics

EM Waves and Light

The EM wave equation is:

$$\nabla^2 \mathbf{E} - \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = 0$$

The harmonic wave solution is:

$$\mathbf{E} = \mathbf{E}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$$

Where \mathbf{k} is the wave vector. It has a magnitude:

$$k = \frac{2\pi}{\lambda}$$

Where λ is the wavelength. If \mathbf{E}_0 is time independent then the harmonic wave describes monochromatic light.

The magnitude of \mathbf{E}_0 determines the amplitude of the field. The intensity (time-averaged energy per unit area per unit time) is proportional to $|\mathbf{E}_0|^2$.

The components of \mathbf{E}_0 :

$$\mathbf{E}_0 = (E_{0x}, E_{0y}, E_{0z})$$

determine the **polarisation**. For light with fixed polarisation, we can replace the vector \mathbf{E}_0 with a scalar E_0 **scalar approximation**.

Phase, Phasors and Phase Fronts

In complex notation the harmonic wave solution is:

$$E = E_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$$

The wave is characterised by an amplitude E_0 and a phase $\phi = i(\mathbf{k} \cdot \mathbf{r} - \omega t)$.

For a **plane wave**, E_0 is independent of position and time.

For a plane wave propagating at angle θ relative to the z axis in the xz plane, the **spatial frequency** along x is:

$$u = \frac{\sin \theta}{\lambda}$$

As $k_x = k \sin \theta$ we find that the x -component of the wave vector is:

$$k_x = 2\pi u$$

The intensity of the wave is given by:

$$\mathcal{I} = \frac{1}{2} \epsilon_0 c |E|^2$$

Spherical Waves, Paraxial Approximation and Lenses

For both plane and spherical waves the phase change in moving a distance r' in the direction of propagation is kr' . For example, the distance between an input point $(x', y', 0)$ and an observation point (x, y, z) is:

$$r' = [z^2 + (x - x')^2 + (y - y')^2]^{1/2}$$

If $z \gg |x - x'|$ then we can use the binomial expansion to make the **Fresnel approximation**:

$$r' = z \left[1 + \frac{(x - x')^2 + (y - y')^2}{z^2} \right]^{1/2} \approx z \left[1 + \frac{1}{2} \frac{(x - x')^2 + (y - y')^2}{z^2} \right]$$

We define the **paraxial distance** as:

$$r_p = z + \frac{(x - x')^2 + (y - y')^2}{2z}$$

The paraxial distance is used to write a paraxial form of the spherical wave. For a spherical wave emitted from the origin, we have $x' = y' = 0$ and:

$$E = \frac{E_s}{ikr} e^{ikr} \approx \frac{E_s}{ikz} e^{ikz} e^{ik\rho^2/2z}$$

Where $\rho^2 = x^2 + y^2$. The parameter after the 2 in the denominator of the ρ^2 -term tells us the radius of curvature of the wavefronts.

A **lens** imprints a phase that changes the curvature of a wave: the field immediately downstream of a thin lens place in the $z = 0$ plane is:

$$E^{(L)} = E^{(0)} e^{-ik\rho^2/2f}$$

Where $E^{(0)}$ is the field immediately before the lens. A lens converts a paraxial spherical wave with radius of curvature s_1 (diverging) to another paraxial spherical wave with curvature $-s_2$ (converging), where:

$$\frac{1}{s_1} + \frac{1}{s_2} = \frac{1}{f}$$

Interference

When two or more waves intersect they interfere. Interference maps the **relative phase** between the two waves into intensity maxima and minima.

The sum of two plane waves is:

$$E = E_1 + E_2 = E_{0,1}e^{i(\mathbf{k}_1 \cdot \mathbf{r} - \omega t)} + E_{0,2}e^{i(\mathbf{k}_2 \cdot \mathbf{r} - \omega t)}$$

Calculated the intensity $\mathcal{I} \propto |E|^2$ gives cross terms like $E_1 \cdot E_2^*$ that give rise to **interference fringes**.

Another way to write the intensity, assuming $E_{0,1} = E_{0,2} = E_0$ is to rewrite the electric field as:

$$E = 2E_0 e^{i(\bar{\mathbf{k}} \cdot \mathbf{r} - \omega t)} \cos\left(\frac{\Delta \mathbf{k} \cdot \mathbf{r}}{2}\right)$$

Where $\bar{\mathbf{k}} = (\mathbf{k}_1 + \mathbf{k}_2)/2$ and $\Delta \mathbf{k} = \mathbf{k}_1 - \mathbf{k}_2$.

The first exponential term is a **global phase** factor when we calculate intensity, The **relative phase** terms survive:

$$\mathcal{I} = 4E_0^2 \cos^2\left(\frac{\Delta \mathbf{k} \cdot \mathbf{r}}{2}\right)$$

If \mathbf{k}_1 and \mathbf{k}_2 are in the xz plane at an angle of $\theta = \pm\theta_0/2$ with respect to the z -axis then the space between the intensity maxima along x is:

$$\Lambda = \frac{\lambda}{2 \sin(\theta_0/2)}$$

For small θ , the spacing frequency of the interference fringed is proportional to angle,

$$\frac{1}{\Lambda} \approx \frac{\theta}{\lambda}$$

Michelson Interferometer

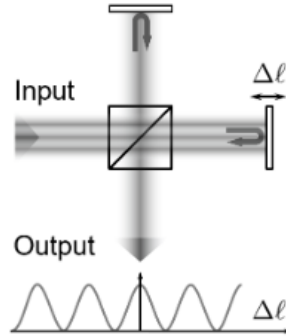


Figure 1: The Michelson interferometer with the output intensity as a function of the path difference shown below.

