Thermal Physics

and

Statistical Mechanics

Lecture Notes

PHY294 · University of Toronto

Compiled April 18, 2026

Preface

I, Amir Koutahi, wrote these notes as my personal study notes for the second half of PHY294 (Thermal Physics) at the University of Toronto, taught by Professor R. J. Dwayne Miller. His faculty profile is available at `chemistry.utoronto.ca/people/directories/all-faculty/dwayne-miller`.

The text aims to capture the full theoretical content of the course, but it necessarily misses the spirit of the many memorable in-class demonstrations Prof. Miller used to bring the material to life – those are best appreciated in person.

Professor Miller's lectures sparked in me the idea of pursuing independent further study in statistical mechanics, and these notes have been structured with that continuation in mind: the final part is set up so that future material – on Bose/Fermi statistics, ensembles beyond the canonical one, and applications in condensed matter and biophysics – can be slotted in naturally.

Because these are working study notes written by a student, there are almost certainly typos and minor errors in both the prose and the equations. If you spot any, I would be very happy to hear about them and fix them. Please email me at `amir.koutahi@mail.utoronto.ca`.

– Amir Koutahi

Contents

Part I

Thermal Physics

CHAPTER 1

PHY294 Lecture Notes

These notes follow the Spring 2025 lecture sequence of PHY294 (Thermal Physics). Each section corresponds to a single class meeting; a brief topic descriptor is given alongside the lecture date to make navigation easier. A consistent convention is used throughout: the Boltzmann constant is written k_B, sample averages with angle brackets $\langle \cdot \rangle$, and definitions / theorems / key results are displayed in coloured callout boxes.

1.1 Lecture 1 – Foundations: Kinetic Theory of the Ideal Gas

Feb 26

Thermal Physics: Scope and Motivation

Thermal physics studies systems containing extremely large numbers of particles, typically of the order of 10^{23} particles (about one mole of matter). The objective is to understand how the microscopic motion of atoms and molecules gives rise to macroscopic properties such as pressure, temperature, and entropy.

Thermal physics therefore connects two levels of description:

- **Microscopic physics** – motion and interactions of individual particles.
- **Macroscopic physics** – observable quantities such as pressure, temperature, and volume.

Key Idea

Thermal physics explains how simple macroscopic laws arise from the collective behaviour of enormous numbers of particles.

Two Complementary Descriptions

Thermal physics is built from two major theoretical frameworks.

Thermodynamics

Thermodynamics is a macroscopic theory describing matter using measurable variables such as

1. P – pressure
2. V – volume
3. T – temperature
4. N – number of particles
5. S – entropy

Thermodynamics does not require knowledge of individual particles.

Statistical Mechanics

Statistical mechanics explains thermodynamics using microscopic particle states.

Definition

A **microstate** is a complete specification of the microscopic configuration of a system, including positions, momenta, and quantum states of all particles.

Macroscopic properties arise from averages over extremely many possible microstates.

Thermal Equilibrium

A system is in **thermal equilibrium** when its macroscopic properties no longer change with time.

Definition

Two systems are in thermal equilibrium if no net heat flows between them when they are placed in contact.

Zeroth Law of Thermodynamics

Theorem – Zeroth Law

If system A is in thermal equilibrium with system C, and system B is in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other.

This law establishes temperature as a measurable physical quantity.

Ideal Gas as a Model System

To understand thermal physics quantitatively, we introduce the **ideal gas model**.

Key Idea

The ideal gas serves as the simplest physical system for connecting microscopic particle motion with macroscopic thermodynamic laws.

The ideal gas assumes:

- particles are point-like;
- particles move randomly;
- collisions are perfectly elastic;
- interactions between particles are negligible.

Empirical Gas Laws

Boyle's Law

At constant temperature,

$$P \propto \frac{1}{V} \qquad \text{or} \qquad PV = \text{constant}.$$

Pressure is inversely proportional to volume.

Charles's Law

For a gas,

$$V \propto T \qquad \text{or} \qquad \frac{V}{T} = \text{constant}.$$

This relation leads to the definition of the **absolute temperature scale**.

Absolute Zero

Extrapolation of gas laws suggests a fundamental lower temperature limit

$$T = 0\,\mathrm{K} = -273.15^\circ\mathrm{C}.$$

At absolute zero, thermal motion would vanish in the classical description.

Ideal Gas Law

Combining the empirical gas laws yields the ideal gas equation.

Theorem – Ideal Gas Law

$$PV = nRT \qquad \text{or equivalently} \qquad PV = Nk_BT,$$

where N is the number of particles and k_B is the Boltzmann constant.

$$k_B = 1.38 \times 10^{-23}\,\mathrm{J/K}, \qquad R = 8.314\,\mathrm{J/(mol \cdot K)}.$$

Kinetic Theory of Gases

The kinetic theory derives macroscopic pressure from microscopic particle motion.

Consider a cubic box with side length L and volume $V = L^3$. Particles move randomly inside the container.

Collision with a Wall

Consider one particle of mass m moving with velocity component v_x. During an elastic collision with the wall,

$$v_x \longrightarrow -v_x.$$

The momentum change is therefore

$$\Delta p_x = 2mv_x.$$

The time between successive collisions with the same wall is

$$\Delta t = \frac{2L}{v_x}.$$

Hence the average force on the wall is

$$F = \frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}.$$

Pressure from Many Particles

For N particles, pressure equals total force divided by area:

$$P = \frac{\sum_i F_i}{A}.$$

Using $A = L^2$ and $V = L^3$,

$$P = \frac{Nm\langle v_x^2\rangle}{V}.$$

Because the motion is isotropic,

$$\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle, \qquad v^2 = v_x^2 + v_y^2 + v_z^2,$$

which implies $\langle v_x^2\rangle = \frac{1}{3}\langle v^2\rangle$. Substituting,

$$PV = \tfrac{1}{3}Nm\langle v^2\rangle.$$

Temperature and Kinetic Energy

The average kinetic energy per particle is

$$E_K = \tfrac{1}{2}m\langle v^2\rangle,$$

so the pressure relation becomes

$$P = \frac{2N}{3V}E_K.$$

Comparing with the ideal gas law $P = Nk_BT/V$,

$$\frac{Nk_BT}{V} = \frac{2N}{3V}E_K \qquad \Longrightarrow \qquad E_K = \tfrac{3}{2}k_BT.$$

Key Idea

Temperature is proportional to the average kinetic energy of particles in a gas.

Physical Interpretation

The kinetic theory shows that thermodynamic laws arise from microscopic particle motion. Macroscopic quantities such as pressure and temperature are statistical properties of extremely large numbers of particles:

$$\text{microscopic motion} \Longrightarrow \text{macroscopic thermodynamics.}$$

1.2 Lecture 2 – Degrees of Freedom and Equipartition

Feb 27

Changing the Energy of a Thermodynamic System

A thermodynamic system is described by four macroscopic variables

$$T, \quad P, \quad V, \quad N.$$

These variables are interrelated. For an ideal gas,

$$PV = Nk_BT.$$

Temperature can be interpreted microscopically as a measure of the average translational kinetic energy of particles,

$$T = \frac{2}{3}\frac{E_K}{k_B}.$$

Equivalently, temperature describes how energy is distributed across the available types of motion.

Total Thermal Energy

At thermal equilibrium a system possesses **thermal energy** stored in different ways depending on the types of motion available to its particles.

Definition

A **degree of freedom** is an independent way in which energy can be stored or exchanged within a physical system.

Translational Degrees of Freedom

A particle moving in three-dimensional space can translate along three independent axes; therefore a monatomic particle has three translational degrees of freedom,

$$E = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2.$$

Each coordinate direction contributes one independent kinetic energy term.

Key Idea

A monatomic gas has 3 translational degrees of freedom.

Rotational Degrees of Freedom

Molecules can also rotate about axes through their centre of mass. For a diatomic molecule there are three possible rotational axes, but the axis along the bond has a vanishingly small moment of inertia and is not excited at ordinary temperatures. Only two rotational modes contribute,

$$E_{\text{rot}} = \tfrac{1}{2}I_y\omega_y^2 + \tfrac{1}{2}I_z\omega_z^2.$$

Key Idea

A diatomic molecule has 2 rotational degrees of freedom.

Vibrational Degrees of Freedom

Vibrational motion occurs when atoms oscillate relative to one another. A simple model is a mass on a spring with spring constant k,

$$E = \tfrac{1}{2}mv^2 + \tfrac{1}{2}kx^2.$$

For a diatomic molecule the vibration occurs along the bond, giving one vibrational degree of freedom,

$$E_{\text{vib}} = \tfrac{1}{2}k\,(r_1 - r_2)^2.$$

Energy Modes of a Diatomic Molecule

The total internal energy is

$$U = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}},$$

with $d_t = 3$, $d_r = 2$, $d_v = 1$ giving $d = 6$ total energy modes.

Equipartition Theorem

Theorem – Equipartition

For a classical system in thermal equilibrium at temperature T, energy is shared equally among all quadratic degrees of freedom, with each contributing $\frac{1}{2}k_BT$ to the average energy.

Average energy contributions:

$$\text{translational mode} = \tfrac{1}{2}k_BT, \qquad \text{rotational mode} = \tfrac{1}{2}k_BT, \qquad \text{vibrational mode} = k_BT.$$

The vibrational mode contributes twice as much because it has both a kinetic and a potential quadratic term.

Key Idea

Each quadratic energy term contributes $\frac{1}{2}k_BT$ to the average energy.

Total Thermal Energy

For a system of N molecules the total thermal energy is

$$U = N\Big(d_t\tfrac{1}{2}k_BT + d_r\tfrac{1}{2}k_BT + d_vk_BT\Big),$$

where d_t, d_r, d_v are the translational, rotational, and vibrational degrees of freedom.

Example: Water Molecule

A water molecule (H_2O) is a non-linear triatomic molecule. The total number of degrees of freedom for an n-atom molecule is $3n$. For non-linear molecules,

$$d_t = 3, \quad d_r = 3, \quad d_v = 3n - 6.$$

For water ($n = 3$), $d_v = 3(3) - 6 = 3$, so water has 3 translational, 3 rotational, and 3 vibrational degrees of freedom.

Example: Carbon Dioxide

Carbon dioxide (CO_2) is a linear molecule, for which

$$d_t = 3, \quad d_r = 2, \quad d_v = 3n - 5.$$

Degrees of Freedom for n-Atomic Molecules

For a molecule with n atoms:

- **Non-linear molecules:** $d = 3 + 3 + (3n - 6)$.
- **Linear molecules:** $d = 3 + 2 + (3n - 5)$.

Heat Transfer Mechanisms

Thermal energy can move between systems through three mechanisms:

- **Conduction** – energy transfer through microscopic collisions.
- **Convection** – energy transfer through bulk fluid motion.
- **Radiation** – energy transfer through electromagnetic waves.

Heat increases atomic and molecular motion and can be converted into mechanical work or vice versa.

Key Idea

Thermodynamics studies how energy moves between a system and its surroundings.

1.3 Lecture 3 – First Law and Thermodynamic Processes

Mar 2

Heat

Heat is **thermal energy in transit**: the spontaneous transfer of energy between systems caused by a temperature difference.

Definition

Heat is energy that flows from a higher-temperature system to a lower-temperature system.

An object does **not** contain heat intrinsically; heat exists only during the transfer process. If two systems with temperatures $T_1 > T_2$ are placed in contact, energy flows until thermal equilibrium is reached.

Work

Energy transfer that is **not** caused by a temperature difference is called work.

Definition

Work is energy transfer produced by an external agent acting on the system. A typical example is compression or expansion of a gas using a piston.

First Law of Thermodynamics

Energy conservation for thermodynamic systems gives:

Theorem – First Law of Thermodynamics

$$\Delta U = Q + W,$$

where U is the internal energy, Q is heat transferred *to* the system, and W is work done *on* the system.

For differential changes,

$$dU = \delta Q - P\,dV.$$

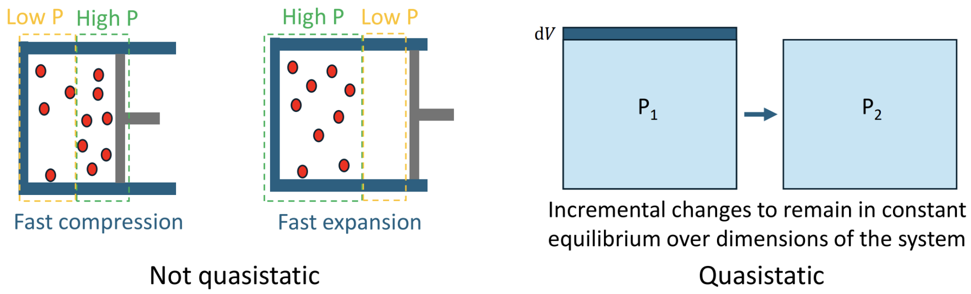
The term $P\,dV$ is the mechanical work during a volume change.

