Properties of Matter

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Chapter 1

Properties of Solids and Liquids

1.1 Introduction

The kinetic energy per particle is $\approx k_B T$. Solids form when,

$$k_B T << \epsilon \tag{1.1}$$

where ϵ is the binding energy. Further, liquids form when,

$$k_B T \approx \epsilon \tag{1.2}$$

and gasses when,

$$k_B T >> \epsilon. \tag{1.3}$$

1.2 Elasticity of Solids

Solids exhibit elastic behaviour, i.e., when stress is applied they deform (strain) and return to their original shape once removed. The way solids resist strain is defined by elastic moduli, which are general defined,

$$\text{Elastic Modulus} = \frac{\text{Stress}}{\text{Strain}}. \tag{1.4}$$

1.2.1 Young's Modulus

Definition. *E - The ability of a solid to resist forces along a given axis.*

Consider a setup like in fig. 1.1. Stress is given by, $\frac{F}{A}$ and strain by, $\frac{\Delta l}{l}$ where Δl is the deformation along the axis of the force. We then have,

$$\boxed{E = \frac{F}{A} \left(\frac{\Delta l}{l} \right)^{-1}.} \tag{1.5}$$
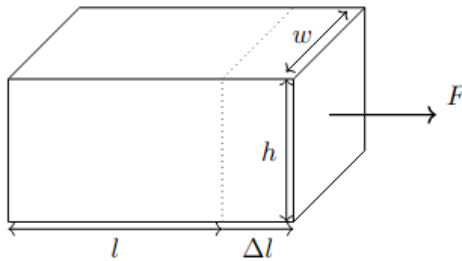
Figure 1.1: Solid undergoing deformation due to a force along its axis.
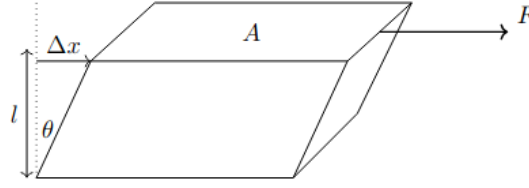
Figure 1.2: A solid undergoing shearing due to a force parallel to and along one of its faces.
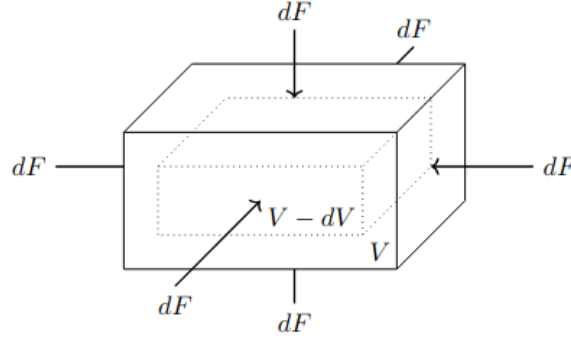
Figure 1.3: A solid of volume V being compressed by a force, dF, leading to an infinitesimal change in its volume dV.

1.2.2 Shear Modulus

Definition. G - *The ability of a solid to resist shearing when a force is applied parallel to the surface of the solid.*

Consider a setup like in fig. 1.2. If the solid shears by Δx due to a force F, then its strain is,

$$\frac{\Delta x}{l} = \tan\theta \cong \theta \tag{1.6}$$

for small θ. The shear modulus is then,

$$\boxed{G = \frac{F}{A}\left(\frac{\Delta x}{l}\right)^{-1} = \frac{F}{A\theta}}. \tag{1.7}$$

1.2.3 Bulk Modulus

Definition. K - *Resistance of a material to compression.*

The bulk modulus describes the stress due to a change in pressure dP. If we consider a setup like in fig. 1.3, the change in volume is $-dV$, the strain is dV/V, so the bulk modulus is,

$$\boxed{K = -V\frac{dP}{dV}}. \tag{1.8}$$

The minus sign indicates that an increase in pressure results in a decrease in volume.

1.3 Properties of Static Liquids

1.3.1 Hydrostatic Pressure

Consider a column of liquid of constant density ρ_l, a depth d, and cross-sectional area A as in fig. 1.4. Since the liquid is static (no net flow), we have $F_{\text{net}} = 0$. The force at d is then,

$$F = P_0 A + \rho dg A = P(d)Am \tag{1.9}$$

so the pressure at d is,

$$\boxed{P(d) = P_0 + \rho g d}. \tag{1.10}$$

$\implies$ as d increases linearly, so does P.
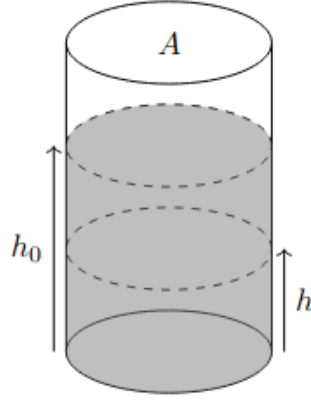
Figure 1.4: A column of liquid of constant density ρ, vertical height h_0, and cross-sectional area A.
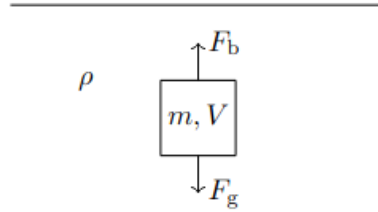
Figure 1.5: An arbitrary hollow shape of volume V filled with liquid of density ρ, immersed in a liquid of the same density.

1.3.2   Buoyancy and Archimedes Principle

Consider an arbitrary hollow shape of volume V filled with liquid of density ρ_l, immersed in a liquid of the same density, as in fig. 1.5. The weight of the object is given by,

$$F_w = \rho_l V g. \tag{1.11}$$

The pressure acting on the body must be equal and opposite to its weight. We call this the *buoyancy force*,

$$\boxed{F_b = \rho_l V g}. \tag{1.12}$$

The buoyancy force is *equal and opposite to the weight of the liquid displaced.* I.e., in the case that the mass has a density ρ_b such that $\rho_l > \rho_b$, the force it feels is still of the form eq. (1.12), so will float above the surface of the water.

1.4   Flow of Incompressible Liquid

The molecules in a liquid or gas can easily flow, with the same time and position dependent velocity, $\mathbf{v}(\mathbf{r}, t)$.

1.4.1   Conservation of mass and the continuity equation

The rate of mass flow through an area element of a surface $d\mathbf{S}$ is $\rho \mathbf{v} \cdot d\mathbf{S}$. The rate of mass flow into a volume bounded by a surface S is this expression evaluated over all space,

$$\frac{dm}{dt} = \rho \int_S \mathbf{v} \cdot d\mathbf{S}. \tag{1.13}$$

For a liquid of constant density, eq. (1.13) must equal 0,

$$\int_S \mathbf{v} \cdot d\mathbf{S} = 0 \tag{1.14}$$
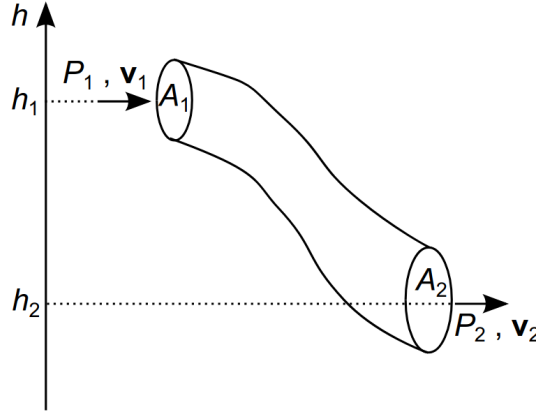
Figure 1.6: Frictionless pipe of arbitrary shape, with each end at a different height h_1 and h_2 such that $h_2 < h_1$.

and by the divergence theorem,

$$\boxed{\boldsymbol{\nabla} \cdot \mathbf{v} = 0} \tag{1.15}$$

In the case of compressible liquids (i.e., where $\rho = \rho(\mathbf{r})$), conservation of mass is satisfied via the continuity equation,

$$\boxed{\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{v}) = 0}. \tag{1.16}$$

1.4.2 Bernoulli's Principle

We will investigate how pressure of a liquid depends on flow speed. We assume no surface or viscous forces, and we assume flow is time independent, i.e., $\mathbf{v} = \mathbf{v}(\mathbf{r})$.

Particles will flow in streamlines. Consider adjacent streamlines which form a tube of arbitrary shape, where each end is at a different vertical height, h_1 and h_2 such that $h_2 < h_1$, and there is no flow in or out of the tube, as in fig. 1.6. The liquid enters at height h_1, with velocity v_1, pressure P_1, through an area A_1. The liquid leaves at height h_1, with velocity h_2, pressure P_2, through an area A_2.

From the conservation of mass,

$$v_1 A_1 = v_2 A_2. \tag{1.17}$$

In a time $\mathrm{d}t$, the work done by pressure P_1 on the liquid at entry is,

$$\mathrm{d}W_1 = P_1 A_1 v_1 \, \mathrm{d}t \tag{1.18}$$

and similarly for the exit,

$$\mathrm{d}W_2 = P_2 A_2 v_2 \, \mathrm{d}t \,. \tag{1.19}$$

The kinetic energy of the liquid is,

$$\mathrm{d}K_1 = \frac{1}{2} \left(\rho v_1 A_1 \, \mathrm{d}t \right) v_1^2, \tag{1.20}$$

and the potential energy,

$$\mathrm{d}V = \left(\rho v_1 A_1 \, \mathrm{d}t \right) g h_1, \tag{1.21}$$

and similarly for the exit. By conservation of energy,

$$\mathrm{d}W_1 + \mathrm{d}K_1 + \mathrm{d}V_1 = \mathrm{d}W_2 + \mathrm{d}K_2 + \mathrm{d}V_2$$

$$A_1 v_1 \left(P_1 + \frac{1}{2} \rho v_1^2 + \rho g h_1 \right) \mathrm{d}t = A_2 v_2 \left(P_2 + \frac{1}{2} \rho v_2^2 + \rho g h_2 \right) \mathrm{d}t \,. \tag{1.22}$$

By eq. (1.17), we can divide eq. (1.22) by $A_1 v_1 \, \mathrm{d}t$,

$$P_1 + \frac{1}{2} \rho v_1^2 + \rho g h_1 = P_2 + \frac{1}{2} \rho v_2^2 + \rho g h_2 \tag{1.23}$$

which leads to Bernoulli's equation,

$$P(h,v) + \rho g h + \frac{1}{2}\rho v^2 = \text{constant}$$

(1.24)

$\implies$ *faster moving liquids have lower pressure.*

1.4.3   Flow Properties and Viscosity

Laminar Flow

Definition. *Smooth, regular streamlines that are locally parallel to each other*

The drag force on a spherical object of radius R inserted into a liquid under laminar flow is caused by the liquid's resistance to shearing, and is given by Stoke's law,

$$\mathbf{F}_D = 6\pi\nu R\mathbf{v}$$

(1.25)

where ν is the viscosity of the liquid.