Young's Interferometer

The **sum of two spherical waves** originating at $(x', z) = (\pm d/2, 0)$ (Young's two holes) is:

$$E = \frac{E_s}{ikr_1} e^{ikr_1} + \frac{E_s}{ikr_2} e^{ikr_2}$$

Where E_s is the effective amplitude of the waves.

In the paraxial limit $d \ll z$ and $x < z$ we can write this as:

$$E = \bar{E}_s e^{ik(\bar{r} + d^2/8z)} \left(e^{ikdx/2z} + e^{-ikdx/2z} \right)$$

Where $\bar{E}_s = E_s/ik\bar{r}$ and $\bar{r} = z + x^2/2z$.

The intensity is:

$$I = 4\bar{I}_s \cos^2\left(\frac{\pi dx}{\lambda z}\right)$$

Note: $dx = d \cdot x$ and is not the differential dx .

For slits rather than circular apertures $\bar{E}_s = E_s/\sqrt{ik\bar{r}}$. For **three slits** at $(x', z) = (0, 0)$ and at $(\pm d, 0)$ the sum of the three paraxial cylindrical waves is:

$$E = \bar{E}_s e^{i(k\bar{r} - \omega t)} \left(e^{ikdx/z} + 1 + e^{-ikdx/z} \right)$$

The intensity is:

$$I = \bar{I}_s \left[1 + 2 \cos\left(\frac{2\pi dx}{\lambda z}\right) \right]^2$$

N Slits: Phasor Sums and Diffraction Gratings

For three slits at $t = 0$:

$$E = \frac{E_0}{\sqrt{ikz}} e^{ik\bar{r}} \left(e^{ikdx/z} + 1 + e^{-ikdx/z} \right)$$

Where the terms inside the bracket are a **discrete phasor sum**. For N-slits, the expression is:

$$\begin{aligned} E &= \frac{E_0}{\sqrt{ikz}} e^{ik\bar{r}} \sum_{m=-(N-1)/2}^{(N-1)/2} e^{ikmdx/z} \\ &= \frac{E_0}{\sqrt{ikz}} e^{ik\bar{r}} e^{-i(N-1)kdx/2z} \sum_{m=0}^{(N-1)/2} e^{ikmdx/z} \end{aligned}$$

As this is a geometric progression it can be summed analytically. The generic feature of the sum are:

1. Positions where all phasors align are known as **principal maxima**. They occur at $x = m(\lambda/d)z$, where m is an integer, and have an intensity proportional to N^2
2. The intensity is zero when the phasors are isotropically distributed in the complex plane. The position of the first zero is $x = [\lambda/(Nd)]z$. There are $N - 1$ zeros between the principal maxima.
3. Positions of partial constructive alignment are known as **subsidiary maxima**. There are $N - 2$ subsidiary maxima between the principal maxima.

Fresnel Diffraction Integral

The light distribution in any plane z can be written as a **sum of paraxial spherical waves** originating from the input plane at $z = 0$ using the **Fresnel diffraction integral**:

$$E^{(z)} = \frac{E_0}{i\lambda z} \iint_{-\infty}^{\infty} f(x', y') e^{ikr_p} dx' dy'$$

Where $f(x', y')$ is the **aperture function** and:

$$r_p = z + \frac{(x - x')^2 + (y - y')^2}{2z}$$

is the **paraxial distance** from the source point $(x', y', 0)$ to the observation point (x, y, z) .

For the case of a circular aperture with radius R_a , the field on axis at $(\rho, z) = (0, z)$ in cylindrical coordinates:

$$\mathcal{E}^{(z)} = \frac{\mathcal{E}_0}{i\lambda z} e^{ikz} \int_0^{R_a} e^{ik\rho'^2/2z} 2\pi\rho' d\rho' = -\mathcal{E}_0 e^{ikz} \left(e^{ikR_a^2/2z} - 1 \right)$$

and the intensity is:

$$\mathcal{I}^{(z)} = 4\mathcal{I}_0 \sin^2\left(\frac{\pi R_a^2}{2\lambda z}\right)$$

The intensity oscillates between 0 and $4\mathcal{I}_0$. This can be explained in terms of **Fresnel zones**:

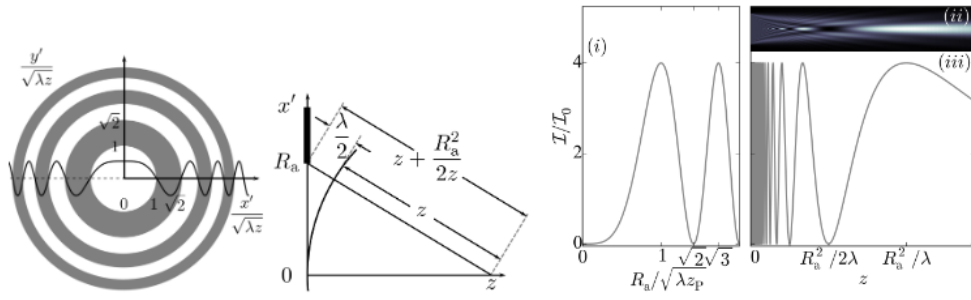


Figure 1: Left: Path difference variation across a circular aperture and how that changes the phase of waves arriving from different points. Middle: Geometry of the 1st Fresnel zone. The field changes sign at the edge of the 1st zone where $R_a = \sqrt{\lambda z}$. Right: The intensity pattern in the xz plane downstream of a circular aperture.