Quasistatic Processes

Definition

A **quasistatic process** occurs infinitely slowly so that the system remains in thermodynamic equilibrium at every stage.

Because the system stays near equilibrium, thermodynamic variables such as P, V, and T are well defined at each step.



Quasistatic compression in a cylinder.

Work in a Quasistatic Compression or Expansion

For a quasistatic process the work done on a gas is

$$W = -\sum_i P_i\,\Delta V_i \xrightarrow{\Delta V \to 0} W = -\int_{V_i}^{V_f} P(V,T)\,dV.$$

Isothermal Processes

Definition

An **isothermal process** occurs at constant temperature.

For an ideal gas $P = Nk_BT/V$, so

$$W = -\int_{V_i}^{V_f} \frac{Nk_BT}{V}\,dV = -Nk_BT\ln\left(\frac{V_f}{V_i}\right).$$

Key Idea

Work done on an isothermal ideal gas:

$$W = -Nk_BT\ln\left(\frac{V_f}{V_i}\right).$$

Since T is constant the internal energy does not change, $\Delta U = 0$, and the first law gives $Q = -W$. Thus:

- Expansion ⇒ heat absorbed.
- Compression ⇒ heat released.

Adiabatic Processes

Definition

An **adiabatic process** occurs with no heat exchange, $\delta Q = 0$.

Energy changes occur only through work, and the first law becomes

$$dU = -P\,dV.$$

Adiabatic processes typically occur in thermally insulated systems.

Internal Energy of an Ideal Gas

For an ideal gas with f quadratic degrees of freedom,

$$U = \tfrac{f}{2}\,Nk_BT, \qquad dU = \tfrac{f}{2}\,Nk_B\,dT.$$

Substituting into the first law gives

$$\tfrac{f}{2}\,Nk_B\,dT = -P\,dV.$$

Using the Ideal Gas Law

From $PV = Nk_BT$, differentiation yields $P\,dV + V\,dP = Nk_B\,dT$, so

$$\tfrac{f}{2}(P\,dV + V\,dP) = -P\,dV,$$

which simplifies to

$$V\,dP = -\left(1 + \frac{2}{f}\right) P\,dV.$$

Adiabatic Relation

Dividing by PV and using $d(\ln x) = dx/x$,

$$d\ln P + \left(1 + \frac{2}{f}\right) d\ln V = 0 \implies P\,V^{1+2/f} = \text{constant}.$$

With the adiabatic index $\gamma = (2+f)/f$,

$$PV^{\gamma} = \text{constant}.$$

Key Idea

Adiabatic process relation:

$$PV^{\gamma} = \text{constant}.$$

Adiabatic vs. Isothermal Paths

In a P–V diagram:

- Isothermal: $P \propto 1/V$.
- Adiabatic: $P \propto 1/V^{1+2/f}$.

Adiabatic curves are steeper because temperature changes during the process.

Common Thermodynamic Processes

Process	**Condition**
Isothermal	$T = \text{constant}$
Adiabatic	$\delta Q = 0$
Isobaric	$P = \text{constant}$
Isochoric	$V = \text{constant}$

1.4 Lecture 4 – Heat Capacity, Latent Heat, and Enthalpy

Mar 5

Heat Capacity

Heat capacity measures how much heat is required to change the temperature of a system.

Definition

$$C = \frac{Q}{\Delta T},$$

where Q is heat added and ΔT is the resulting temperature change.

Useful normalisations:

$$\text{per particle: } \frac{C}{N}, \qquad \text{per unit mass: } \frac{C}{m}.$$

Heat Capacity at Constant Volume and Pressure

Two experimental conditions are common.

Constant volume (C_V)

The gas is confined to a rigid container, so $W = 0$ and

$$C_V = \frac{Q}{\Delta T} = \left.\frac{\partial U}{\partial T}\right|_V .$$

Constant pressure (C_P)

The gas expands as it is heated, performing work $W = -P\Delta V$, so

$$C_P = \left.\frac{\partial U}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P .$$

Key Idea

Because some heat goes into expansion work, $C_P > C_V$.

Heat Capacity of Ideal Gases

For an ideal gas $U = \frac{f}{2}Nk_BT$, so

$$C_V = \frac{f}{2}\,Nk_B, \qquad \frac{C_V}{N} = \frac{f}{2}\,k_B.$$

Examples:

$$\text{monatomic: } f = 3 \;\Rightarrow\; C_V = \frac{3}{2}\,Nk_B, \qquad \text{diatomic: } f = 7 \;\Rightarrow\; C_V = \frac{7}{2}\,Nk_B.$$

For constant pressure

$$\frac{C_P}{N} = \left(\frac{f}{2} + 1\right) k_B, \qquad C_P = C_V + Nk_B.$$

Latent Heat

During a phase transition, energy added to the system does not change its temperature.

Definition

Latent heat is the heat required to convert a substance from one phase to another at constant temperature.

At a phase transition $\Delta T = 0$, so $C \to \infty$. Instead we define the latent heat per unit mass

$$L = \frac{Q}{m}.$$

Example: water boiling has $L_{\text{vap}} \approx 2260\,\text{J/g}$. Phase changes require large energies because intermolecular forces must be overcome.

Enthalpy

Internal energy U describes microscopic energy within the system but does not include the work required to create space for it in the environment. To include this effect we define enthalpy.

Definition

$$H = U + PV.$$

The PV term represents the energy needed to push the atmosphere aside as the system expands.

Enthalpy at Constant Pressure

Using the first law $dU = \delta Q - P\,dV$, $\delta Q = dU + P\,dV$. Since $H = U + PV$, $dH = dU + P\,dV$ at constant pressure. Therefore

Key Idea

At constant pressure, $\Delta H = Q$.

Heat measured in constant-pressure experiments directly gives the enthalpy change.

Heat Capacity and Enthalpy

For constant-pressure processes

$$C_P = \left.\frac{\partial H}{\partial T}\right|_P,$$

so C_P describes how enthalpy changes with temperature.

Hess's Law

Theorem – Hess's Law

The total enthalpy change of a reaction equals the sum of the enthalpy changes of the individual steps.

If a reaction occurs through multiple steps,

$$\Delta H = \sum_i \Delta H_i.$$

This follows because enthalpy is a **state function** that depends only on the initial and final states.

Standard Enthalpy of Formation

Tables of thermodynamic data list standard enthalpies of formation ΔH_f° for substances at $P = 1\,\mathrm{atm}$, $T = 298\,\mathrm{K}$. These values allow direct calculation of reaction enthalpies.

Example: Combustion of Methane

$$\mathrm{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O}$$

Standard enthalpies of formation:

$$\Delta H_f^\circ(\mathrm{CH_4}) = -74.8\,\mathrm{kJ/mol}, \quad \Delta H_f^\circ(\mathrm{CO_2}) = -393.5\,\mathrm{kJ/mol},$$

$$\Delta H_f^\circ(\mathrm{H_2O}(g)) = -241.8\,\mathrm{kJ/mol}, \quad \Delta H_f^\circ(\mathrm{O_2}) = 0.$$

By Hess's law,

$$\Delta H_{\mathrm{rxn}} = [(-393.5) + 2(-241.8)] - [(-74.8) + 2(0)] = -802.3\,\mathrm{kJ/mol}.$$

If the water condenses to liquid, additional energy is released and $\Delta H_{\mathrm{rxn}} \approx -890.4\,\mathrm{kJ/mol}$. Accounting for compression work gives $\approx -885.4\,\mathrm{kJ/mol}$.

Phase Transitions and Energy Storage

Large amounts of energy can be stored in intermolecular forces and released during phase transitions. For example, dry ice sublimes according to

$$\mathrm{CO_2}(s) \rightarrow \mathrm{CO_2}(g), \qquad \Delta H_{\mathrm{sub}} = 26.1\,\mathrm{kJ/mol},$$

at $T = -78.5°\mathrm{C}$.

Key Idea

Phase transitions convert stored molecular energy into macroscopic work and motion.

1.5 Lecture 5 – Microstates, Multiplicity, and the Einstein Solid Mar 6

Two-State Systems

A two-state system is one in which each particle can exist in one of two possible states. The simplest example is a flip of a coin.

Assumptions:

- Heads and tails are equally probable.
- Each flip is independent of the others.

For three coins there are $2^3 = 8$ possible outcomes (microstates):

$$HHH,\ HHT,\ HTH,\ THH,\ HTT,\ THT,\ TTH,\ TTT.$$

Microstates and Macrostates

Definition

A **microstate** is a specific microscopic configuration of a system, e.g. HTH.

Definition

A **macrostate** is defined by macroscopic quantities and may correspond to many microstates, e.g. "2 heads".

The number of microstates corresponding to a macrostate is called the *multiplicity*.

Definition

The **multiplicity** Ω is the number of microstates corresponding to a given macrostate.

For three coins:

Macrostate	Ω
$3H$	1
$2H$	3
$1H$	3
$0H$	1

Multiplicity of a Two-State System

For a system of N atoms with n excited atoms, the multiplicity is the number of ways to choose which n of the N atoms are excited:

$$\Omega(n) = \binom{N}{n} = \frac{N!}{n!\,(N-n)!}.$$

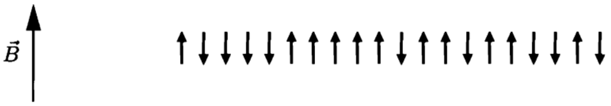
The total number of microstates is 2^N.

Paramagnet as a Two-State System

A paramagnet consists of magnetic dipoles in an external magnetic field. Each dipole points in one of two directions:

- parallel to the field (lower energy);
- anti-parallel to the field (higher energy).

Let $N_\uparrow$ and $N_\downarrow$ be the numbers of up and down dipoles, with $N = N_\uparrow + N_\downarrow$. The total energy depends only on the number of dipoles aligned with or against the field.



Two-state paramagnet in an external magnetic field $\mathbf{B}$.

Multiplicity and Probability

For a macrostate with multiplicity Ω, $P(\text{microstate}) = 1/\Omega$ assuming all microstates are equally probable.

Key Idea

Fundamental assumption of statistical mechanics: all accessible microstates of an isolated system in equilibrium are equally probable.

Einstein Model of a Solid

A solid can be modelled as a collection of N independent quantum harmonic oscillators. Each oscillator can store discrete quanta of energy,

$$E = \left(q + \tfrac{1}{2}\right) \hbar\omega,$$

where q is the number of quanta and $\omega = \sqrt{k/m}$. Energy levels are equally spaced.

Energy Quanta Distribution

For N oscillators sharing q quanta, the macrostate is defined by the total energy q. A microstate specifies how the quanta are distributed:

$$(q_1, q_2, q_3) = (2, 0, 0) \quad \text{or} \quad (1, 1, 0),$$

both correspond to the same macrostate.

Example: Three Oscillators with Three Quanta

For $N = 3$, $q = 3$, the microstates are

$$(3,0,0),\ (0,3,0),\ (0,0,3),$$

$$(2,1,0),\ (2,0,1),\ (1,2,0),\ (1,0,2),\ (0,2,1),\ (0,1,2),$$

$$(1,1,1),$$

giving $\Omega = 10$.

Multiplicity of an Einstein Solid

The multiplicity for q quanta distributed among N oscillators is

$$\Omega(N,q) = \frac{(q+N-1)!}{q!\,(N-1)!}.$$

Each microstate has probability $P = 1/\Omega(N,q)$.

Two Einstein Solids in Thermal Contact

Consider two solids $A(N_A, q_A)$ and $B(N_B, q_B)$ with conserved total energy $q = q_A + q_B$.

When the solids come into thermal contact they exchange energy until equilibrium is reached.

Assumptions:

- weak coupling between the two solids;
- energy exchange inside each solid is much faster than between them.

At equilibrium the system reaches the macrostate with the **largest total multiplicity**.

Key Idea

Thermodynamic equilibrium corresponds to the most probable macrostate (maximum multiplicity).