Turbulent Flow

Definition. *Streamlines are irregular and chaotic due to formation of eddies in the flow.*

The drag force on an object placed in the stream occurs due to the inertial force required to push the liquid out of the way of the object. The drag force is given by,

$$\mathbf{F}_D = \frac{1}{2}\rho v^2 C_D A\hat{\mathbf{v}}$$

(1.26)

where A is the cross-sectional area of the object and C_D is a dimensionless drag coefficient.

Laminar-Turbulent Transition and Reynold's Number

Whether a liquid experiences laminar or turbulent flow depends on the ratio of inertial force to viscous force. This ratio is given by Reynold's number,

$$Re = \frac{\rho L v}{\nu}$$

(1.27)

where L is the length of the object moving through the liquid.

1.5   Liquid Surfaces

Free Surface: The surface interface of a liquid is characterised by the surface free energy γ. This is the energy required to increase the surface area of the interface.

Liquid-Liquid Interface: At the interface between two liquids, it is only energetically favourable for them to mix if $\gamma < 0$.

Liquid-Solid Interface: For $\gamma < 0$, it is energetically favourable for the liquid to spread over the surface of the solid.

1.5.1   Liquids in a Container

Contact Angle

We are interested in the way a liquid-gas interface meets the solid wall of a container. The shape of the liquid near the wall is known as the meniscus, as in fig. 1.7. We can approximate the meniscus as linear, where the liquid meets the wall at the contact angle θ, at a height h, and horizontal distance l from the surface of the liquid.

Let us consider the following surface-free energies,
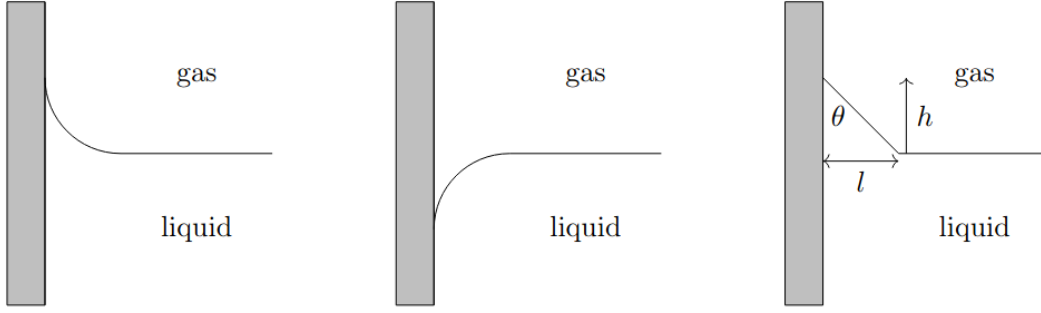
Figure 1.7

1. Solid-gas γ_{sg},

2. Solid-liquid γ_{sl},

3. Liquid-gas γ_{lg}.

The meniscus free energy (per unit length of the meniscus, thus having dimensions of force) is given by,

$$F_{\text{men}} = (\gamma_{sl} - \gamma_{sg}) + \gamma_{lg} \left(\sqrt{h^2 + l^2} - l \right). \tag{1.28}$$

The free energy is minimised when,

$$\frac{\partial F_{\text{men}}}{\partial h} = (\gamma_{sl} - \gamma_{sg}) + \gamma_{lg} \left(\frac{1}{2} \frac{2h}{\sqrt{h^2 + l^2}} \right) = 0. \tag{1.29}$$

We have that,

$$\frac{h}{\sqrt{h^2 + l^2}} = \cos\theta \tag{1.30}$$

which allows us to find Young's equation relating contact angle to surface free energy,

$$\boxed{\gamma_{lg} \cos\theta = \gamma_{sg} - \gamma_{sl}}. \tag{1.31}$$

When $\theta < \frac{\pi}{2}$, we say the liquid wets the solid.

Capillary Action

This occurs when a column of liquid is placed in a narrow tube. Consider a tube of radius R at height h relative to the surface of the bulk liquid. The surface free energy gain is,

$$\Delta F_s = 2\pi rh \left(\gamma_{sl} - \gamma_{sg} \right) \tag{1.32}$$

while the increase in gravitational potential energy is,

$$\Delta F_g = \pi R^2 h \rho g \frac{h}{2} \tag{1.33}$$

where $h/2$ is used as that is the location of the centre of mass.

The total free energy is,

$$F = \Delta F_s + \Delta F_g = \frac{\pi}{2} R^2 h^2 \rho g + 2\pi Rh \left(\gamma_{sl} - \gamma_{sg} \right) \tag{1.34}$$

which is minimised when,

$$\frac{\partial F}{\partial h} = \pi R^2 h \rho g + 2\pi R \left(\gamma_{sl} - \gamma_{sg} \right) = 0, \tag{1.35}$$

which can be rearranged to give a function for h,

$$\boxed{h = -\frac{2}{(\gamma_{sl} - \gamma_{sg})} \rho g R = \frac{2\gamma_{lg} \cos\theta}{\rho g R}} \tag{1.36}$$

1.5.2   Surface Tension and Surface Free Energy

Consider a wire frame, with one side of length l, free to move in the x direction. A thing film of liquid covers the space within the frame and shifts the wire a distance $\mathrm{d}x$ in order to minimise the overall free energy.

The work done on the wire to move a distance $\mathrm{d}x$ due to a force F applied by the thin film of liquid is,

$$\mathrm{d}W = F \, \mathrm{d}x \, . \tag{1.37}$$

The work also contributes to increasing the surface area of the liquid by,

$$\mathrm{d}A = sl \, \mathrm{d}x \, . \tag{1.38}$$

The energy increase is given by,

$$\mathrm{d}E_s = \gamma \, \mathrm{d}A = 2\gamma l \, \mathrm{d}x \, . \tag{1.39}$$

Equating eq. (1.37) and eq. (1.39) gives an expression for the *surface tension*,

$$\boxed{F = 2\gamma l} \, . \tag{1.40}$$

Chapter 2

Thermodynamics

In this chapter we deal with analysing the macroscopic properties of objects composed of many microscopic atoms and particles. We will first consider an idea gas, i.e., one in which,

- the particles have no volume,

- and the particles have no interatomic forces acting between them.

This allows us to write down the ideal gas equation in two forms,

$$\underbrace{P}_{\text{Pressure}} \overbrace{V}^{\text{Volume}} = \underbrace{n}_{\text{Moles}} \overbrace{R}^{\substack{\text{Molar gas} \\ \text{constant}}} \underbrace{T}_{\text{Temperature}} \tag{2.1}$$

$$PV = \underbrace{N}_{\substack{\text{Number of} \\ \text{molecules}}} \overbrace{k_b}^{\substack{\text{Boltzmann} \\ \text{constant}}} T. \tag{2.2}$$

1 mole of substance contains N_A (Avogadro's number) amount of molecules. We further have a relation between the molar gas constant and the Boltzmann constant which states,

$$R = N_A k_b. \tag{2.3}$$

In this course, we will often discuss 2 different variables,

1. **Intensive Variables** - Value is not proportional to the amount of substance.

2. **Extensive Variables** - Value is linearly proportional to the amount of substance.

2.1 First law of thermodynamics

Law 1.

$$\underbrace{\Delta E}_{\substack{\text{Change in} \\ \text{internal energy}}} = \underbrace{W}_{\substack{\text{Work done} \\ \text{on the system}}} + \underbrace{Q}_{\substack{\text{Heat supplied} \\ \text{to a system}}} \tag{2.4}$$

We say that E is a function of state, meaning that the value of E is path independent. For an ideal gas, we have that $E = E(T)$ which is the energy due to the kinetic energy of the particles. If we take the limit as $\Delta E \to 0$,

$$\boxed{\mathrm{d}E = \mathrm{d}Q + \mathrm{d}W}. \tag{2.5}$$

Furthermore, W and Q are not functions of state, meaning that their values are path dependent. This means that,

$$\Delta E = W + Q \equiv \text{Const} \tag{2.6}$$

however, W and Q will not be constant as they depend on the shape of the function they take on.
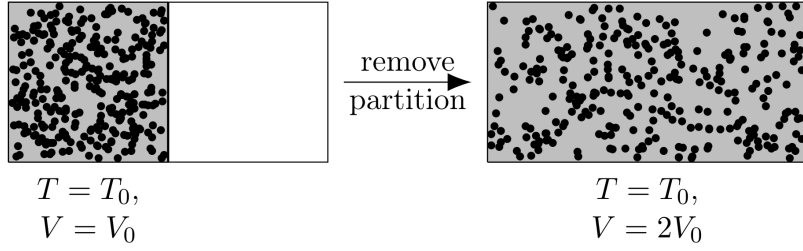
Figure 2.1

2.1.1   Cyclic Process

This is a process which starts and ends in the same equilibrium state, so there is no change in energy over the cycle,

$$\oint \mathrm{d}E = E_{\text{final}} - E_{\text{initial}} = 0. \tag{2.7}$$

From the first law,

$$\oint \mathrm{d}W + \oint \mathrm{d}Q = 0 \tag{2.8}$$

and thus,

$$\boxed{\oint \mathrm{d}W = -\oint \mathrm{d}Q} \tag{2.9}$$

for a cyclic process.

2.1.2   Quasistatic Process

This is a process that occurs so slowly that the system is always instantaneously in thermal equilibrium. For a quasistatic process. the force applied is approximately equal to the pressure of the fluid itself,

$$\boxed{\frac{|\mathbf{F}|}{A} \simeq P}. \tag{2.10}$$

2.1.3   Reversible Processes

For a reversible process, we require,

1. The process must be *quasistatic*.

2. There is no external friction.

3. The process must not cause permanent change to the system.

Free expansion of an isolated gas

Let us consider a gas confined in a volume which is separated in half, with the gas initially in only one part of the volume as in fig. 2.1. If we remove the partition instantaneously, we have,

$$W = 0 \qquad\qquad Q = 0 \qquad\qquad \implies \qquad\qquad \Delta E = 0. \tag{2.11}$$

However, this process is *non-reversible*, as we have caused a permanent change to the system.