1.6 Lecture 6 – Multiplicity in Large Systems

Mar 9

Multiplicity Functions & Large Systems

- **Multiplicity function:** models the occupation of specific states or conditions of a system (e.g. how many molecules have a given energy, how many coins are heads).
- **Ideal gas:** particles that interact only through elastic collisions; multiplicity counts position–momentum microstates.
- **Einstein solid:** crystalline solid of N atoms acting as independent oscillators; multiplicity counts the distribution of energy quanta.
- **Debye solid:** crystalline solid of N atoms interacting via quantised sound waves (phonons); multiplicity counts phonon distributions.

Large systems contain extremely large numbers of particles, $N \sim 10^{23}$.

Definition

For very large N we use Stirling's approximation

$$N! \approx N^N e^{-N}\sqrt{2\pi N}, \qquad \ln N! \approx N\ln N - N.$$

Large Einstein Solid: Compact Derivation

Starting from

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!\,(N-1)!} \approx \frac{(q+N)!}{q!\,N!},$$

take the logarithm

$$\ln\Omega \approx (q+N)\ln(q+N) - q\ln q - N\ln N.$$

For $q \gg N$, $\ln(q+N) \approx \ln q + N/q$, so

$$\ln\Omega \approx (q+N)\left(\ln q + \tfrac{N}{q}\right) - q\ln q - N\ln N \approx N\ln\left(\tfrac{q}{N}\right) + N + \tfrac{N^2}{q} \xrightarrow{q\gg N} N\ln\left(\tfrac{q}{N}\right) + N.$$

Hence

$$\boxed{\Omega(N,q) \;\approx\; \left(\frac{e\,q}{N}\right)^N}.$$

Two Einstein Solids

For two identical solids of N oscillators each,

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N.$$

Writing $q_A = q/2 + x$, $q_B = q/2 - x$,

$$q_A q_B = (q/2)^2 - x^2 \implies \Omega = \left(\frac{e}{N}\right)^{2N} \left[(q/2)^2 - x^2\right]^N.$$

Taking the logarithm and expanding for small x,

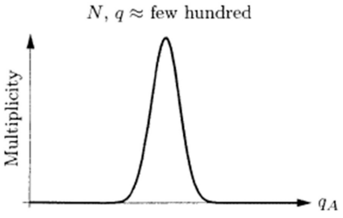
$$\ln\Omega = N\Big[\ln(q/2)^2 + \ln\Big(1-\tfrac{4x^2}{q^2}\Big)\Big] \approx N\Big[\ln(q/2)^2 - \Big(\tfrac{2x}{q}\Big)^2\Big].$$

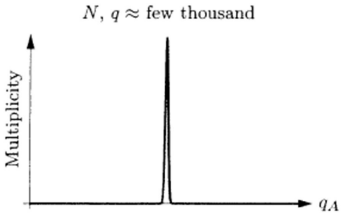
Therefore

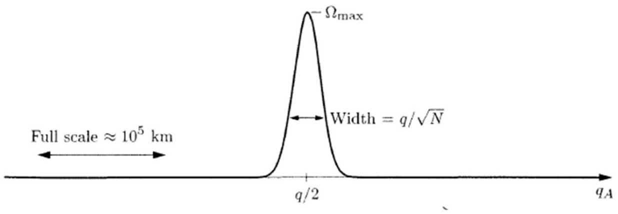
$$\boxed{\Omega = \Omega_{\max}\exp\Big[-N\Big(\tfrac{2x}{q}\Big)^2\Big]}, \qquad \text{Width} \sim \frac{q}{\sqrt{N}}.$$

The distribution narrows like $1/\sqrt{N}$ as N increases.

For large N, any random fluctuation away from the most likely microstate will be *utterly unmissable!*







Gaussian Distributions in Physics

When all microstates are equally probable, macroscopic variables often follow Gaussian distributions. This appears in many physical systems including molecular spectra (e.g. vibrational linewidths of water, where line broadening reflects a distribution of molecular configurations).

Multiplicity of a Two-State Paramagnet

For a paramagnet with N spins of which $N_\downarrow$ are down,

$$\Omega = \binom{N}{N_\downarrow} = \frac{N!}{N_\downarrow!(N-N_\downarrow)!}.$$

Using Stirling's approximation $n! \approx (n/e)^n$,

$$\Omega \approx \frac{(N/e)^N}{(N_\downarrow/e)^{N_\downarrow}((N-N_\downarrow)/e)^{N-N_\downarrow}} = \frac{N^N}{N_\downarrow^{N_\downarrow}(N-N_\downarrow)^{N-N_\downarrow}}.$$

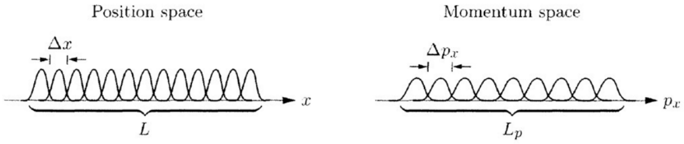
$$\ln\Omega \approx N\ln N - N_\downarrow \ln N_\downarrow - (N-N_\downarrow)\ln(N-N_\downarrow).$$

For $N_\downarrow \ll N$,

$$\ln\Omega \approx N_\downarrow \ln\left(\frac{N}{N_\downarrow}\right) + N_\downarrow, \qquad \Omega \approx \left(\frac{Ne}{N_\downarrow}\right)^{N_\downarrow}.$$

Multiplicity of a 1D Ideal Gas

Consider a particle confined to a line of length L.



One-dimensional phase space for a confined particle.

The uncertainty principle gives $\Delta x\,\Delta p_x \gtrsim h$, so

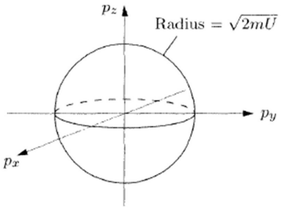
$$N_x = \frac{L}{\Delta x}, \qquad N_p = \frac{p_x}{\Delta p_x}, \qquad \Omega \approx \frac{L\,p_x}{h}.$$

Multiplicity of a 3D Ideal Gas

In three dimensions

$$\Omega \sim \frac{V_{\text{space}}\,V_{\text{momentum}}}{h^3}, \qquad V_{\text{space}} = XYZ.$$

Using kinetic energy $U = (p_x^2 + p_y^2 + p_z^2)/(2m)$, the momentum states lie on a sphere of radius $\sqrt{2mU}$:



Momentum-space sphere for a single particle.

so

$$V_{\text{momentum}} = \tfrac{4}{3}\pi(2mU)^{3/2}, \qquad \Omega = \frac{V \cdot \frac{4}{3}\pi(2mU)^{3/2}}{h^3}.$$

Two Molecules in an Ideal Gas

For two distinguishable molecules,

$$U = \frac{1}{2m}\left(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2 + p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2\right),$$

and momentum space becomes a hypersphere in six dimensions:

$$\Omega \sim \frac{V_{\text{space}}^2\,V_{\text{momentum}}}{h^6}.$$

For indistinguishable particles we must divide by 2!.

Multiplicity of an Ideal Gas with N Particles

Generalising,

$$\Omega_N(U, V) = f(N)\, V^N\, U^{3N/2},$$

where $f(N)$ depends only on N.

Two Interacting Ideal Gases

For two gases exchanging energy,

$$\Omega_{\text{total}} = f(N)^2\, V_A^N V_B^N\, U_A^{3N/2} U_B^{3N/2},$$

with peak width

$$\text{width} \sim \frac{U_A + U_B}{3N/2}.$$

For macroscopic N this width is vanishingly small.

Key Idea

Macroscopic systems remain extremely close to their equilibrium energy distribution.

1.7 Lecture 7 – Entropy and the Second Law

Mar 12

Entropy and Multiplicity

Energy in a system rearranges over time. Systems evolve toward configurations with higher multiplicity Ω. When a barrier between two systems is removed,

$$q_{\text{total}} = \text{constant}, \qquad \Omega_{\text{total}} = \Omega_1\Omega_2.$$

As energy redistributes, the number of accessible microstates increases dramatically.

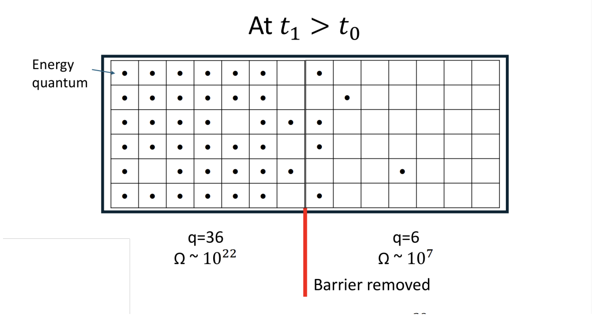
Einstein Solid

Multiplicity:

$$\Omega(N,q) = \frac{(q+N-1)!}{q!\,(N-1)!}.$$

Using Stirling's approximation $\ln N! \approx N\ln N - N$,

$$\ln\Omega = \ln\frac{(q+N-1)!}{q!\,(N-1)!}.$$

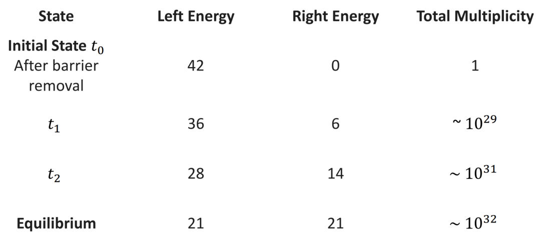


Worked example: 42 oscillators in each box, 42 quanta total.

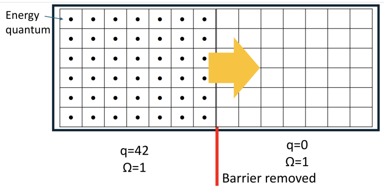
$$\ln\Omega = (77\ln 77 - 77) - (36\ln 36 - 36) - (41\ln 41 - 41) \approx 53.21,$$
$$\Omega \sim 10^{22}\text{–}10^{23}.$$

Time Evolution Toward Equilibrium

Energy distribution evolves toward the maximum-multiplicity configuration:



State	Left Energy	Right Energy	Total Multiplicity
Initial State t_0 After barrier removal	42	0	1
t_1	36	6	~ 10^{29}
t_2	28	14	~ 10^{31}
Equilibrium	21	21	~ 10^{32}



Higher multiplicity ⇒ higher probability. The equilibrium state is overwhelmingly more likely than any individual non-equilibrium state – in this example, roughly 2,700× more likely. Even with only 42 oscillators per box and 42 quanta, the numbers become astronomical. To make these numbers manageable, we work with the logarithm of Ω, i.e. the entropy.

Definition of Entropy

Key Idea

$$S = k_B \ln \Omega.$$

Key properties:

1. The total entropy of a composite system is the sum of the entropies of its parts. For our two-box example,
$$S_{\text{total}} = k_B \ln(\Omega_1 \Omega_2) = S_1 + S_2.$$
2. The logarithmic scaling makes very large systems easier to manage.

Second Law of Thermodynamics

Equivalent statements:

- Heat flows from hot to cold.
- A system in equilibrium is found in the macrostate with the greatest entropy.
- The entropy of an isolated system never decreases: $\Delta S \geq 0$.

Entropy and the Arrow of Time

If a physical process increases the total entropy of an isolated system, the reverse process cannot occur spontaneously, since it would violate the second law. In our previous example, this means that the 42 quanta cannot all spontaneously return to a single box. A familiar example is perfume: once sprayed, the aerosol spreads throughout the room and never returns to the bottle. As entropy increases we identify a temporal evolution of the system – this is the origin of the thermodynamic arrow of time.

Entropy of an Ideal Gas

Multiplicity (with the indistinguishability factor):

$$\Omega \approx \frac{1}{N!}\frac{V^N}{h^{3N}}\left(\frac{4\pi m U}{3N}\right)^{3N/2}.$$

Using Stirling's approximation,

$$\boxed{S = Nk_B \ln\left[\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right] + \tfrac{5}{2}Nk_B} \qquad \text{(Sackur–Tetrode equation).}$$

Dependence of Entropy

The entropy of an ideal gas depends on its volume, energy, and number of particles. Increasing any of these increases the entropy:

- more volume ⇒ more spatial configurations;
- more particles ⇒ more combinatorial configurations;
- more energy ⇒ more energy redistributions.

Example: Helium Gas

One mole of helium at room temperature and atmospheric pressure in a volume of $0.025\,\mathrm{m}^3$ has

$$U = \tfrac{3}{2}nRT \approx 3700\,\mathrm{J}, \qquad S = Nk_B \cdot 15.2 \approx 126\,\mathrm{J/K}.$$

Entropy of a Volume Change: Free Expansion

When a gas freely expands into a larger volume, no work is done and no heat flows in or out. What is the entropy change?

Using Sackur–Tetrode,

$$\Delta S = S_f - S_i = Nk_B\left[\ln\left(\tfrac{V_f}{N}\beta\right) + \tfrac{5}{2}\right] - Nk_B\left[\ln\left(\tfrac{V_i}{N}\beta\right) + \tfrac{5}{2}\right],$$

where

$$\beta = \left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}.$$

The temperature-dependent terms cancel, leaving

$$\boxed{\Delta S = Nk_B \ln\left(\frac{V_f}{V_i}\right)}.$$

Entropy of Mixing

Another way to increase entropy is to allow different materials to interact. For example, smells diffusing in air during cooking. To find the increased entropy of two gases mixing, treat the situation as a free expansion for each gas. Gas A expands to twice its initial volume:

$$\Delta S_A = N k_B \ln\left(\frac{V_f}{V_i}\right) = N k_B \ln\left(\frac{2V}{V}\right) = N k_B \ln 2.$$

Similarly $\Delta S_B = N k_B \ln 2$. The total entropy increase is

$$\Delta S_{\text{total}} = 2 N k_B \ln 2.$$

Gibbs Paradox

If the two gases are *identical*, the same equation predicts $\Delta S_{\text{total}} = 2N k_B \ln 2$. But physically, removing a partition between two equal volumes of the same gas at the same temperature and pressure produces no observable change. Mathematically

$$\Delta S_{\text{total}} = 2 N k_B \ln 2, \qquad \text{but physically} \qquad \Delta S_{\text{total}} = 0.$$

No observable change $\Rightarrow$ already at equilibrium.

Resolution: Indistinguishability

The resolution is that identical particles are *indistinguishable*. The corrected multiplicity is

$$\Omega_{\text{corr}} = \frac{1}{N!}\,\Omega = \frac{1}{N!}\,\frac{V^N}{h^{3N}},$$

which removes the over-counting and resolves the paradox. Swapping identical particles does not produce a new physical state, so the naive counting V^N over-counts configurations by $N!$. Note that the physical volume occupied by the gas does not change, $V_A = V_{A'}$; the correction only modifies how microstates are counted.

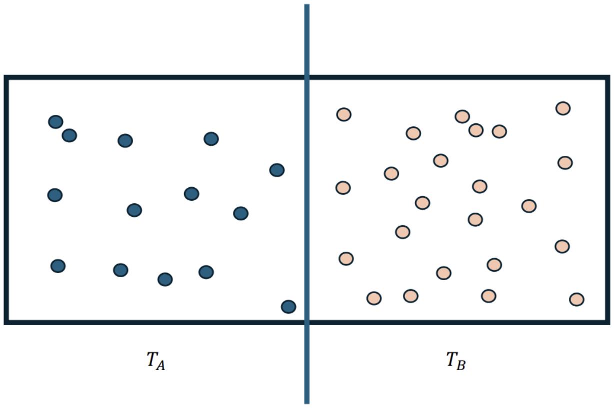
$$\boxed{\text{Indistinguishability changes counting, not physical volume.}}$$

1.8 Lecture 8 – Temperature, Equilibrium, and the Thermodynamic Identity

Mar 13

Thermal Equilibrium and Entropy

At equilibrium $T_A = T_B$, and the second law says systems evolve toward maximum entropy.



Two systems in thermal contact exchanging energy.

Total energy is conserved, $U = U_A + U_B = \text{constant}$, so $dU_A = -dU_B$. At equilibrium the total entropy is stationary:

$$\frac{dS_{\text{total}}}{dU_A} = 0.$$

Derivation of Temperature

$$\frac{dS_{\text{total}}}{dU_A} = \frac{dS_A}{dU_A} + \frac{dS_B}{dU_A} = 0.$$

Using $dU_B = -dU_A$,

$$\frac{dS_A}{dU_A} - \frac{dS_B}{dU_B} = 0 \implies \frac{dS_A}{dU_A} = \frac{dS_B}{dU_B}.$$

The change in entropy per unit energy is the same for two systems in thermal equilibrium.

Definition of temperature:

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}}$$

Physical Interpretation of Temperature

- Units: $S/U \Rightarrow \text{J/K/J} = 1/\text{K}$.
- As $T \to \infty$, $dS/dU \to 0$.
- A large entropy increase per small energy increase ⇒ low temperature.

Entropy as a Function of State Variables

Entropy depends on $S = S(U, V, N)$.

Definition

Total differential of S:

$$dS = \left(\frac{\partial S}{\partial U}\right) dU + \left(\frac{\partial S}{\partial V}\right) dV + \left(\frac{\partial S}{\partial N}\right) dN.$$

For fixed N,

$$dS = \frac{\partial S}{\partial U}\, dU + \frac{\partial S}{\partial V}\, dV.$$

Thermodynamic Identity

First law $dU = \delta Q + \delta W$. For reversible processes $\delta Q = T\, dS$ and $\delta W = -P\, dV$, so

$$\boxed{dU = T\, dS - P\, dV.}$$

Because U, S, V are state functions, this identity holds for *all* processes, not just reversible ones. The internal energy U thus changes with entropy S and volume V.

Entropy Differential Form

Rearranging,

$$dS = \frac{1}{T}\, dU + \frac{P}{T}\, dV.$$

Example: Two-System Interaction

Two systems A and B exchange internal energy and volume. If ΔU and ΔV associated with ΔT are transferred from A to B, what is the entropy change? Show that equilibrium occurs when $T_A = T_B$ and $P_A = P_B$.

$$\Delta S = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \Delta U + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) \Delta V.$$

At equilibrium $\Delta S \to 0$ for arbitrary $\Delta U, \Delta V$, which requires $T_A = T_B$ and $P_A = P_B$.

Heat Capacity and Entropy

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

Using the chain rule,

$$C_V = \frac{dU}{dS} \cdot \frac{dS}{dT} = T\left(\frac{\partial S}{\partial T}\right)_V.$$

Thus C_V measures how much entropy is gained per unit temperature increase.

Low-temperature behaviour: although C_V is often nearly constant over the range of interest,

$$C_V \to 0 \quad \text{as } T \to 0.$$

At absolute zero nothing can be thermally excited, so no energy can be absorbed and the heat capacity must vanish.

A Conundrum

Observation 1. Many spontaneous processes release energy (combustion, exothermic reactions): $\Delta U < 0$. So it appears that nature prefers lower energy.

Observation 2. Ice melts spontaneously at room temperature, but melting requires energy input: $\Delta U > 0$. This contradicts the "lower energy" idea.

Energy alone does not determine spontaneity:

$$\Rightarrow \text{ entropy increase drives the process.}$$

Spontaneity and the Role of Entropy

The correct thermodynamic criterion for spontaneity is

$$\Delta S_{\text{total}} > 0,$$

or equivalently, at constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S < 0.$$

Melting of Ice

Energy: $\Delta H > 0$ (endothermic, requires heat input).
Entropy: $\Delta S \gg 0$ (ice is ordered, liquid water is much more disordered).

Competition Between Energy and Entropy

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

- $\Delta H > 0$: energetically unfavourable.
- $\Delta S > 0$: entropically favourable.

At sufficiently high temperature $T\Delta S > \Delta H$, so $\Delta G < 0$ and melting becomes spontaneous.

1.9 Lecture 9 – Microscopic Heat Capacity and Chemical Potential

Mar 16

Microscopic Origin of Heat Capacity and Estimation of ε

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

Thus C_V measures how much energy (or entropy) a system gains per unit increase in temperature.

Degrees of Freedom and C_V

For a diatomic molecule such as H_2, different degrees of freedom contribute to the heat capacity:

- Translation $\to \frac{3}{2}R$.
- Rotation $\to R$.
- Vibration $\to R$ (kinetic + potential).

At low temperatures only translation contributes, $C_V = \frac{3}{2}R$. As T rises, rotation activates, $C_V = \frac{5}{2}R$. At even higher temperatures vibration activates, $C_V = \frac{7}{2}R$.

Why Vibrations Turn On Gradually

Unlike classical systems, vibrational energy is quantised:

$$E_n = \left(n + \tfrac{1}{2}\right)\varepsilon,$$

where ε is the quantum spacing. The key comparison is between thermal energy and quantum spacing:

- $k_B T \ll \varepsilon$: vibrations frozen, C_V contribution ≈ 0.
- $k_B T \sim \varepsilon$: vibrations begin to activate.
- $k_B T \gg \varepsilon$: full classical contribution recovered.

Hence the vibrational contribution to C_V rises smoothly rather than abruptly.

Estimating ε from the Graph

From the heat capacity curve, the vibrational contribution rises from 0 to its full value R over a range of temperatures. A useful rule is that half-activation occurs near $k_B T \approx \varepsilon/3$. The midpoint of the rise occurs near $T \approx 2000\,\mathrm{K}$, so

$$k_B T \approx \frac{\varepsilon}{3} \implies \varepsilon \approx 3k_B T.$$

Numerical Estimate

Using $k_B = 8.6 \times 10^{-5}\,\mathrm{eV/K}$,

$$\varepsilon \approx 3 \times 2000 \times 8.6 \times 10^{-5} \approx 0.51\,\mathrm{eV}.$$

Connection to Experimental Values

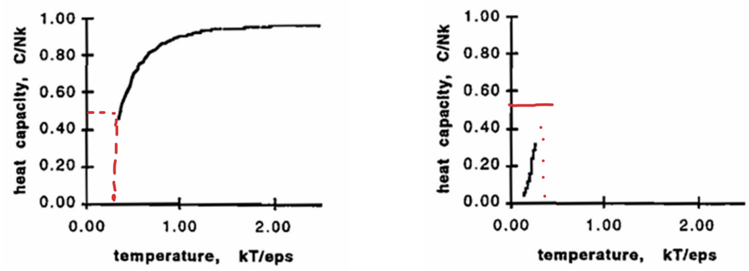
Experimentally, for H_2 vibration,

$$\varepsilon = h\nu \approx 4161\,\mathrm{cm}^{-1}.$$

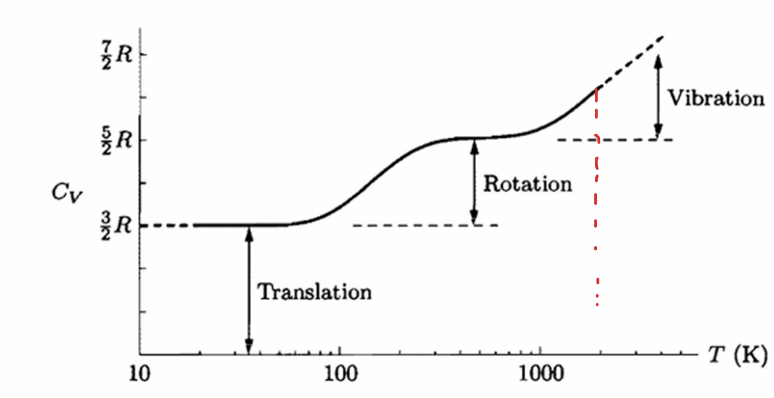
Using $1\,\mathrm{eV} = 8065\,\mathrm{cm}^{-1}$, $\varepsilon \approx 0.51\,\mathrm{eV}$, which agrees very well with the heat-capacity estimate.

Physical Interpretation

The temperature at which C_V rises reveals the underlying quantum energy scale, $k_B T \sim \varepsilon$. Thus macroscopic thermodynamic measurements (heat capacity) directly probe microscopic quantum structure.



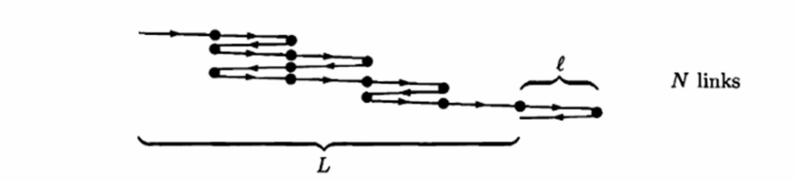
Heat capacity of H_2 as a function of temperature.



Quantised vibrational levels turning on with rising T.

Problem 3.34 – Rubber-Band Polymer

Polymers, like rubber, are made of very long molecules, usually tangled into a configuration with lots of entropy. As a very crude model of a rubber band, consider a chain of N links each of length ℓ (see Figure 3.17). Each link has only two possible states, pointing either left or right. The total length L of the rubber band is the net displacement from the start of the first link to the end of the last link.



Schematic rubber-band model: a chain of N two-state links.