Isothermal expansion of an ideal gas

Now consider a setup as in fig. 2.2, where we use a piston to change the volume of the container, and we use a source to keep the temperature of the gas constant. We have,

$$W < 0 \qquad Q > 0 \qquad \implies (Q + W) = 0 \qquad \implies \Delta E = 0. \tag{2.12}$$

This process is *reversible* given that,
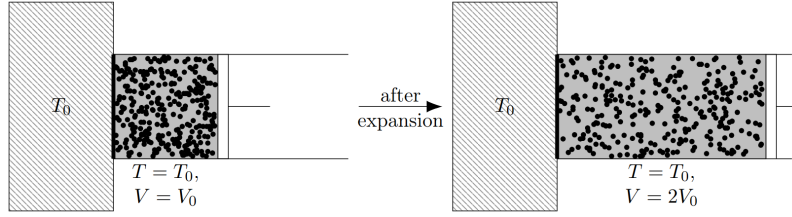
- The piston is frictionless,

- The piston moves slowly.

Figure 2.2

2.1.4 Work Done

Generally, the work done on a fluid is represented by an the area under the curve on an *indicator diagram*, which plots pressure against volume. If we consider a piston of cross-sectional area A compressing a fluid, we can write the work done as,

$$\mathrm{d}W = \mathbf{F} \cdot \mathrm{d}\mathbf{x} = \underbrace{\frac{|\mathbf{F}|}{A}}_{P} \underbrace{A \,\mathrm{d}x}_{-\mathrm{d}V} = -P \,\mathrm{d}V \,. \tag{2.13}$$

For an ideal gas at temperature, we can evaluate this as,

$$\begin{aligned} W &= -\int_{V_i}^{V_f} \frac{nRT}{V} \,\mathrm{d}V \\ &= nRT \ln\left(\frac{V_i}{V_f}\right). \end{aligned} \tag{2.14}$$

For a cyclic process, the net work done is an enclosed area on the $P - V$ diagram.

Reversible Work

Stretching of a wire

If we have a string under tension Γ which undergoes an infinitesimal change in length $\mathrm{d}\ell$, we have,

$$\mathrm{d}W = \Gamma \,\mathrm{d}\ell \,. \tag{2.15}$$

Increase in surface area

For a surface tension γ and a change in area $\mathrm{d}A$,

$$\mathrm{d}W = \gamma \,\mathrm{d}A \,. \tag{2.16}$$

2.1.5 Heat Capacity

Heat capacity C is the amount of energy required to raise the temperature by $\mathrm{d}T$,

$$\mathrm{d}Q = C \,\mathrm{d}T \,. \tag{2.17}$$

Heat capacity at constant volume

Rewriting the first law,

$$\mathrm{d}Q = C_V \,\mathrm{d}T = \mathrm{d}E - \mathrm{d}W = \mathrm{d}E + \underbrace{P \,\mathrm{d}V}_{0} \tag{2.18}$$

where the subscript V indicates volume is being held constant. We can take $P \,\mathrm{d}V = 0$ since V is constant, and $\Delta V \to 0, \mathrm{d}V = 0$. Let us write $E = (V, T)$,

$$\mathrm{d}E = \frac{\partial E}{\partial T} \,\mathrm{d}T + \underbrace{\frac{\partial E}{\partial T}}_{0} \,\mathrm{d}V \,. \tag{2.19}$$

Equating eq. (2.18) to (2.19), we get,

$$\dj Q = C_V \, dT = \frac{\partial E}{\partial T} \, dT \tag{2.20}$$

from which we obtain our final expression,

$$C_V = \frac{\partial E}{\partial T}. \tag{2.21}$$

Heat capacity at constant pressure

Rewriting the first law,

$$\dj Q = C_P \, dT = dE + P \, dV. \tag{2.22}$$

Writing $E = E(T, P)$,

$$dE = \frac{\partial E}{\partial T} \, dT + \underbrace{\frac{\partial E}{\partial P}}_{0} \, dP. \tag{2.23}$$

We can then obtain our final relation,

$$\boxed{C_P = \frac{\partial E}{\partial T} + P\frac{\partial V}{\partial T}} \tag{2.24}$$

Ideal Gas

In an ideal gas, $E = E(T)$, i.e., energy has sole dependence on temperature. Thus,

$$\frac{dE}{dT} = \frac{\partial E}{\partial T} = C_V(T). \tag{2.25}$$

From the ideal gas law,

$$P\frac{\partial V}{\partial T} = nR. \tag{2.26}$$

From which we get the relation,

$$\boxed{C_P(T) = C_V(T) + nR}. \tag{2.27}$$

2.1.6   Adiabatic Processes

For an adiabatic process, there is *no heat transfer*, i.e., $Q = 0$. From the first law and eq. (2.25),

$$dE - \dj W = C_V \, dT - \dj W = 0. \tag{2.28}$$

From the ideal gas equation,

$$T = \frac{PV}{nR} \tag{2.29}$$

whose differential is,

$$dT = \frac{1}{nR} \left(P \, dV + V \, dP \right) \tag{2.30}$$

from which the differential of E follows,

$$dE = \frac{C_V}{nR} \left(P \, dV + V \, dP \right). \tag{2.31}$$

Substituting eq. (2.31) into eq. (2.25) and assuming a reversible process ($\dj W = -P \, dV$), we obtain,

$$\begin{aligned} C_V \, dT + P \, dV = \frac{C_V}{nR}(P \, dV + V \, dP) + P \, dV &= 0 \\ C_V V \, dP + \underbrace{(C_V nR)}_{C_P} P \, dV &= 0 \\ \implies \frac{1}{P} \, dP + \frac{C_P}{C_V}\frac{1}{V} \, dV &= 0. \end{aligned} \tag{2.32}$$
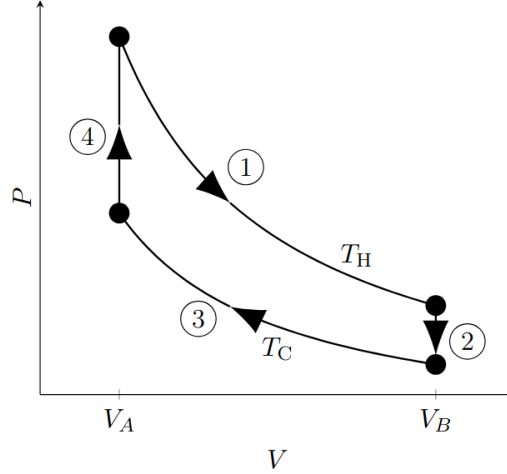
Figure 2.3

If we have that C_P and C_V are constant, let us define,

$$\gamma = \frac{C_P}{C_V} \tag{2.33}$$

which is also constant. We can integrate eq. (2.32) from $(P_1, V_1) \rightarrow (P_2, V_2)$,

$$\int_{P_1}^{P_2} \frac{1}{P} \, dP + \gamma \int_{V_1}^{V_2} \frac{1}{V} \, dV = 0 \implies \ln\left(\frac{P_2 V_2^{\gamma}}{P_1 V_1^{\gamma}}\right) = 0 \tag{2.34}$$

Removing the logarithm from eq. (2.34), we obtain an expression relating the initial and final pressure and volume for an adiabatic process,

$$\boxed{P_2 V_2^{\gamma} = P_1 V_2^{\gamma}} \tag{2.35}$$

and by using the ideal gas law, we can eliminate variables and find expressions involving temperature,

$$\boxed{T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}} \tag{2.36}$$

$$\boxed{T_2 P_2^{\frac{1}{\gamma}-1} = T_1 P_1^{\frac{1}{\gamma}-1}} \tag{2.37}$$

2.2 Second Law of Thermodynamics

Law 2. *The direction of heat flow approaches equilibrium, such that,*

- *Systems at an intermediate temperature reach equilibrium at an intermediate temperature.*

- *Heat naturally flows from hot bodies to cold bodies,*

- *We require an engine to produce work from heat.*

2.2.1 Heat engines

Heat engines produce work from heat. They operate in a cyclic process such that,

$$\Delta E = \oint dE = 0. \tag{2.38}$$

Sterling Engine

The Sterling engine is a piston operating between two heat reservoirs, with a hot reservoir at temperature T_H and a hot reservoir at temperature T_C where $T_C < T_H$ and contains an ideal gas. It works in a cycle such that,

1. *Isothermal expansion*

   - Work done *by* gas,
   $$W_1 = nRT_H \ln\left(\frac{V_B}{V_A}\right) \tag{2.39}$$

   - Heat *absorbed*,
   $$Q_1 = W_1 \tag{2.40}$$

2. *Contact cooling*

   - No work done.
   - Heat *ejected*,
   $$Q_2 = E(T_H) - E(T_C) \tag{2.41}$$

3. *Isothermal compression*

   - Work done *on* gas,
   $$W_3 = nRT_C \ln\left(\frac{V_B}{V_A}\right) \tag{2.42}$$

   - Heat *ejected*
   $$Q_3 = W_3 \tag{2.43}$$

4. *Contact heating*

   - No work done
   - Heat *absorbed*,
   $$Q_4 = E(T_H) - E(T_C) \tag{2.44}$$

This cycle can be visualised on an indicator diagram as in fig. 2.3. Furthermore, this cycle can all be derived from the first law and $\mathrm{d}W = -P\,\mathrm{d}V$.

Let us look at the cycle in more detail. The net work done *by* the gas is,

$$W = W_1 - W_3 = nR(T_H - T_C)\ln\left(\frac{V_B}{V_A}\right). \tag{2.45}$$

The heat absorbed from the reservoir is at T_H is,

$$Q_H = Q_1 + Q_4. \tag{2.46}$$

The heat ejected *to* the hot reservoir is,

$$Q_C = Q_2 + Q_3. \tag{2.47}$$

From the first law,

$$\Delta E = (-W) + (Q_H - Q_C) = 0 \tag{2.48}$$

and therefore,

$$W = Q_H - Q_C = nR\ln\left(\frac{V_B}{V_A}\right)T_H + C_V\Delta T - nR\ln\left(\frac{V_B}{V_A}\right)T_C = nR\ln\left(\frac{V_B}{V_A}\right)\Delta T. \tag{2.49}$$

where $\Delta T = T_H - T_C$. The efficiency of the engine is the ratio of desired output to required input, so,

$$\eta_E = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = \frac{nR\ln\left(\frac{V_B}{V_A}\right)\Delta T}{nR\ln\left(\frac{V_B}{V_A}\right)T_H + C_V\Delta T}. \tag{2.50}$$

A schematic of the heat flow of a Sterling engine is shown in fig. 2.4.