Example – (a) Entropy in terms of N and N_R

Each link can point either left or right. If exactly N_R links point right, then $N_L = N - N_R$ point left. The number of arrangements is

$$\Omega = \binom{N}{N_R} = \frac{N!}{N_R!(N-N_R)!},$$

so the entropy is

$$S = k_B \ln \Omega = k_B \ln\left(\frac{N!}{N_R!(N-N_R)!}\right),$$

i.e.

$$\frac{S}{k_B} = \ln N! - \ln N_R! - \ln(N-N_R)!.$$

For large N, Stirling's approximation $\ln n! \approx n \ln n - n$ gives

$$\frac{S}{k_B} \approx N \ln N - N_R \ln N_R - (N-N_R)\ln(N-N_R),$$

so

$$\boxed{S \approx k_B[N \ln N - N_R \ln N_R - (N-N_R)\ln(N-N_R)]\,.}$$

Example – (b) Length L in terms of N and N_R

Each right link contributes $+\ell$ and each left link $-\ell$. With $N_L = N - N_R$,

$$L = \ell(N_R - N_L) = \ell(2N_R - N),$$

and equivalently $N_R = \frac{1}{2}(L/\ell + N)$.

Example – (c) Thermodynamic identity

For an ordinary system, $dU = T\,dS - P\,dV$. Here L plays the role of V and the inward tension F plays the role of $-P$. Stretching the band quasistatically by $dL > 0$ does positive work, $dW = F\,dL$, so the appropriate identity is

$$\boxed{dU = T\,dS + F\,dL.}$$

Example – (d) Tension in terms of L, T, N, ℓ

For a process at constant U, $dU = 0$, so $F\,dL = -T\,dS$ and

$$F = -T\left(\frac{\partial S}{\partial L}\right)_U .$$

By the chain rule, $\frac{\partial S}{\partial L} = \frac{\partial S}{\partial N_R} \cdot \frac{\partial N_R}{\partial L}$, with $\partial N_R/\partial L = 1/(2\ell)$ and

$$\frac{\partial S}{\partial N_R} = k_B \ln\left(\frac{N - N_R}{N_R}\right).$$

Therefore

$$F = -\frac{k_B T}{2\ell} \ln\left(\frac{N - N_R}{N_R}\right).$$

Substituting $N_R = (L/\ell + N)/2$,

$$\frac{N - N_R}{N_R} = \frac{1 - L/(N\ell)}{1 + L/(N\ell)},$$

which gives

$$\boxed{F = \frac{k_B T}{2\ell} \ln\left(\frac{1 + L/(N\ell)}{1 - L/(N\ell)}\right).}$$

Example – (e) Hooke's law in the limit $L \ll N\ell$

Let $x = L/(N\ell)$. For $|x| \ll 1$, $\ln\left(\frac{1+x}{1-x}\right) \approx 2x$, so

$$F \approx \frac{k_B T}{2\ell} \cdot 2x = \frac{k_B T}{N\ell^2} L,$$

which is Hooke's law $F \propto L$.

$$\boxed{F \approx \frac{k_B T}{N\ell^2} L \quad (L \ll N\ell).}$$

Example – (f) Temperature dependence

For fixed L, $F \propto T$. So holding L fixed, increasing T increases F. Equivalently, holding F fixed, the band must *contract* when heated. This makes sense in the entropy picture: a stretched band has fewer accessible configurations, so stretching lowers configurational entropy. At higher temperatures entropic effects dominate, favouring shorter, more disordered configurations.

Example – (g) Sudden stretching

A sudden stretch is approximately adiabatic, so the total entropy is approximately constant. But stretching reduces configurational entropy. To keep the total entropy constant, the vibrational entropy (which depends on U) must increase, so U – and thus T – increases.

$$\boxed{\text{The temperature increases when the band is suddenly stretched.}}$$

This is a striking example of elasticity driven primarily by entropy rather than by potential energy.

Variable Particle Number and Chemical Potential

Allowing Particle Exchange

So far we have considered systems with fixed N. Just as energy and volume can change to maximise entropy, particles can also move between systems to increase entropy.

For reversible processes in a closed system,

$$dU = T\,dS - P\,dV.$$

We now relax the assumption that N is constant.

Why a New Term is Needed

Particles are not "empty": each carries energy. So even if $dS = dV = 0$, the internal energy can still change when $dN \neq 0$. Hence $U = U(S, V, N)$.

General Differential of U

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN.$$

We already know $(\partial U/\partial S)_{V,N} = T$, $(\partial U/\partial V)_{S,N} = -P$. Define the remaining term as the **chemical potential**:

$$\mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

Physically, μ is the energy change when one particle is added at fixed entropy and volume.

Extended Thermodynamic Identity

$$\boxed{dU = T\,dS - P\,dV + \mu\,dN.}$$

Entropy Representation

Rewriting in terms of dS,

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN.$$

Matching coefficients with $dS = (\partial S/\partial U)dU + \cdots$ gives

$$\boxed{\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}.}$$

Physical Interpretation of μ

- If adding particles **decreases** entropy, then $(\partial S/\partial N)_{U,V} < 0$ and $\mu > 0$: the system tends to **expel** particles.
- If adding particles **increases** entropy, then $(\partial S/\partial N)_{U,V} > 0$ and $\mu < 0$: the system tends to **attract** particles.

Particle Flow and Equilibrium

Systems evolve toward maximum entropy. From $\mu/T = -(\partial S/\partial N)_{U,V}$,

$$\boxed{\text{Particles flow from regions of high } \mu \text{ to low } \mu.}$$

This is analogous to heat flowing from high T to low T, or volume expanding against pressure differences.

Equilibrium

At equilibrium there is no net particle flow, so $\mu_A = \mu_B = \cdots = \mu_i$, and the total particle number is conserved,

$$\boxed{N_{\text{total}} = N_A + N_B + \cdots = \text{constant.}}$$

Key Idea

Chemical potential plays the same role for particles as temperature does for energy.

Example: Osmotic Pressure

Osmosis is a fundamental process in biological and physical systems. Water (H_2O) diffuses across a semipermeable membrane into a region containing solute molecules, lowering the system's free energy and increasing entropy in two ways:

- energy redistribution (more ways to distribute energy ⇒ higher entropy);
- increased configurational disorder of solvent and solute.

This entropy-driven process manifests as a real macroscopic force that drives mass transport.

Definition

The **osmotic pressure** Π is the external pressure required to stop the net flow of solvent into the solution – the pressure needed to oppose the entropy-driven mixing.

Connection to Chemical Potential

Changes in entropy with respect to particle number govern particle flow, $\mu/T = -(\partial S/\partial N)_{U,V}$, so osmotic flow can be understood as solvent molecules moving in response to differences in μ.

Chemical Potential of an Ideal Gas

For a monatomic ideal gas, the entropy is given by Sackur–Tetrode. Defining the thermal de Broglie wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}},$$

the entropy can be written

$$S = N k_B \left[\ln\left(\frac{V}{N\lambda^3} \right) + \tfrac{5}{2} \right].$$

Derivative of S with respect to N

$$\frac{\partial S}{\partial N} = k_B \left[\ln\left(\frac{V}{N\lambda^3} \right) + \tfrac{5}{2} \right] + N k_B \frac{\partial}{\partial N} \ln\left(\frac{V}{N\lambda^3} \right).$$

Since $\partial/\partial N \, \ln(V/(N\lambda^3)) = -1/N$,

$$\frac{\partial S}{\partial N} = k_B \ln\left(\frac{V}{N\lambda^3} \right) + \tfrac{3}{2} k_B.$$

Chemical Potential

Recall $\mu = -T(\partial S/\partial N)$, so

$$\boxed{\mu = -k_B T \left[\ln\left(\frac{V}{N\lambda^3} \right) + \tfrac{3}{2} \right].}$$

Physical Interpretation

- λ is the spatial extent of a particle's quantum wave packet.
- λ^3 is the effective quantum volume per particle.

- $V/(N\lambda^3)$ measures the available space per particle relative to the quantum uncertainty.

- As density N/V increases, μ increases.
- A system with higher μ pushes particles outward.
- For an ideal gas μ is typically negative.
- Increasing T makes μ more negative – adding particles becomes entropically favourable.

Diffusive Equilibrium

Consider two systems A and B that can exchange energy, volume, and particles. The total entropy change is

$$\Delta S_{\text{total}} = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\Delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)\Delta V_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right)\Delta N_A.$$

Equilibrium Conditions

At equilibrium $\Delta S_{\text{total}} = 0$ for arbitrary exchanges, which requires

$$T_A = T_B \quad \text{(thermal equilibrium)},$$

$$P_A = P_B \quad \text{(mechanical equilibrium)},$$

$$\boxed{\mu_A = \mu_B \quad \text{(diffusive equilibrium).}}$$

1.10 Lecture 10 – Heat Engines, Carnot, and Stirling Cycles

Mar 19

Industrial Origins of Thermodynamics

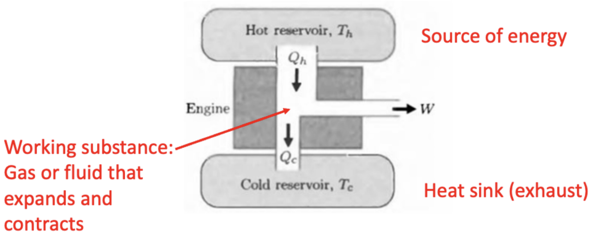
Before thermodynamics was a science it was an engineering challenge. Steam engines were revolutionary but inefficient; the key question was how much work can be extracted from a given amount of heat (e.g., from coal).

Sadi Carnot

Carnot showed that engines move heat from a hot reservoir to a cold reservoir, and that the work produced by this "fall" of heat is analogous to a water-wheel. Crucially, the efficiency depends only on the two reservoir temperatures, not on the working substance.

Heat Engine

A heat engine converts heat into mechanical work in a cyclic process.



Schematic of a heat engine operating between two reservoirs.

By the first law,

$$W = Q_h - Q_c,$$

and the efficiency is

$$e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h}.$$

Can $Q_c \to 0$, giving 100% efficiency? The second law says no: total entropy must not decrease,

$$\Delta S_{\text{total}} = \Delta S_h + \Delta S_c \geq 0.$$

Over a cycle the engine must return to its initial state, so the entropy expelled must be at least the entropy absorbed,

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \implies \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}.$$

The maximum possible efficiency is therefore

$$e \leq 1 - \frac{T_c}{T_h}.$$

Carnot Efficiency

$$\boxed{e_{\text{Carnot}} = 1 - \frac{T_c}{T_h}.}$$

Achieved only by reversible engines ($\Delta S_{\text{total}} = 0$).

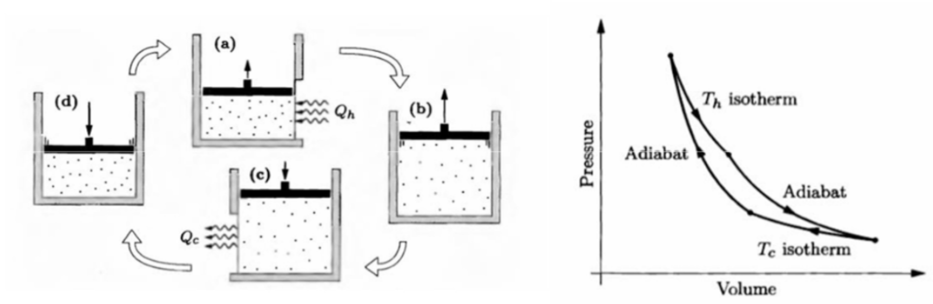
Why Real Engines Fall Short of Carnot

Real engines suffer irreversibilities – friction, turbulence, finite temperature gradients, heat leaks – that generate entropy ($\Delta S_{\text{total}} > 0$) and so reduce the maximum achievable efficiency below the Carnot limit.

Can a Reversible Engine Be Built?

In principle a reversible engine reaches $e_{\max} = 1 - T_c/T_h$, but perfectly reversible processes require infinitely slow (quasistatic) operation and no dissipation. Real engines can therefore approach but never reach the limit.

Carnot Cycle



The Carnot cycle on the P–V diagram.

The four strokes are:

- Isothermal expansion: heat absorbed from hot reservoir.
- Adiabatic expansion: temperature drops with no heat exchange.
- Isothermal compression: heat released to cold reservoir.
- Adiabatic compression: temperature rises with no heat exchange.

Stirling Engine

A Stirling engine converts thermal energy differences into kinetic energy and works even with small temperature gradients.

Key feature: a regenerator stores heat and reuses it, improving efficiency. Applications include space-based power systems.

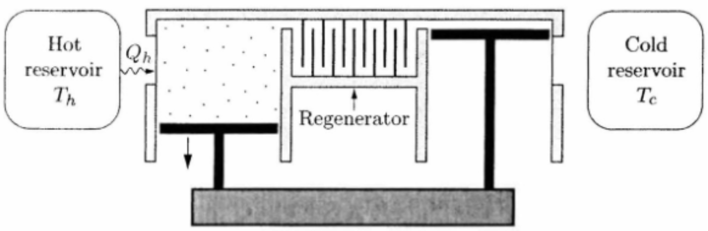


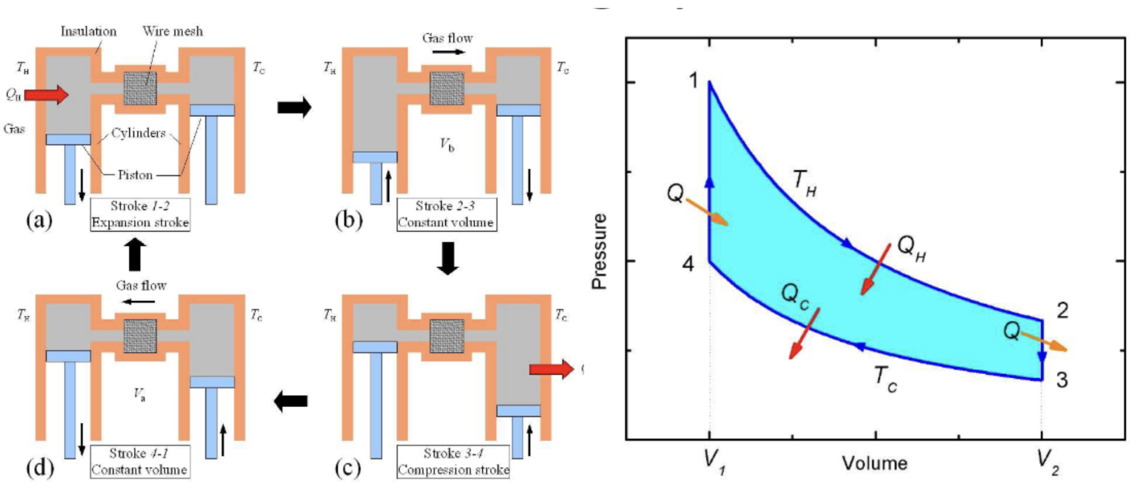
Figure 4.7. A Stirling engine, shown during the power stroke when the hot piston is moving outward and the cold piston is at rest. (For simplicity, the linkages between the two pistons are not shown.)

Regenerator stores gas in folds that act as thermal reservoir gradient that stores Q and cancels power/compression strokes

Schematic of a Stirling engine.

Stirling Engine Properties

- Safer alternative to high-pressure steam engines.
- Closed-cycle external-combustion engine: the working gas (air, helium, or hydrogen) never leaves the engine.
- The regenerator (typically a wire mesh) stores heat during the cooling phase and returns it during the heating phase. This internal recycling allows the Stirling engine to *theoretically* match the Carnot efficiency.



Stirling cycle: isothermal expansion, isochoric cooling, isothermal compression, isochoric heating.

Stirling Cycle (Ideal)

Steps:

1. Isothermal expansion at T_h.
2. Isochoric cooling (heat stored in regenerator).
3. Isothermal compression at T_c.
4. Isochoric heating (heat returned from regenerator).

Stirling Cycle Without a Regenerator (Ideal Gas)

Step 1: Isothermal expansion at T_h.

$$Q_1 = Nk_BT_h \ln\left(\frac{V_2}{V_1}\right).$$

Step 2: Isochoric cooling.

$$Q_2 = NC_v(T_c - T_h).$$

Step 3: Isothermal compression at T_c.

$$Q_3 = -Nk_BT_c \ln\left(\frac{V_2}{V_1}\right).$$

Step 4: Isochoric heating.

$$Q_4 = NC_v(T_h - T_c).$$

Total work:

$$W = \sum_{n=1}^{4} Q_n = Nk_B(T_h - T_c)\ln\left(\frac{V_2}{V_1}\right).$$

Efficiency:

$$\eta = \frac{W}{Q_{\text{in}}} = \frac{Nk_B(T_h - T_c)\ln(V_2/V_1)}{Nk_BT_h\ln(V_2/V_1) + NC_v(T_h - T_c)} < 1 - \frac{T_c}{T_h}.$$

The Ideal Stirling Cycle (with Regenerator)

The four heats are the same, but now Q_2 is stored in the regenerator and returned in Q_4, so they cancel as far as net heat input is concerned:

$$Q_{\text{in}} = Nk_BT_h \ln\left(\frac{V_2}{V_1}\right).$$

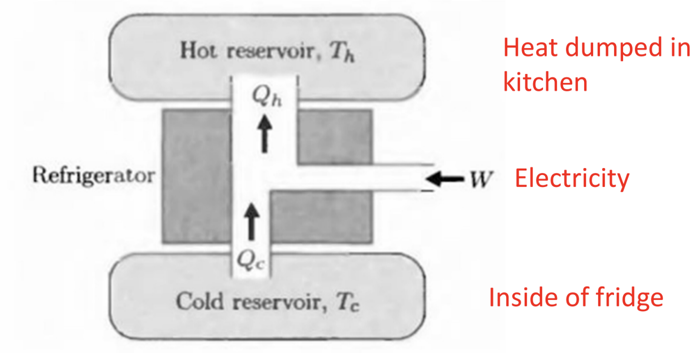
The efficiency therefore reduces to

$$\eta = \frac{Nk_B(T_h - T_c)\ln(V_2/V_1)}{Nk_BT_h\ln(V_2/V_1)} = 1 - \frac{T_c}{T_h}.$$

The Stirling engine with an ideal regenerator achieves Carnot efficiency.

Reversible Engines and Refrigerators

A refrigerator is a heat engine run in reverse: work input forces heat to flow from cold to hot. The objective is to remove as much heat as possible from the cold space.



Refrigerator schematic.

Coefficient of Performance (COP)

Instead of efficiency, refrigerators are characterised by a coefficient of performance,

$$\text{COP} = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{Q_h/Q_c - 1}.$$

COP can exceed 1.

COP limit from the second law. Entropy gives $Q_h/T_h \geq Q_c/T_c$, so

$$\text{COP} \leq \frac{T_c}{T_h - T_c}.$$

As $T_h - T_c \to 0$ the COP grows without bound: it is easy to keep a fridge cool in a cold room and very hard in a hot one.

Heat vs. Work: Space Heater vs. Heat Pump

Example – Toronto winter

On a cold winter day in Toronto you need to deliver 1000 J of heat to your room using 100 J of electrical work. Compare:

- Space heater: 100% conversion of work to heat.
- Heat pump (Carnot refrigerator run in reverse) extracting heat from $T_c = -10°\text{C}$ and delivering at $T_h = 20°\text{C}$.

Space heater. By the first law $Q_{\text{room}} = W = 100\,\text{J}$.
Heat pump. The output is Q_h with

$$\text{COP} = \frac{Q_h}{W} = \frac{T_h}{T_h - T_c} = \frac{293}{293 - 263} = 9.77,$$

so

$$Q_h = \text{COP} \times W = 9.77 \times 100\,\text{J} = 977\,\text{J}.$$

The heat pump delivers nearly 10× as much heat as the space heater for the same electrical input.

1.11 Lecture 11 – Real Engines: Otto, Diesel, Rankine, and Throttling

Mar 20

Beyond the Carnot Cycle

Last class we found the theoretical limits for ideal heat engines and refrigerators,

$$e \le 1 - \frac{T_c}{T_h}, \qquad \text{COP} \le \frac{T_c}{T_h - T_c}.$$

How do real engines and refrigerators actually function?

Internal Combustion Engines: The Otto Cycle

The Otto cycle describes how gasoline engines operate:

1. Air–gas mixture is injected into the chamber.
2. The mixture is compressed adiabatically by the piston.
3. A spark plug ignites the mixture.
4. High-pressure gas expands adiabatically and pushes the piston.
5. Hot gases are exhausted and replaced with new gas.

There is no external hot reservoir; thermal energy is produced internally by combustion.

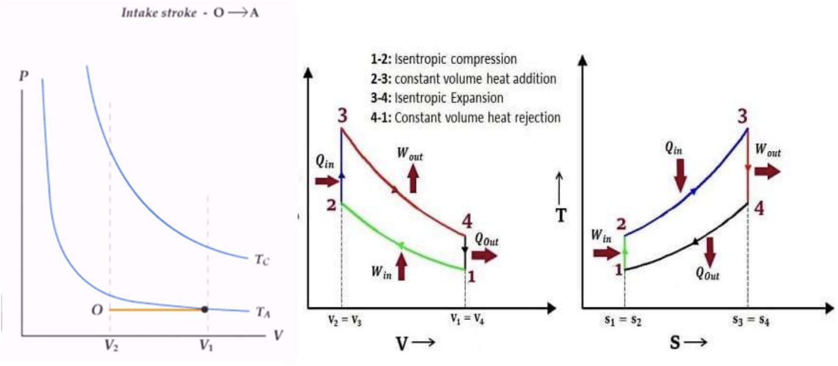
The efficiency of the Otto cycle is

$$e = 1 - \frac{1}{r^{\gamma-1}},$$

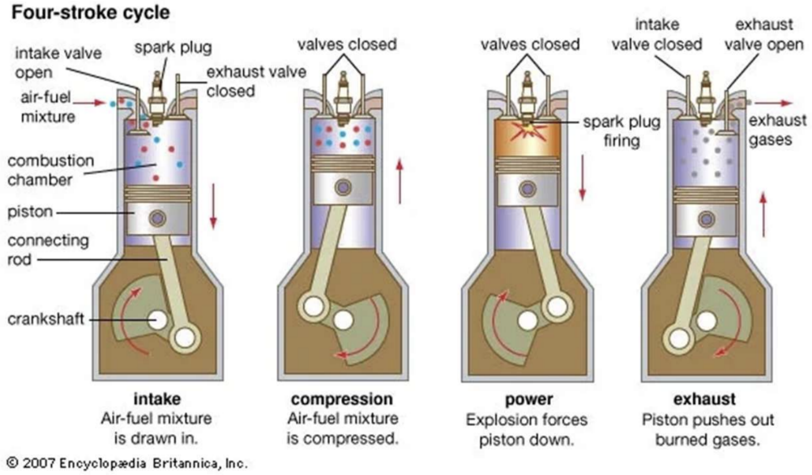
where $r = V_1/V_2$ is the compression ratio and γ is the adiabatic exponent. For air ($\gamma = 7/5$) and $r = 8$,

$$e \approx 1 - \frac{1}{8^{2/5}} \approx 0.56.$$

In practice, real engines achieve $\sim 30\%$ efficiency due to friction, heat loss, and incomplete combustion.



Otto cycle on the P–V diagram.



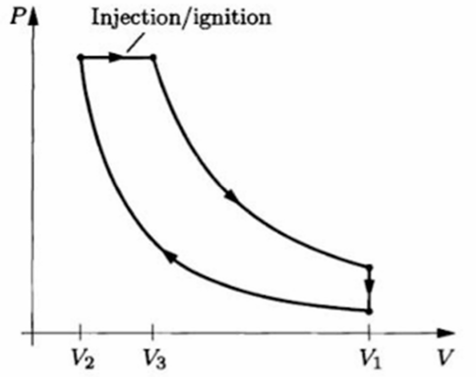
Idealised Otto cycle thermodynamics.

Diesel Engine

If the fuel–air mixture becomes too hot during compression it can ignite prematurely. Diesel engines avoid this by compressing only air and then injecting fuel into the hot cylinder, where it auto-ignites without a spark.

Diesel Cycle

1. Isentropic compression: pure air compressed adiabatically.
2. Isobaric expansion: fuel injected and burns at constant pressure.
3. Isentropic expansion: hot gas expands adiabatically.
4. Isochoric cooling: exhaust and intake.



Diesel cycle on the P–V diagram.