2.2.2   Heat pumps and refrigerators

These are the opposite of engines, they do work on a system to extract heat.
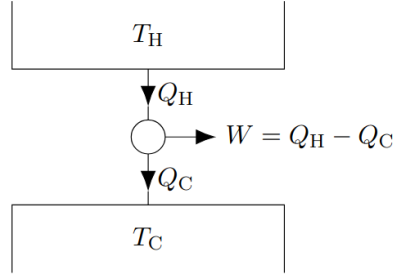
Figure 2.4

Refrigerator

Work is done to extract heat Q_C from a system to lower its temperature T_C. In this case, the efficiency of the system is given as,

$$\eta_R = \frac{Q_C}{Q_H - Q_C}. \tag{2.51}$$

Heat Pump

In a heat pump, we extract heat from a cooler reservoir at T_C to heat a system to T_H. The desired output is Q_H, so,

$$\eta_P = \frac{Q_H}{Q_H - Q_W}. \tag{2.52}$$

If an engine is reversible, then,

$$\eta_P = \frac{1}{\eta_E}. \tag{2.53}$$

2.2.3 Carnot's Cycle

Carnot's theorem states,

Theorem.

1. *A reversible engine is most efficient.*

2. *All reversible engines, operating between two heat baths, have the same efficiency, η_C depending only on T_H and T_C.*

This type of engine can be constructed using the Carnot cycle (whose P-V diagram is shown in fig. 2.5),

1. **Isothermal Expansion** at T_H,

   - $\Delta T = 0, \Delta E = 0$.
   - $\mathrm{d}W = nRT_H \ln\left(\frac{V_B}{V_A}\right)$.

2. **Adiabatic Expansion**

   - $\mathrm{d}Q \implies \mathrm{d}E = \mathrm{d}W$
   - $PV^\gamma = \text{Const.} \implies P \propto V^{-\gamma}$
   - By the ideal gas law, $P = \frac{nRT}{V} \implies \frac{nRT}{V}V^\gamma = \text{Const.} \implies T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1}$.

3. **Isothermal Compression**

   - $Q = nRT_C \ln\left(\frac{V_C}{V_D}\right)$

4. **Adiabatic Compression**

   - $T_H V_A^{\gamma-1} = T_C V_D^{\gamma-1}$.

Figure 2.5

From the cycle above, we find that the ratio,

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} \tag{2.54}$$
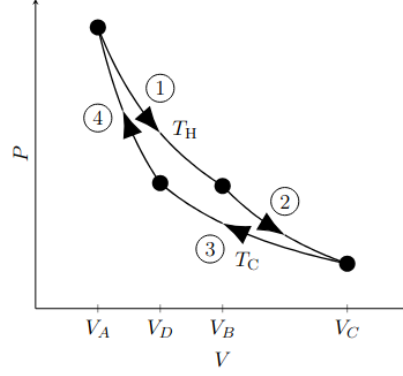
holds. From this, we can write down the efficiency of this engine,

$$\eta_C = \frac{W}{Q_H} = \frac{nRT_H \ln\left(\frac{V_B}{V_A}\right) - nRT_C \ln\left(\frac{V_C}{V_D}\right)}{nRT_H \ln\left(\frac{V_B}{V_A}\right)} = \frac{nRT_H \ln\left(\frac{V_B}{V_A}\right) - nRT_C \ln\left(\frac{V_B}{V_A}\right)}{nRT_H \ln\left(\frac{V_B}{V_A}\right)} \tag{2.55}$$

from which we can write down the final expression for the *Carnot efficiency*,

$$\boxed{\eta_C = 1 - \frac{T_C}{T_H}}. \tag{2.56}$$

Let us note that we find that the Stirling cycle approaches Carnot efficiency for small values of C_V.

2.2.4   Statements of the Second Law

It is difficult to state the second law in a concise, general way through only understanding heat. However, below are two common formulations.

Kelvin-Planck Statement

> It is impossible to construct an engine which, operating in a cycle, produces no effect other than the extraction of heat from the reservoir and the performance of an equivalent amount of work.

Clausius Statement

> It is impossible to construct a refrigerator which, operating in a cycle, produces no effect other than the transfer of heat from a cooler body to a hotter one.

2.3   Entropy

Entropy is encoded into Clausius's inequality, which states that if a system is taken over a cycle, absorbing infinitesimal amounts of heat đQ, from various reservoirs at raving temperatures T, throughout, then

$$\oint \frac{đQ}{T} \leq 0. \tag{2.57}$$
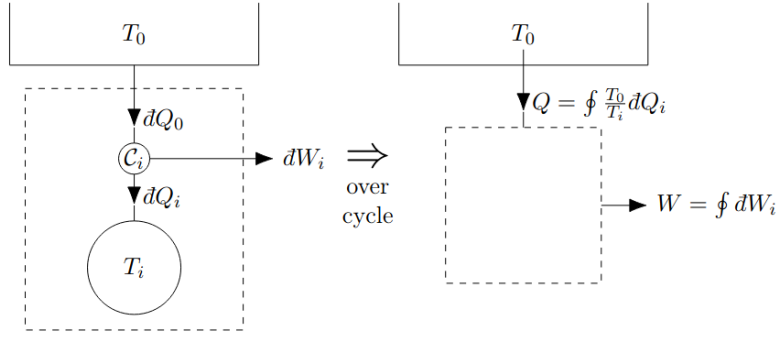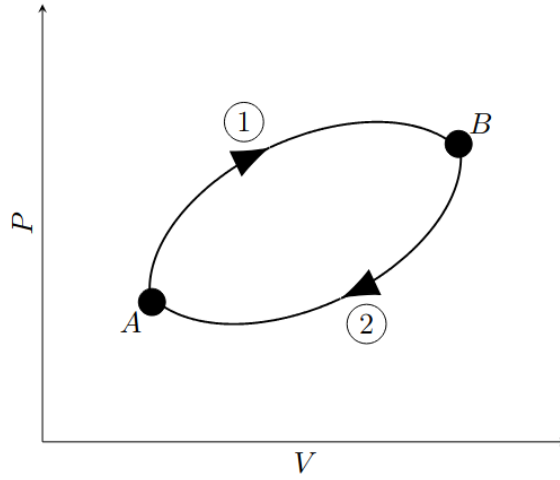
Figure 2.6

Figure 2.7

2.3.1 Proof

Let us consider a cycle as in fig. 2.6. We have that the heat input is,

$$Q_H = \oint \dj Q_H = T_H \oint \frac{\dj Q_i}{T_i} \tag{2.58}$$

and the total work done is,

$$W = \oint \dj W_i. \tag{2.59}$$

The only way for this cycle to be possible is if the work done is 0 or negative. Thus,

$$\oint \dj W_i \leq 0. \tag{2.60}$$

We can write $\oint \dj W_i = \oint \dj Q_i$ and,

$$\oint \frac{\dj Q_i}{T_i} \leq 0. \tag{2.61}$$

2.3.2 Mathematical definition of entropy

We define infinitesimal entropy of a system,

$$\mathrm{d}S = \frac{\dj Q}{T}. \tag{2.62}$$

We only have constant entropy in equilibrium. Let us consider a process like in fig. 2.7. The total

entropy of this system is,

$$\oint \frac{\text{d}Q}{T} = \int_A^B \frac{\text{d}Q}{T} + \int_B^A \frac{\text{d}Q}{T} = 0$$

$$\implies \int_A^B \frac{\text{d}Q}{T} - \int_A^B \frac{\text{d}Q}{T} = 0 \tag{2.63}$$

thus we have shown that entropy is path independent and thus is a function of state. Let us now define entropy further. Let us consider a reference state O as we go from A to B. We have,

$$\int_A^B = \int_A^O \frac{\text{d}Q}{T} + \int_B^A \frac{\text{d}Q}{T}$$

$$= \int_O^B \frac{\text{d}Q}{T} - \int_O^A \frac{\text{d}Q}{T} \tag{2.64}$$

$$= S(B) - S(A).$$

We can then define the entropy,

$$\boxed{S(A) = \int_O^A \frac{\text{d}Q_{\text{rev}}}{T}}. \tag{2.65}$$

NOTE: Entropy is defined in terms of a reversible process.

2.3.3   The law of increase in entropy

Let us now consider a similar scenario to fig. 2.7, but we have an irreversible process as we go from A to B. Applying Clausius' inequality,

$$\int_A^B \frac{\text{d}Q_{\text{irrev}}}{T} + \int_B^A \frac{\text{d}Q_{\text{rev}}}{T} \leq 0$$

$$\int_A^B \frac{\text{d}Q_{\text{irrev}}}{T} \geq \int_A^B \frac{\text{d}Q_{\text{rev}}}{T} \tag{2.66}$$

which gives us our final statement,

$$S(B) - S(A) \geq \int_A^B \frac{\text{d}Q_{\text{irrev}}}{T} \tag{2.67}$$

2.3.4   Thermally Isolated Systems

For thermally isolated systems, it always holds that,

$$S(B) - S(A) \geq 0. \tag{2.68}$$

For a system doing the maximum amount of work, we have that,

$$S(B) - S(A) = 0. \tag{2.69}$$

For a system acting between two finite reservoirs, they will reach a final temperature given by,

$$T_f = \sqrt{T_H T_C}. \tag{2.70}$$

2.3.5   Entropy and Heat Capacity

Entropy can be used to define the heat capacity of for a given constant variable X. This is given by,

$$C_X = T \left(\frac{\partial S}{\partial T} \right)_X \tag{2.71}$$

which, integrating, gives,

$$S(T, X) - S(T_0, X) = \int_{T_0}^T \frac{C_X(T', X)}{T'} \, \text{d}T'. \tag{2.72}$$

2.3.6 Fundamental Relation of Thermodynamics

The fundamental theorem of thermodynamics is a restatement of the second law,

$$\boxed{\mathrm{d}E = T\,\mathrm{d}S + \mathrm{d}W_{\mathrm{rev}}}. \tag{2.73}$$

For an ideal gas, this is,

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V. \tag{2.74}$$

If we think of the second law, and energy being of the form $E \equiv E(S, V)$, we can write,

$$\mathrm{d}E = \left(\frac{\partial E}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial E}{\partial V}\right)_S \mathrm{d}V \tag{2.75}$$

which wen equating coefficients allows us to find,

$$\boxed{T = \left(\frac{\partial E}{\partial S}\right)_V} \qquad\qquad \boxed{P = -\left(\frac{\partial E}{\partial V}\right)_S} \tag{2.76}$$

2.4 Thermodynamic Potentials

From the fundamental relation of thermodynamics, we are able to derive different thermodynamic potentials, which allow us to state whether a reaction can happen spontaneously.