Diesel efficiency:

$$e_{\text{diesel}} = 1 - \frac{1}{r^{\gamma-1}} \cdot \frac{\alpha^{\gamma} - 1}{\gamma(\alpha - 1)},$$

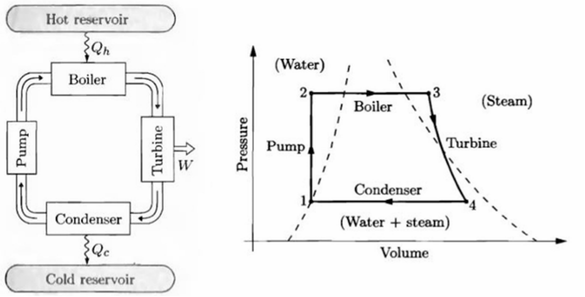
where $\alpha = V_3/V_2$ is the cutoff ratio. Although Otto cycles are theoretically more efficient at the same compression ratio, Diesel engines achieve higher practical efficiencies (up to $\sim 40\%$).

Steam Engines: The Rankine Cycle

The Rankine cycle is a practical model for steam engines and power plants. A working fluid (usually water) undergoes phase changes to convert heat into work.

Cycle Steps

1. Pump: increases pressure of liquid.
2. Boiler: heat added at constant pressure (liquid → super-heated vapour).
3. Turbine: steam expands adiabatically and does work.
4. Condenser: heat rejected at constant pressure (vapour → liquid).



Rankine cycle.

Efficiency

The pump adds very little energy because the PV contribution to H is small for liquids:

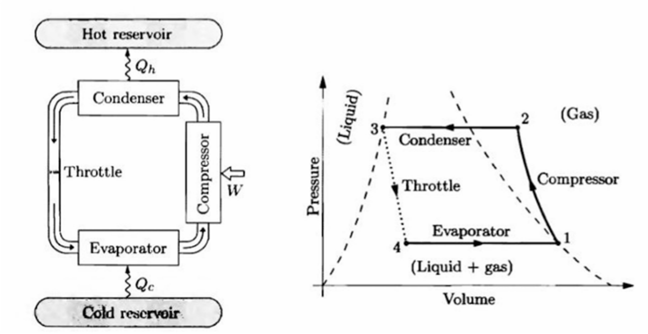
$$W_{\text{net}} = (H_3 - H_4) - (H_2 - H_1), \qquad Q_{\text{in}} = H_3 - H_2,$$

so

$$e_{\text{rankine}} = \frac{W_{\text{net}}}{Q_{\text{in}}} = 1 - \frac{H_4 - H_1}{H_3 - H_2}.$$

With $H_2 \approx H_1$, this simplifies further.

Real Refrigerators: Reversing the Rankine Cycle



Reverse-Rankine refrigeration cycle.

$$Q_{\text{absorbed}} = H_1 - H_4, \qquad Q_{\text{expelled}} = H_2 - H_3,$$

$$\text{COP} = \frac{Q_{\text{absorbed}}}{Q_{\text{expelled}} - Q_{\text{absorbed}}} = \frac{H_1 - H_4}{H_2 - H_3 - H_1 + H_4}.$$

Values of H_1, H_2, H_3 are obtained from steam tables; H_4 requires analysis of the throttling process.

The Throttling / Joule–Thomson Process

A throttling process occurs when a fluid at high pressure passes through a restriction into a region of lower pressure.

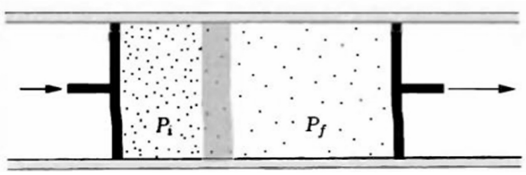
- No heat transfer: $Q = 0$.
- Only pressure-volume work, no shaft work.

$$U_f - U_i = Q + W = W_{\text{high}} + W_{\text{low}} = P_i V_i - P_f V_f,$$

which rearranges to $U_f + P_f V_f = U_i + P_i V_i$, i.e.

$$H_f = H_i.$$

The enthalpy is conserved – the process is **isenthalpic**.



Throttling: pressure drop with constant enthalpy.

Why Does the Temperature Drop?

For an ideal gas $\Delta H = 0 \Rightarrow \Delta T = 0$, so throttling does not cool an ideal gas. In real gases or liquids, there is a potential-energy contribution to H from intermolecular forces (e.g. van der Waals):

$$H = U_{\text{pot}} + U_{\text{kin}} + PV.$$

Most intermolecular forces are weakly attractive at the relevant length scale. For attractive forces $U_{\text{pot}} < 0$. As the pressure drops and molecules move apart, $|U_{\text{pot}}|$ decreases and U_{pot} becomes less negative – i.e. it *increases*. To compensate, the kinetic energy drops and the fluid cools.

Application to Refrigeration

Since $H_3 = H_4$ in the refrigeration cycle,

$$\text{COP} = \frac{H_1 - H_3}{H_2 - H_1}.$$

This explains how real refrigerators achieve cooling using throttling combined with phase changes.

1.12 Lecture 12 – Free Energies and Chemical Driving Forces

Mar 23

Free Energy and Real Systems

In real physical systems we are rarely dealing with isolated systems. Most are in contact with a reservoir such as the atmosphere or a thermal bath, so T and P are often constant while U, S, V can change.

In isolated systems U is constant and S is maximised. In non-isolated systems the environment plays an active role: the reservoir can supply or absorb energy, affecting the work the system can perform.

Enthalpy

At constant pressure there is an "atmospheric tax" to make room for the system itself, so the enthalpy of the system is

$$H = U + PV.$$

But if our system is not isolated, it can extract energy from its surroundings.

Helmholtz Free Energy

If the system is in thermal contact with a reservoir at temperature T, it can extract energy from the surroundings as heat Q. This "free" energy from the environment reduces the energy we must provide to create the system. We don't need to provide the full internal energy U; we only need to provide what is not already supplied by the environment:

$$F = U - TS.$$

The environment provides $Q = TS$ where S is the system's final entropy. So F is the energy we must put in to "create" the system from nothing, given that we get TS worth of heat for free.

Free energy lets us predict the state of matter without computing the entropy of the entire universe each time.

Maximum Work from a System

What is the maximum work extractable from a system? From the first law, $dU = Q + W$, where W is work done *on* the system. From the second law,

$$dS_{\text{total}} = dS_{\text{sys}} + dS_{\text{res}} \geq 0,$$

and at constant reservoir temperature $dS_{\text{res}} = -Q/T$, so $Q \leq T\,dS$. Substituting into the first law,

$$dU \leq T\,dS + W \implies W \geq dU - T\,dS = dF.$$

The work done *by* the system is therefore

$$W_{\text{by}} = -W \leq -\Delta F.$$

$$\boxed{\text{Maximum work extractable at constant } T = -\Delta F.}$$

Gibbs Free Energy

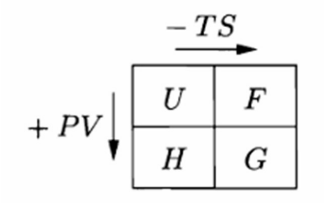
Battery example. When a battery discharges, a chemical reaction occurs that changes the structural entropy of the molecules.

- If the products have higher entropy than the reactants, the system absorbs heat from the environment.
- If the products have lower entropy (e.g. a gas → solid), the system dumps the excess disorder as heat into the environment.

When both temperature and pressure are constant (most real systems), we define

$$G = U - TS + PV.$$

In words: you need U to build the system, you get TS for free from the environment's heat, and you must pay PV to make room for the system in the surroundings.



U, F, H, and G are called thermodynamic potentials.

Free-energy diagram and accounting.

Relation to Work

Starting from $\Delta G = \Delta U - T\Delta S + P\Delta V$ and splitting $W = -P\Delta V + W_{\text{other}}$ together with $Q - T\Delta S \leq 0$ gives

$$\Delta G \leq W_{\text{other}}.$$

$$\boxed{\Delta G = \text{maximum non-expansion work at constant } T, P.}$$

Key Idea

Quantity	Conditions	Meaning
ΔF	constant T, V	maximum total work
ΔG	constant T, P	maximum useful (non-PV) work

Electrolysis Example

Example – Splitting water electrolytically

$$(H_2O)_{\text{liq}} \to (H_2)_{\text{gas}} + \tfrac{1}{2}(O_2)_{\text{gas}}.$$

From reference tables, $\Delta H = 286\,\text{kJ}$. Some of this energy goes into expansion work, $P\Delta V = 4\,\text{kJ}$, leaving $282\,\text{kJ}$ in the system.

Entropy change.

$$S_{H_2O} = 70\,\text{J/K},\ S_{H_2} = 131\,\text{J/K},\ S_{O_2} = 205\,\text{J/K},$$

$$\Delta S = S_{\text{prod}} - S_{\text{react}} = (131 + \tfrac{1}{2}\cdot 205) - 70 = 163\,\text{J/K}.$$

Heat from the environment. $T\Delta S = (298)(163) = 49\,\text{kJ}$. So $49\,\text{kJ}$ enters the system as heat from the environment.

Gibbs free energy. Total energy input is $286\,\text{kJ}$; heat contribution is $49\,\text{kJ}$; remaining required work is $286 - 49 = 237\,\text{kJ}$, i.e.

$$\Delta G = \Delta H - T\Delta S = 237\,\text{kJ}.$$

$$\boxed{\Delta G = \text{minimum electrical work for the reaction.}}$$

Reversing the Process: The Fuel Cell

Example – Hydrogen–oxygen fuel cell

Run the reaction in reverse:

$$H_2 + \tfrac{1}{2}O_2 \to H_2O.$$

Combining hydrogen with oxygen to form water lets us extract $237\,\text{kJ}$.

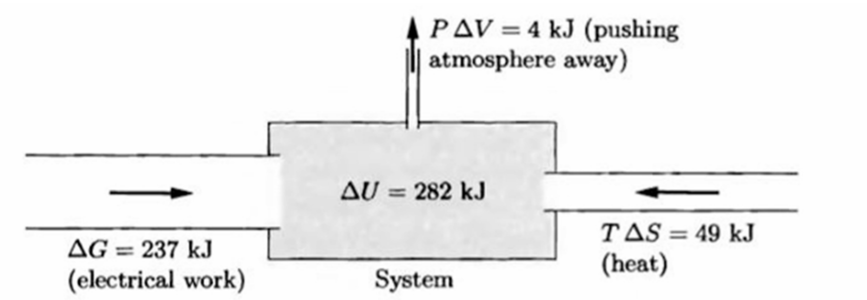
Energy balance. The fuel cell also releases heat:

- Electrical work extracted: $237\,\text{kJ}$.
- Heat expelled: $49\,\text{kJ}$.
- Total energy change: $286\,\text{kJ}$.

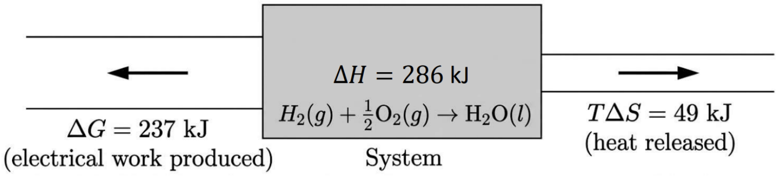
$$e = \frac{286 - 49}{286} = \frac{237}{286} \approx 83\%.$$

- Fuel cells convert chemical energy directly to electrical energy.
- Some energy must be released as heat due to entropy.
- Efficiency is significantly higher than conventional heat engines.

$$\boxed{\text{Fuel cells are not limited by Carnot efficiency.}}$$



Electrolysis



Fuel cell

Fuel-cell schematic and energy flow.

Numerical Battery Example: Lead–Acid Cell

Lead–acid cells in car batteries run on

$$2\mathrm{SO}_4^{2-} + 2\mathrm{H}^+ \to 2\mathrm{HSO}_4^-.$$

At the anode (−):

$$\mathrm{Pb} + \mathrm{HSO}_4^- \to \mathrm{PbSO}_4 + \mathrm{H}^+ + 2e^-.$$

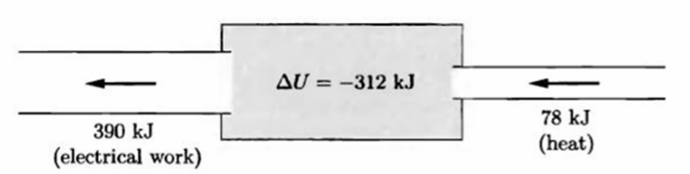
At the cathode (+):

$$\mathrm{PbO}_2 + \mathrm{HSO}_4^- + 3\mathrm{H}^+ + 2e^- \to \mathrm{PbSO}_4 + 2\mathrm{H}_2\mathrm{O}.$$

For this reaction at standard pressure, temperature, and concentration:

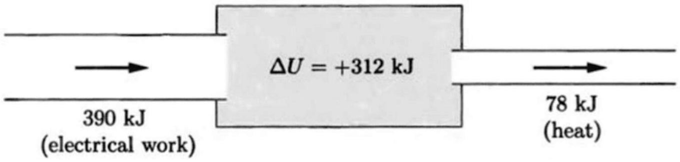
$$\Delta G = -390\,\mathrm{kJ}, \qquad \Delta H = -312\,\mathrm{kJ}.$$

(a) The electrical work produced is 390 kJ. The exothermic enthalpic energy is less than the maximum work by 78 kJ. This extra energy comes into the system as heat from the environment. We use ΔU rather than ΔH here because no gases are involved in this reaction, so $\Delta U \approx \Delta H$.