2.4.1 Work Availability

We wish to find the maximum amount of work we can extract from a system initially out of equilibrium with the surroundings. A system like this will always increases its entropy if it can. We have that, for a system with the environment at pressure P_0 and temperature T_0, we have,

$$\begin{aligned}
\Delta S_{\mathrm{tot}} &= \Delta S_{\mathrm{sys}} + \Delta S_{\mathrm{env}} \\
&= \Delta S + \frac{Q}{T_0} \\
&= \Delta S + \frac{-\Delta E - P\,\mathrm{d}V}{T_0} \\
&= \frac{T_0\Delta S - \Delta E - P\,\mathrm{d}V}{T_0} \geq 0
\end{aligned} \tag{2.77}$$

From this we can define the *availability* of a system,

$$-\Delta A = T_0\Delta S - \Delta E - P\,\mathrm{d}V \geq 0, \tag{2.78}$$

for which we have that the entropy of a system increases given that $\Delta A \leq 0$. We can further interpret the availability as the useful work done by a system. We have that,

$$\boxed{W_{\mathrm{useful}} \leq -\Delta A}. \tag{2.79}$$

We can further relate available work to thermodynamic potentials (described in detail in sections below).

- For a process at constant temperature and pressure, the availability is related to the Gibbs free energy,

$$\boxed{W_{\mathrm{useful}} \leq -\Delta G} \tag{2.80}$$

- For a process at constant volume and temperature, the availability is related to the Helmholtz free energy,

$$\boxed{W_{\mathrm{useful}} \leq -\Delta F}. \tag{2.81}$$

2.4.2 Helmholtz Free Energy

We can derive this from the Helmholtz free energy from the fundamental relation of thermodynamics,

$$
\begin{aligned}
\mathrm{d}E &= T\,\mathrm{d}S - P\,\mathrm{d}V \\
&= T\,\mathrm{d}S + S\,\mathrm{d}T - S\,\mathrm{d}T - P\,\mathrm{d}V \\
&= \mathrm{d}(TS) - S\,\mathrm{d}T - P\,\mathrm{d}V \\
\implies \underbrace{\mathrm{d}E - TS}_{\mathrm{d}F} &= \underbrace{-S\,\mathrm{d}T - P\,\mathrm{d}V}_{\mathrm{d}T=0,\mathrm{d}V=0}
\end{aligned}
\tag{2.82}
$$

From this we can define the Helmholtz free energy,

$$
\boxed{F(T,V) = E - TS}.
\tag{2.83}
$$

Which holds for constant T and V. We can further consider the expansion of $\mathrm{d}F$,

$$
\mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial F}{\partial V}\right)_T \mathrm{d}V
\tag{2.84}
$$

and equating coefficients,

$$
S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad\qquad P = -\left(\frac{\partial F}{\partial V}\right)_T.
\tag{2.85}
$$

We then have that,

$$
\mathrm{d}F \leq 0
\tag{2.86}
$$

where equality holds for equilibrium, and spontaneous change for $\mathrm{d}F < 0$.

2.4.3 Gibbs Free Energy

We derive the Gibbs free energy from the Helmholtz free energy. We have,

$$
\begin{aligned}
\mathrm{d}F = \mathrm{d}(E - TS) &= -S\,\mathrm{d}T - P\,\mathrm{d}V \\
&= -S\,\mathrm{d}T - p\,\mathrm{d}V - v\,\mathrm{d}P + V\,\mathrm{d}P \\
&= -S\,\mathrm{d}T - \mathrm{d}(PV) + V\,\mathrm{d}P = \mathrm{d}(E - TS) \\
\implies \underbrace{\mathrm{d}(E - TS + PV)}_{\mathrm{d}G} &= -S\,\mathrm{d}T + V\,\mathrm{d}P
\end{aligned}
\tag{2.87}
$$

The Gibbs free energy is then,

$$
\boxed{G(T,P) = E - TS + PV}.
\tag{2.88}
$$

The Gibbs free energy tells us about the non-reversible work in the system. Expanding $\mathrm{d}(E - TS + PV)$,

$$
\begin{aligned}
\mathrm{d}E - \cancel{S\,\mathrm{d}T}^{\,0} - T\,\mathrm{d}S + P\,\mathrm{d}V + \cancel{V\,\mathrm{d}P}^{\,0} &= -\cancel{S\,\mathrm{d}T}^{\,0} + \cancel{V\,\mathrm{d}P}^{\,0} \\
\implies \underbrace{\mathrm{d}E - T\,\mathrm{d}S}_{\mathrm{d}W_{\mathrm{rev}}} + \underbrace{P\,\mathrm{d}V}_{\mathrm{d}W_{\mathrm{vol}}} &= \mathrm{d}W_{\mathrm{other}}
\end{aligned}
\tag{2.89}
$$

2.4.4 Enthalpy

Enthalpy is derived from the Gibbs free energy. We consider enthalpy at constant entropy and pressure. Furthermore, for a system at constant pressure, the enthalpy is interpreted as the heat released during the process. The derivation is shown below,

$$
\begin{aligned}
\mathrm{d}(E - TS + PV) &= -S\,\mathrm{d}T + V\,\mathrm{d}P \\
&= -S\,\mathrm{d}T - T\,\mathrm{d}S + T\,\mathrm{d}S + V\,\mathrm{d}P \\
&= -\mathrm{d}(TS) + T\,\mathrm{d}S + V\,\mathrm{d}P \\
\implies \mathrm{d}(E + PV) &= T\,\mathrm{d}S + V\,\mathrm{d}P
\end{aligned}
\tag{2.90}
$$

we then define the enthalpy H,

$$H = E + PV \tag{2.91}$$

where we have,

$$\boxed{\mathrm{d}H = T\,\mathrm{d}S\,V\,\mathrm{d}P} \tag{2.92}$$

and the relations,

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad\qquad \left(\frac{\partial H}{\partial P}\right)_S = V. \tag{2.93}$$

We can further define the Gibbs free energy in terms of enthalpy,

$$\mathrm{d}G = \mathrm{d}H - T\,\mathrm{d}S \tag{2.94}$$

where we require $\mathrm{d}G \leq 0$ for spontaneous change.

2.4.5 Interpretation of Thermodynamic Potentials

Internal Energy

For thermally isolated systems, $(Q = 0)$,

$$\begin{aligned} \Delta A &= \Delta E + P_0\Delta V = 0 \\ \Longrightarrow \Delta E &= -P_0\Delta V. \end{aligned} \tag{2.95}$$

Entropy

For thermally isolated systems at fixed volume,

$$\Delta A = -T_0\Delta S \tag{2.96}$$

thus,

$$(\Delta S)_{E,V} \geq 0 \tag{2.97}$$

for spontaneous change. I.e., entropy must be maximised.

Helmholtz Free Energy

For a system that starts and ends at the same temperature, with constant volume,

$$\Delta A = \Delta(E - T_0 S) = \Delta F \tag{2.98}$$

so,

$$(\Delta F)_{T,V} \leq 0 \tag{2.99}$$

for spontaneous change.

Gibbs Free Energy

If the system starts and ends at the same pressure and temperature, the availability becomes,

$$\Delta A = \Delta(E - T_0 S + P_0 V) = \Delta G \tag{2.100}$$

thus for spontaneous change,

$$(\Delta G)_{T,P} \leq 0 \tag{2.101}$$

and for equilibrium, we minimise the Gibbs free energy.

Enthalpy

For a system at constant pressure, the work done is $P_0\Delta V$. From the first law,

$$\Delta E = Q - P_0\Delta V. \tag{2.102}$$

The change in enthalpy is,

$$\Delta H = \Delta E + P_0\Delta V \tag{2.103}$$

and we therefore have,

$$(\Delta H)_P = Q \tag{2.104}$$

so the change in enthalpy is the heat released during a process.

2.4.6   Maxwell Relations

The Maxwell relations are given below, with proof given for the first below,

$$\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S \tag{2.105}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{2.106}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{2.107}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{2.108}$$

We will show the proof for eq. (2.105), but the proofs for all other relations follow similarly.

Proof.

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V = \left(\frac{\partial E}{\partial S}\right)\mathrm{d}S + \left(\frac{\partial E}{\partial V}\right)_S \mathrm{d}V$$

$$T = (\frac{\partial E}{\partial S})_V \qquad\qquad\qquad P = -\left(\frac{\partial E}{\partial V}\right)_S$$

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

$$\implies \left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$$

$\square$

2.5   Phase Transitions

In order to consider phase transitions, we must consider *open systems*, i.e., systems where the number of particles can change. We can then write the internal energy to account for open systems,

$$E = TS - PV + \mu N \tag{2.109}$$

where μ is the chemical potential. We can then write the FTR,

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}N\,. \tag{2.110}$$

We can visualise phase transitions on a P-T diagram, as in figure 2.8,

2.5.1   Phase Transition Conditions

For a substance to transition from one state to another, it must be possible for the two states to be in equilibrium. Considering a total isolated systems composed of two systems in two different states,

$$S(E,V,N) = S_1(E_1,V_1,N_1) + S_2(E_2,V_2,N_2) \tag{2.111}$$

Considering $\mathrm{d}S$ for each part of the system, we obtain the differentials,

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{V_1,N_1} = \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2,N_2} \tag{2.112}$$

$$\left(\frac{\partial S_1}{\partial V_1}\right)_{E_1,N_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2,N_2} \tag{2.113}$$

$$\left(\frac{\partial S_1}{\partial N_1}\right)_{E_1,V_1} = \left(\frac{\partial S_2}{\partial N_2}\right)_{E_2,V_2} \tag{2.114}$$
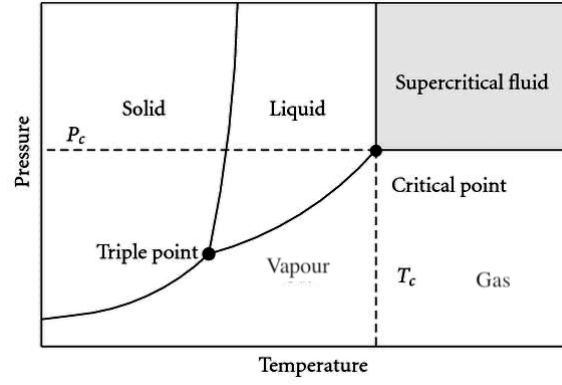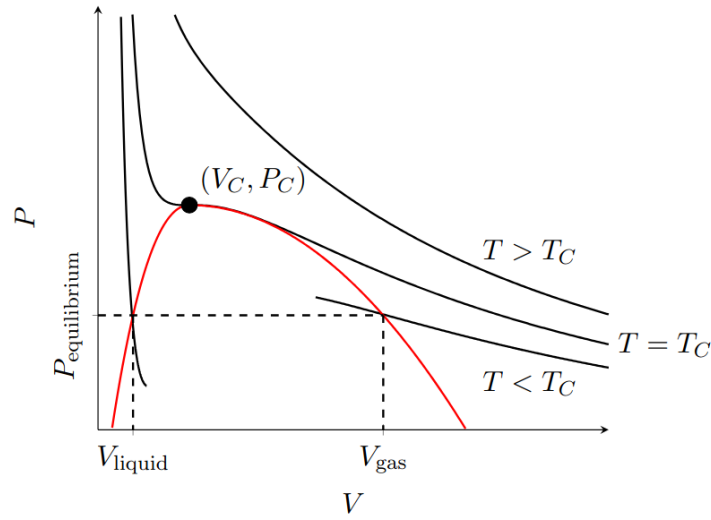
Figure 2.8

Figure 2.9

These lead to the conditions for phase equilibrium,

- $T_1 = T_2$, no heat flow between systems.

- $P_1 = P_2$, the systems are at mechanical equilibrium.

- $\mu_1 = \mu_2$, there is no preference to be in one state over another.

2.5.2   Clausius-Clapeyron Relation

If we approximate the interface line between two states as being linear, such that we go from points $(T, P) \rightarrow (T + \delta T, P + \delta P)$, we can write the Clausius-Clapeyron relation as,

$$\frac{\delta P}{\delta T} = \frac{\Delta H}{T \Delta \mathcal{V}} \tag{2.115}$$

where $\mathcal{V}$ is the molar volume, and ΔH is the molar change in enthalpy, often written as L, and referred to as the latent heat.

2.5.3   Liquid Gas-Transition

We wish to analyse the liquid-gas transition more carefully. With the liquid-gas coexistence line ending at the critical point, we can infer that it is possible we can reach the gas phase from the liquid phase
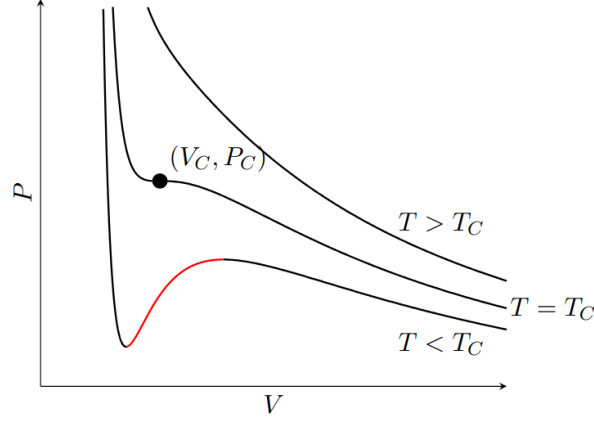
Figure 2.10

without a phase transition. Thus, we could describe both liquid and gas with the same equation of state. If we inspect the $P - V$ diagram in figure 2.9, we see that at there is a saddle point at the critical point,

$$\left(\frac{\partial P}{\partial V}\right)_{T_C} = 0 \qquad\qquad\qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = 0 \qquad\qquad (2.116)$$

Below the critical point, we see there is a region where we have unstable states, known as supercooled or superheated states.

2.5.4   Real Gasses

In order to describe the liquid phase, we must take into account interactions between molecules. This is encoded in the van der Walls equation,

$$\boxed{\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = RT}. \qquad\qquad (2.117)$$

The Van der Walls equation reduces to the ideal gas equation when $V > nb$, where in turn $V >> \sqrt{a/P}$. If we apply eq. (2.116) to the Van der Wall's equation, we obtain the critical values for a fluid at the critical point,

$$V_c = 3b, \qquad\qquad T_C = \frac{8a}{27Rb}, \qquad\qquad P_c = \frac{a}{27b^2} \qquad\qquad (2.118)$$

If we analyse the isotherms produces by the Van der Wall's equation, as in figure 2.10, we find that instability occurs due to positive gradients on the PV diagram.

Chapter 3

Kinetic Theory of Gasses

3.1 Probability Distributions

Given a probability distribution $p(\mathbf{v})$,

$$P = \int p(\mathbf{v}) \mathrm{d}^3 v \tag{3.1}$$

is the probability of a particle having a velocity vector $\mathbf{v}$ between $\mathbf{v}$ and $\mathbf{v} + \mathrm{d}^3 v$, i.e., that the particle's velocity will be found in a box of dimensions $\mathrm{d}v_x \, \mathrm{d}v_y \, \mathrm{d}v_z$. Below are listed some properties of probability distributions,

- $p(\mathbf{v}) \geq 0 \; \forall \mathbf{v}$.

- The distribution is normalised, $\int_{-\infty}^{\infty} p(\mathbf{v}) \mathrm{d}^3 v = 1$.

- For independent, uncorrelated variables,

$$p(\mathbf{v}) = p(v_x) p(v_y) p(v_z) \tag{3.2}$$

- The mean value of a quantity described by $f(\mathbf{v})$ is given by,

$$\langle f \rangle = \int f(\mathbf{v}) p(\mathbf{v}) \mathrm{d}^3 v. \tag{3.3}$$

- The variance is given by,

$$\sigma^2(f) = \left\langle f^2 \right\rangle - \langle f \rangle^2 . \tag{3.4}$$

3.1.1 Gaussian Integrals

Gaussian integrals of the mth order have the form,

$$I_m = \int_{-\infty}^{\infty} x^m e^{-ax^2} \, \mathrm{d}x \tag{3.5}$$

for $a > 0$. We can relate even Gaussian integrals by,

$$I_{2n} = \frac{\mathrm{d}^n}{\mathrm{d}a^n} I_0. \tag{3.6}$$

3.2 The Boltzmann Factor

For a fixed number of particles in thermal equilibrium at temperature T,

$$\boxed{p(\text{state}) \propto \exp\left(-\frac{E(\text{state})}{k_B T} \right)} \tag{3.7}$$

- As $T \to \infty$, all states have equal probability

- As $T \to 9$, lowest energy states have higher probability.

If we wish to use this probability distribution, we must first normalise it, such that,

$$p(\mathrm{s}) = \frac{1}{Z} \exp\left(-\frac{E(\mathrm{s})}{k_B T}\right) \tag{3.8}$$

where the normalisation constant is,

$$Z = \int_{\text{all states}} \exp\left(-\frac{E(\mathrm{s})}{k_B T}\right) \mathrm{d}s \tag{3.9}$$

3.2.1   Example: Isothermal Atmosphere

If we consider a planet that has an atmosphere consisting of a gas of non-interacting molecules with mass m, temperature T, with an acceleration due to gravity g at a height y above the planet's surface, we can describe the probability of finding a particle at a height y using the Boltzmann factor. A single particle will be subject to a potential mgy, so its probability distribution will be,

$$p(y) = \frac{1}{Z} \exp\left(-\frac{mgy}{k_B T}\right) \tag{3.10}$$

which is normalised by,

$$Z = \int_0^\infty \exp\left(-\frac{mgy}{k_B T}\right) \mathrm{d}y = \frac{k_B T}{mg}. \tag{3.11}$$

We understand that an atmosphere is made up of more than 1 molecule of gas. For non-interacting molecules, we can say that the density of the gas is proportional to its probability density, $\rho(y) \propto p(y)$, such that,

$$\rho(y) = \rho_0 \exp\left(-\frac{mgy}{k_B T}\right). \tag{3.12}$$

If we consider pressure due to the weight of the particles, for an incremental increase in height $\mathrm{d}y$, the change in pressure is given by $\mathrm{d}P = -\rho g\, \mathrm{d}y$. We can then write,

$$\begin{aligned}
P(y) &= \int_\infty^y -\mathrm{d}P = -g\rho_0 \int_{-\infty}^y \exp\left(-\frac{mgy}{k_B T}\right) \\
&= \frac{k_B T}{m} \rho_0 \exp\left(-\frac{mgy}{k_B T}\right) = \frac{k_B T}{m} \rho(y).
\end{aligned} \tag{3.13}$$

If we consider $\frac{\rho}{m} = \frac{N}{V}$ where N is the number of molecules, we get

$$PV = N k_B T \tag{3.14}$$

which is the ideal gas law.

3.2.2   Equation of State of an Ideal Gas

Let us find the equation of an ideal gas more generally using the velocity distribution of an ideal, homogeneous, isotropic gas in a cubic container. Particles in a gas have velocities,

$$\mathbf{v} = (\dot{x}, \dot{y}, \dot{z}) \tag{3.15}$$

and kinetic energy,

$$K = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right). \tag{3.16}$$

The velocity distribution is going to be given by $p(\mathbf{v}) = p(\dot{x})p(\dot{y})p(\dot{z})$. Inserting $\dot{x}$ into the Boltzmann distribution,

$$p(\dot{x}) = \frac{1}{Z} \exp\left(\frac{\frac{1}{2} m \dot{x}^2}{k_B T}\right). \tag{3.17}$$
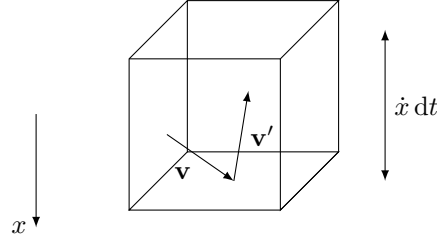
Figure 3.1: Incoming particle undergoes an elastic collision with one surface of the box.

Normalising this integral,

$$Z = \int_{-\infty}^{\infty} \exp\left(\frac{\frac{1}{2}m\dot{x}^2}{k_B T}\right) dx$$
$$= \left(\frac{2\pi K_b T}{m}\right)^{\frac{1}{2}} \tag{3.18}$$

which we evaluate by a standard solution to the 0th order Gaussian integral. The probability distribution is then,

$$p(\dot{x}) = \left(\frac{m}{2\pi K_b T}\right)^{\frac{1}{2}} \exp\left(\frac{\frac{1}{2}m\dot{x}^2}{k_B T}\right). \tag{3.19}$$

Following similar steps for $\dot{y}$ and $\dot{z}$, the probability distribution is given by,

$$p(\mathbf{v}) = \left(\frac{m}{2\pi K_b T}\right)^{\frac{1}{2}} \exp\left(\frac{\frac{1}{2}mv^2}{k_B T}\right). \tag{3.20}$$

If we evaluate the average velocity for each component, we find that,

$$\langle \dot{x} \rangle = \langle \dot{y} \rangle = \langle \dot{z} \rangle = 0 \tag{3.21}$$

which is expected, as given that the gas is homogeneous and isotropic, we expect the particles to move in all directions equally.

Pressure in container

Consider an elastic collision with one surface of area A of the box in a small time dt as in figure 3.1. The volume from which the particles collide is $\dot{x} A \, dt$. Given the number density $n = N/V$, the total number of particles colliding with the surface in a time dt is,

$$N_{\text{col}} = n\dot{x} A \, dt. \tag{3.22}$$

Each collision transfers $2m\dot{x}$ of momentum to the surface due to elastic collisions. The average momentum transfer in a time dt is given by,

$$d\bar{p}_m = nA \, dt \, 2m \langle \dot{x}^2 \rangle$$
$$= 2mnA \, dt \int_0^{\infty} \dot{x}^2 p(\dot{x}) \, d\dot{x}. \tag{3.23}$$
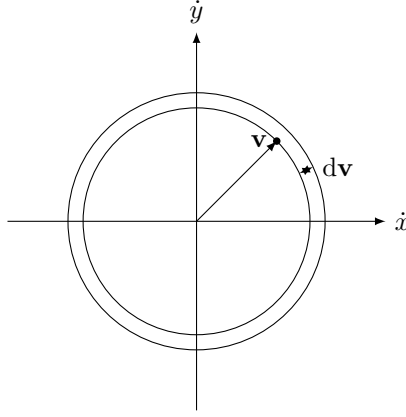
The force on the surface is,

$$F = \frac{d\bar{p}_m}{dt} = 2mnA \int_0^{\infty} \dot{x}^2 p(\dot{x}) \, d\dot{x}. \tag{3.24}$$

The total pressure is then,

$$P = \frac{F}{A} = 2mn \left(\frac{m}{2\pi K_b T}\right)^{\frac{1}{2}} \int_0^{\infty} \dot{x}^2 \exp\left(\frac{\frac{1}{2}m\dot{x}^2}{k_B T}\right) d\dot{x}$$
$$= 2mn \left(\frac{m}{2\pi K_b T}\right)^{\frac{1}{2}} \frac{1}{4} \left(\frac{\pi(2k_B T)^3}{m^3}\right) \tag{3.25}$$
$$= nk_B T = \frac{N}{V} k_B T \implies \boxed{PV = Nk_B T}$$

and thus we have derived the ideal gas law from statistical considerations.

Figure 3.2: Sphere in velocity space at $\dot{z} = 0$.

3.2.3   Internal Energy of an Ideal Gas

In an ideal gas, the only energy that exists is kinetic energy. So, the mean energy is given by,

$$
\begin{aligned}
\langle E \rangle &= N \int \frac{1}{2} m v^2 p(\mathbf{v}) \mathrm{d}^3 v \\
&= \frac{1}{2} N m \left(\frac{m}{2\pi k_B T} \right) \int v^2 \exp\left(-\frac{m v^2}{2 k_b T} \right) \mathrm{d}^3 v.
\end{aligned}
\tag{3.26}
$$

This integral is difficult to perform. Let us consider the velocity of a particle in velocity space. Particles of velocity $\mathbf{v}$ all have equal probability, and form a sphere in velocity space. If we consider a thin shell of this sphere, we find,

$$
\mathrm{d}^3 v = 4\pi v^2 \, \mathrm{d}v .
\tag{3.27}
$$

which allows us to more readily evaluate the integral,

$$
\begin{aligned}
\langle E \rangle &= 2\pi N m \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty v^4 \exp\left(-\frac{m v^2}{2 k_B T} \right) \mathrm{d}v \\
&= \pi N m \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \frac{3}{4} \left(\frac{\pi}{\left(\frac{m}{2} k_B T \right)^5} \right)^{\frac{1}{2}} \\
&= \frac{3}{2} N k_B T.
\end{aligned}
\tag{3.28}
$$

Considering the average energy per particle, we obtain,

$$
\frac{\langle E \rangle}{N} = 3 \cdot \frac{1}{2} k_B T.
\tag{3.29}
$$

3.3   Maxwell-Boltzmann Speed Distribution

In order to find the speed distribution, we must consider a spherical shell of thickness $\mathrm{d}v$ in velocity space. We want to find the probability has a speed between v and $v + \mathrm{d}v$,

$$
\int p(v) \, \mathrm{d}v = \int 4\pi v^2 p(\mathbf{v}) \, \mathrm{d}v .
\tag{3.30}
$$

By observation, we can conclude that the distribution of molecular speeds is given by,

$$
\boxed{ p(v) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{\frac{3}{2}} v^2 \exp\left(-\frac{m v^2}{2 k_B T} \right) }
\tag{3.31}
$$

which is the Maxwell-Boltzmann speed distribution. From this we can obtain several different values,
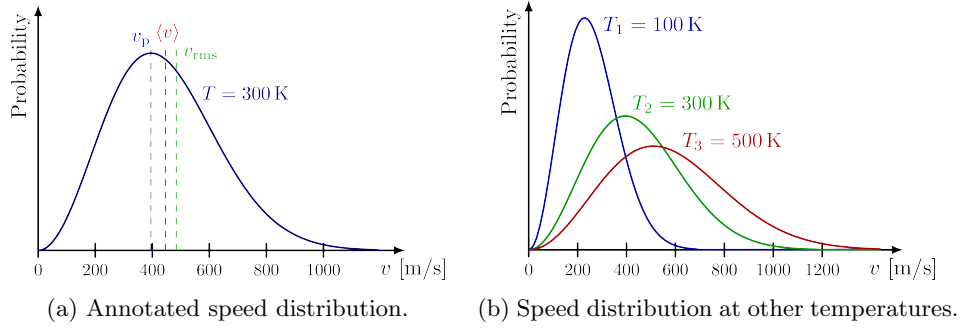
(a) Annotated speed distribution.

(b) Speed distribution at other temperatures.

Figure 3.3

which are visualised in figure 3.3a,

$$v_p = \sqrt{\frac{2k_BT}{m}} \qquad \langle v \rangle = \int_0^\infty v p(v)\,\mathrm{d}v = \sqrt{\frac{8k_BT}{\pi m}} \qquad v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_BT}{m}} \tag{3.32}$$

The shape of the distribution changes with temperature, as in figure 3.3b.

3.4 Equipartition Theorem

Theorem. *The average energy due to each degree of freedom that contributes quadratically to the total energy of a classical system in thermal equilibrium at some temperature T is $\frac{1}{2}k_BT$ per particle.*

For monatomic molecules, there are only translational degrees of freedom, i.e., 3 translational degrees of freedom. If we go through with the equipartition theorem,

$$\frac{\langle E \rangle}{N} = 3 \times \frac{1}{2}k_BT = \frac{3}{2}k_BT \tag{3.33}$$

which agrees with (3.29).

3.4.1 Diatomic Molecules

If we consider a diatomic molecule composed of identical atoms with some bond between them of an effective spring constant k and relative distance Δ as in figure 3.4, we can separate the degrees of freedom into three categories and 3 different energies,

1. 3 translational degrees of freedom, $E_T = \frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right)$.

2. 2 rotational degrees of freedom, $E_{\mathrm{rot}} = \frac{1}{2}I_1\dot{\theta}_1^2 + \frac{1}{2}I_2\dot{\theta}_2^2$.

3. 2 vibrational degrees of freedom, $E_{\mathrm{vib}} = \frac{1}{2}m\dot{\Delta}^2 + \frac{1}{2}k\Delta^2$.

Let us note that the equipartition theorem only applies to classical systems, i.e., when $k_BT >> \Delta E$ where ΔE is the separation between discrete energy levels. Furthermore, at lower temperatures, certain degrees of freedom do not contribute to the internal energy. These are,

$$\text{Vibrational} \qquad\qquad \text{Rotational} \qquad\qquad\qquad \text{Translational} \tag{3.34}$$

$$k_BT \sim \Delta E_{\mathrm{vib}} \simeq \hbar\omega \qquad k_BT \sim \Delta E_{\mathrm{rot}} \simeq \frac{\hbar^2}{I} \qquad k_BT \sim \Delta E_{\mathrm{trans}} \simeq \frac{\hbar^2}{mV^{\frac{2}{3}}} \tag{3.35}$$
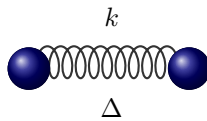

Figure 3.4: Diatomic molecule of two molecules separated by a relative distance Δ, connected by a bond of effective spring constant k.

Chapter 4

Transport Properties of Gasses

It can be shown that the relative speed between particles in a gas is given by,

$$\langle v_r \rangle = \sqrt{2} \langle v \rangle \tag{4.1}$$

which underpins all topics on the discussion of transport properties.

4.1 Mean Collision Time and Mean Free Path

Consider molecule 1 moving at velocity v_r in the rest frame of molecule 2. We can define their collision cross-section as,

$$\sigma = \pi (2r_m)^2 \tag{4.2}$$

where r_m is the radius of the molecule. Let us consider the area the molecule sweeps out in a time $\mathrm{d}t$ as $\sigma v_r \, \mathrm{d}t$. If molecule is present in a cylinder of this volume, a collision will occur. The probability of a collision occurring is then,

$$P = \frac{N}{V} \sigma v_r \, \mathrm{d}t \,. \tag{4.3}$$

Let us define the survival probability distribution $p_s(t)$ as the probability of molecule 1 "surviving" for time t with no collision. The probability of a collision between t and $t + \mathrm{d}t$ is,

$$\mathrm{d}p_s = p_s \cdot \frac{N}{V} \sigma v_r \, \mathrm{d}t \,. \tag{4.4}$$

This can be rearranged and solved trivially,

$$\boxed{p_s = \exp\left(-\frac{N}{V} \sigma v_r \, \mathrm{d}t\right) = \exp\left(\frac{t}{\tau}\right)} \tag{4.5}$$

where τ is the *mean collision time*,

$$\boxed{\tau = \frac{1}{\frac{N}{V} \sigma v_r} = \frac{1}{\frac{N}{V} \sigma \langle v \rangle}} \,. \tag{4.6}$$

We can then define the *mean free path* as the mean distance between collisions,

$$\boxed{\lambda = \tau \langle v \rangle = \frac{1}{\sqrt{2} \frac{N}{V} \sigma}} \,. \tag{4.7}$$

4.2 Effusion

Effusion is the rate of change of escape of gas molecules through a small hole in a container. Assume the hole has an area $\mathrm{d}S$ with radius $<< \lambda$ so that collisions at the vicinity of the hole do not have to be considered. The mean number of collisions per unit time is given by,

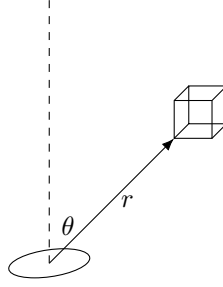$$\frac{1}{\tau} = \frac{\langle v \rangle}{\lambda} \,. \tag{4.8}$$

Figure 4.1: A small hole of area dS a distance r away from a small volume of gas dV.

In a small, arbitrary volume, there are $\frac{N}{V} dV$ molecules. The number of molecules scattered randomly out of dV per unit time is,

$$\frac{N}{V} \langle v \rangle \frac{dV}{\lambda}. \tag{4.9}$$

If we consider that this volume is a distance r away from the hole at an angle θ as in figure 4.1, we find that the fraction of molecules scattered from dV to dS is,

$$\frac{dS \cos \theta}{4\pi r^2}. \tag{4.10}$$

The probability that a molecule will reach dS without collision is $\exp\left(-\frac{r}{\lambda}\right)$. The number of molecules from dV reaching dS per unit time is then given by,

$$\frac{N}{V} \langle v \rangle \frac{dV}{\lambda} \frac{dS \cos \theta}{4\pi r^2} \exp\left(-\frac{r}{\lambda}\right). \tag{4.11}$$

Integrating this expression over all space will allow us to obtain the number of molecules leaving through dS per unit time,

$$\frac{N}{V} \langle v \rangle dS \int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} \sin \theta \cos \theta \, d\theta \int_0^{\infty} \exp\left(-\frac{r}{\lambda}\right) dr$$
$$= \frac{N}{V} \frac{\langle v \rangle \, dS}{4\pi \lambda} \frac{2\pi \lambda}{2} = \frac{N}{V} \langle v \rangle \frac{dS}{4}. \tag{4.12}$$

We can then obtain a flux through the hole (molecules leaving per unit time),

$$\boxed{\Phi = \frac{1}{4} \frac{N}{V} \langle v \rangle}. \tag{4.13}$$

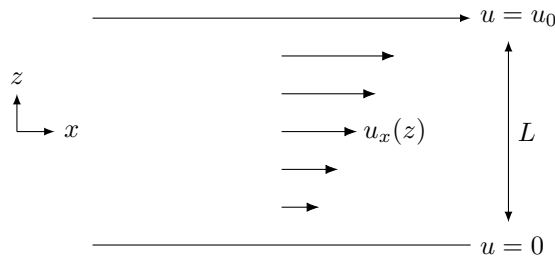The rate at which molecules pass through the area is $A\Phi$.

Figure 4.2: Gas between two plates, the top plate moving at a velocity u_0 and the bottom plate stationary.
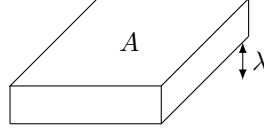
Figure 4.3: Slice of gas of thickness $\lambda << L$, with top and bottom surface area A.

4.3   Viscosity

Consider a gas between two plates as in figure 4.2. The gas exerts a stress on the top plate,

$$F_{xz} = -\eta \frac{\partial u_x}{\partial z} \tag{4.14}$$

where F_{zx} is the rate of change of momentum per unit area. Let us consider a thin slice of the gas of volume $A\lambda$ as in figure 4.3. By simple averaging, we assume that $\frac{1}{6}$ of the molecules are moving in any given direction. Thus, the average number of molecules moving through the top surface of area A is given by,

$$\frac{1}{6}\left(\frac{N}{V}\right) A\lambda. \tag{4.15}$$

The number of molecules passing through the volume per unit time per unit area is,

$$\frac{1}{6}\left(\frac{N}{V}\right) A\lambda \frac{1}{A} \frac{\langle v \rangle}{\lambda} = \frac{1}{6} \frac{N}{V} \langle v \rangle. \tag{4.16}$$

The additional momentum gained per molecule is given by,

$$m\delta u_x = m \frac{\partial u_x}{\partial z} \lambda, \tag{4.17}$$

which also applies to molecules moving through the bottom area, so we multiply by a factor of 2. We can then write the stress on the top plate as,

$$F_{xz} = -2 \frac{1}{6}\left(\frac{N}{V}\right) \langle v \rangle\, m\lambda \frac{\partial u_x}{\partial z} \implies \boxed{\eta = \frac{1}{3} \frac{N}{V} m \langle v \rangle}. \tag{4.18}$$

Some notes on viscosity,

- We can rewrite viscosity as

$$\eta = \frac{1}{3\sqrt{2}} \frac{\langle v \rangle\, m}{\sigma} \tag{4.19}$$

  by eq. (4.7).

- Thus, η is independent of pressure, which holds under the conditions $\sqrt{\sigma} << \lambda << L$.

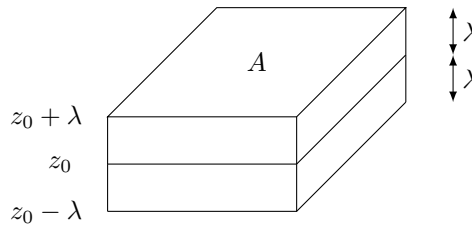- $\eta \propto \langle v \rangle \propto \sqrt{T}$.

Figure 4.4: Thin slice of gas of volume $2\lambda A$ centered on the z_0 plane.

4.4 Transport of Energy (Thermal Conductivity)

We will assume position dependent temperature, i.e., $T \equiv T(\mathbf{r})$. Heat flows along a temperature gradient, thus we can define the heat flux as,

$$\mathbf{q} = -\kappa \boldsymbol{\nabla} \mathbf{T}. \tag{4.20}$$

where κ is the conductivity. If we approximate our heat flow as begin 1 dimensional, we can write,

$$q = -\kappa \frac{\partial T}{\partial z}. \tag{4.21}$$

Let us consider a slice of gas at the z_0 plane, with thickness $A\lambda$ above and below as in figure 4.4. $\frac{1}{6}$ of the molecules move up through the z_0 plane from the bottom layer, and $\frac{1}{6}$ move down from the bottom layer. It takes the molecules $\frac{1}{\tau}$ time to move through the layer, and their mean energy is $\langle E(z) \rangle$. Thus, the average energy flux across the z_0 plane is given by,

$$q_z = \frac{1}{6} \left(\frac{N}{V} \right) A\lambda \cdot \frac{\langle v \rangle}{\tau} \cdot \frac{1}{A} \left(\langle E(z_0 - \lambda) \rangle - \langle E(z_0 + \lambda) \rangle \right). \tag{4.22}$$

Recall that $\mathrm{d}E = C_V \, \mathrm{d}T$. If we consider the expansion,

$$\mathrm{d}E = \frac{\partial E}{\partial z} \, \mathrm{d}z \implies \Delta E = \frac{\partial E}{\partial z} \Delta z \tag{4.23}$$

and then consider,

$$\Delta E = \langle E(z_0 + \lambda) \rangle - \langle E(z_0 - \lambda) \rangle = 2\lambda \frac{\partial E}{\partial z} = 2\lambda c_v \frac{\partial T}{\partial z} \tag{4.24}$$

where we obtain the final expression by the heat capacity relation. We then obtain our final relation for heat flow,

$$q_z = -\frac{1}{6} \left(\frac{N}{V} \right) \langle v \rangle \cdot 2\lambda C_V \frac{\partial T}{\partial z} \tag{4.25}$$

and by observation, we obtain our final expression for thermal conductivity,

$$\kappa = \frac{1}{3} \left(\frac{N}{V} \right) \langle v \rangle \lambda C_V. \tag{4.26}$$

By substituting eq. (4.7), we find that κ is independent of pressure and $\kappa \propto \sqrt{T}$ for $\sqrt{\sigma} << \lambda << L$.

4.5 Self-Diffusion

Consider a mass of "labelled" molecules of gas at constant pressure, (i.e., air freshener sprayed into air). At constant pressure, the molecules undergo random motion, so there is a net flux from high to low concentration. The flux of molecules is,

$$\mathbf{J} = -D\boldsymbol{\nabla} n \tag{4.27}$$

where n is the number density of the labelled molecules, and D is the diffusion coefficient with units $\left[\mathrm{m}^2 \, \mathrm{t}^{-1} \right]$. Let us consider the number density to be position dependent in 1 dimension $n \equiv n(z)$ to reduce eq. (4.27) to $J = -D\frac{\partial n}{\partial z}$. Consider a slice of the gas as in figure 4.4. The mean flux of of molecules through the z_0 plane is,

$$\begin{aligned} J_z &= \frac{1}{6} \langle v \rangle \left(n(z_0 - \lambda) - n(z_0 + \lambda) \right) \\ &= \frac{1}{6} \langle v \rangle \left(-2\lambda \frac{\partial n}{\partial z} \right). \end{aligned} \tag{4.28}$$

Therefore, we can write the diffusivity as,

$$\boxed{D = \frac{\langle v \rangle \lambda}{3}} \qquad \qquad \boxed{D = \frac{\langle v \rangle}{3\sqrt{2} \left(\frac{N}{V} \right) \sigma}} \tag{4.29}$$

We find that D has pressure dependence as $\frac{N}{V} \propto P \implies D \propto P^{-1}$, as well as temperature dependence $\langle v \rangle \propto \sqrt{T}, \frac{N}{V} \propto T \implies D \propto T^{\frac{3}{2}}$.

Appendix A

Definitions

Isothermal Process: Happens at constant temperature, $\Delta E = 0$ for an ideal gas.

Isobaric Process: Happens at constant pressure.

Isochoric Process: Happens at constant volume $\implies \text{d}W = 0$.

Adiabatic Process: Happens with no heat flow $\implies đQ = 0$.

Heat Capacity: Relates heat flow to temperature change $đQ = C\,\text{d}T$.

For an ideal gas at constant volume, the change in energy $\text{d}E$ is always given by,

$$\text{d}E = C_V\,\text{d}T \qquad\qquad (A.1)$$