Discharging the lead-acid cell.

(b) When we reverse the process to charge the battery, we take the system back to its initial state. We then have to pump 78 kJ of heat back into the environment – this is why your phone gets hot when charging.



Charging the lead-acid cell.

(c) We can also use G to compute the cell voltage. We need to know how many electrons it pushes around the circuit per molecule reacted; the reaction shows 2 electrons per cycle. The electrical work per electron is

$$\frac{\Delta G}{n_\mathrm{e}\,N_A} = \frac{390\,\mathrm{kJ}}{2 \cdot 6.02 \times 10^{23}} = 2.02\,\mathrm{eV}.$$

$$\boxed{\text{Cell voltage} = 2.02\,\mathrm{V}.}$$

Problem 5.6 – Glucose Metabolism

A muscle can be thought of as a fuel cell, producing work from the metabolism of glucose:

$$\mathrm{C_6H_{12}O_6} + 6\mathrm{O_2} \to 6\mathrm{CO_2} + 6\mathrm{H_2O}.$$

Example – (a) ΔH and ΔG per mole of glucose

At standard conditions:

	ΔH (kJ)	ΔG (kJ)	S (J/K)
Glucose	-1273	-910	212
$O_2(g)$	0	0	205
$CO_2(g)$	-393.5	-394.4	214
$H_2O(l)$	-285.8	-237.1	70

Subtracting reactants from products:

$$\Delta H = 6(-393.5) + 6(-285.8) - (-1273) = -2803\,\text{kJ},$$

$$\Delta G = 6(-394.4) + 6(-237.1) - (-910) = -2879\,\text{kJ}.$$

Example – (b) Maximum work per mole

Under ideal operation,

$$W_{\text{max}} = -\Delta G = 2879\,\text{kJ per mole of glucose.}$$

Example – (c) Heat exchanged

The net work output ($-\Delta G = 2879\,\text{kJ}$) exceeds the decrease in enthalpy ($-\Delta H = 2803\,\text{kJ}$) by 76 kJ. So 76 kJ of heat must flow *into* the system from the environment.

Example – (d) Entropy explanation

Reactant entropy: $S_{\text{react}} = 212 + 6(205) = 1442\,\text{J/K}$.
Product entropy: $S_{\text{prod}} = 6(214) + 6(70) = 1704\,\text{J/K}$.

$$\Delta S = 1704 - 1442 = 262\,\text{J/K} > 0.$$

The entropy of the system increases, which permits heat to flow into the system from the environment without violating the second law.

Non-ideal operation. Under non-ideal operation new entropy is created during the reaction, so less heat enters (or heat must even be expelled if the entropy created exceeds 262 J/K). Thus less energy leaves as “other” work. The values of ΔH and ΔG themselves are unchanged.

Redefining the Thermodynamic Identities

Using G and F, the identities can be rewritten as:

Key Idea

$$dF = -S\,dT - P\,dV + \mu\,dN,$$

$$dG = -S\,dT + V\,dP + \mu\,dN.$$

From these we read off

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V},$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}.$$

Revisiting the Chemical Potential

From $dG = -S\,dT + V\,dP + \mu\,dN$, at constant T and P, $dG = \mu\,dN$. For a single-component system, $G = \mu N$, so

$$\mu = \frac{G}{N},$$

i.e. the chemical potential is the Gibbs free energy per particle. Recall: if two boxes A, B are in contact and $\mu_A > \mu_B$, particles move from A to B, lowering total G.

Gibbs Free Energy: Driving Forces of Living Systems

We know $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$ and $\Delta S_{\text{surr}} = -\Delta H/T$, so

$$\Delta S_{\text{sys}} - \frac{\Delta H}{T} \geq 0 \implies \Delta H - T\Delta S \leq 0 \implies \Delta G \leq 0.$$

This is the spontaneity criterion: a reaction is spontaneous only if it lowers the Gibbs free energy of the system. Nature minimises G, much as a ball rolls downhill – think of G as a free-energy potential.

Key Idea

If	then	result
$\Delta G < 0$	$\Delta S_{\text{total}} > 0$	spontaneous
$\Delta G = 0$	$\Delta S_{\text{total}} = 0$	equilibrium
$\Delta G > 0$	$\Delta S_{\text{total}} < 0$	impossible

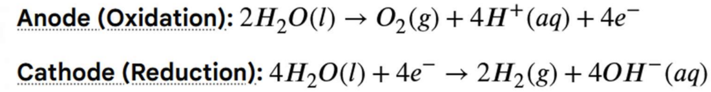
1.13 Lecture 13 – Phase Transformations and Mixtures

Mar 26

Gibbs Free Energy

$$G = U - TS + PV, \qquad \Delta G = \Delta H - T\Delta S, \qquad \Delta G \leq 0 \Rightarrow \text{spontaneous direction.}$$

Example. $(\mathrm{H_2O})_{\mathrm{liq}} \to (\mathrm{H_2})_{\mathrm{gas}} + \frac{1}{2}(\mathrm{O_2})_{\mathrm{gas}}$.



Anode (Oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode (Reduction): $4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$

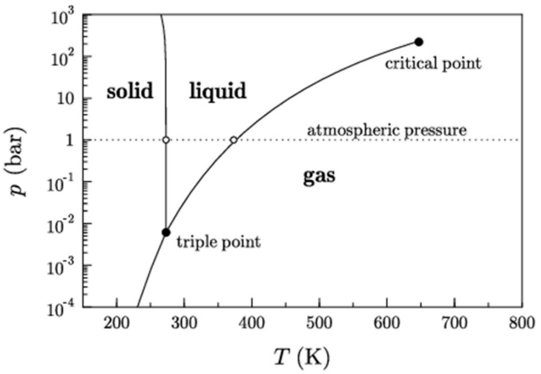
Gibbs free energy along a reaction coordinate.

Phase Transformations

Free energy G does work and drives reactions; some of the most important examples are liquid–gas phase transitions. Nature minimises G, and at different temperatures and pressures different phases "win".

$$G = H - TS.$$

At low T, enthalpy dominates and solids (with strong bonds) are favoured. At high T, entropy dominates and gases (high disorder) are favoured.

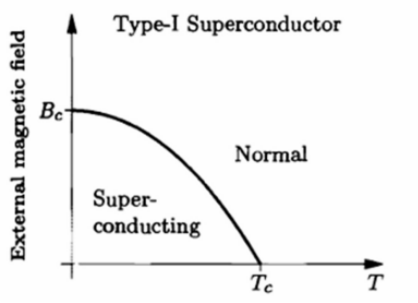


Reading a phase diagram:

1. The lines show coexistence of phases where $\Delta G = 0$ – this is where phase transitions occur.
2. The triple point is the unique (P, T) at which all three phases have the same G.
3. The critical point is the (P, T) above which the distinction between liquid and gas vanishes (super-critical fluid).

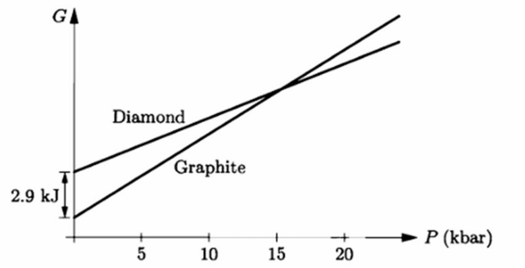
Superconductors

Besides T and P, changing other variables such as the external magnetic field can drive phase transitions. Even with no field, below a critical temperature T_c a new phase emerges where electrical resistance drops to exactly zero. The system prefers the ordered super-conducting state because it has lower G than the disordered normal state at low temperatures – a transition driven by the minimisation of a thermodynamic potential, but involving electron pairing rather than molecular bonds.



Diamond vs. Graphite

In contrast to super-conductors, diamond has the highest thermal conductivity of any bulk material. But at room temperature and pressure, graphite has *lower* G than diamond – so why don't diamonds turn into graphite?



To convert sp^3 diamond into sp^2 graphite, every covalent bond in the lattice must break simultaneously. Diamonds want to become graphite, but the kinetic barrier is enormous. **Thermodynamics tells us where the system wants to go; kinetics tells us when it gets there** (within our lifetime, in this case – no).

Pressure Effect: Diamond vs. Graphite

To shift the equilibrium toward diamond we increase the pressure. Recall $G = U + PV - TS$. Diamond is much denser than graphite:

$$\rho_{\text{diamond}} \approx 3.5\,\text{g/cm}^3, \qquad \rho_{\text{graphite}} \approx 2.2\,\text{g/cm}^3.$$

For constant T, N, $\partial G/\partial P = V$. Graphite occupies a larger volume than diamond, so as pressure increases the relative free energy

$$\Delta G = G_{\text{diamond}} - G_{\text{graphite}}$$

decreases until $G_{\text{diamond}} < G_{\text{graphite}}$, i.e. $\Delta G < 0$. High pressure favours diamond.

$$G = U + PV - TS.$$

Definition

Pressure dependence: $\partial G/\partial P = V$.
Temperature dependence: $\partial G/\partial T = -S$.

Entropy determines the temperature dependence; volume determines the pressure dependence.

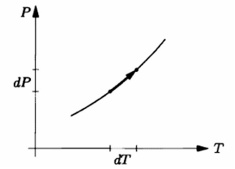
Phase Transition Condition

How do we get the phase-transition lines from a phase diagram? Transitions occur at the boundary where

$$G_{\text{liq}} = G_{\text{gas}}.$$

If we increase T by dT and P by dP keeping the two phases in equilibrium, $dG_{\text{liq}} = dG_{\text{gas}}$, i.e.

$$-S_l\,dT + V_l\,dP = -S_g\,dT + V_g\,dP.$$



Phase boundary in the P–T plane.

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}.$$

Using the latent heat $\Delta S = L/T$:

Definition

Clausius–Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} = \frac{\Delta S}{\Delta V}.$$

Ice–Water Phase Boundary

The density of ice is $\rho_{\text{ice}} \approx 917\,\text{kg/m}^3$, less than liquid water, $\rho_{\text{water}} \approx 1000\,\text{kg/m}^3$, so $V_{\text{ice}} > V_{\text{water}}$.

Clausius–Clapeyron Relation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}.$$

For melting (ice → water),

$$\Delta S = S_{\text{liq}} - S_{\text{sol}} > 0, \qquad \Delta V = V_{\text{liq}} - V_{\text{sol}} < 0,$$

since liquid water occupies less volume than ice.

Slope of the Phase Boundary

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} < 0.$$

Example – Lowering the melting point of ice

What pressure is needed to lower the melting point of ice by 1°C? For 1 g of ice/water, $V = 1.091 \times 10^{-6}\,\text{m}^3$ and $L = 333\,\text{J}$:

$$\frac{dP}{dT} = \frac{333}{273 \cdot (-0.091 \times 10^{-6})} = -1.35 \times 10^7\,\text{Pa/K} = -135\,\text{bar/K}.$$

Thus $\Delta T = -1^\circ\text{C} \Rightarrow \Delta P = +135\,\text{bar}$.

Pressure and Entropy Relation

Rewriting,

Key Idea

$$P = T\left(\frac{\partial S}{\partial V}\right).$$

i.e. pressure pushes the equilibrium toward the phase that occupies *less* volume – a Le Chatelier-type response.

Classic Physics of Ice Skating (Not Quite Right)

The blade of an ice skate is roughly a few mm wide and on average 25 cm long, giving area $\approx 10\,\text{cm}^2$ per the textbook (hockey skates, with hollow + rocker, contact only $< 0.1\,\text{mm}$, so the area is closer to $0.1\,\text{cm}^2$).

If the skater has mass 100 kg, weight $\approx 1000\,\text{N}$, the pressure under the blade is

$$\frac{1000\,\text{N}}{10^{-5}\,\text{m}^2} = 1 \times 10^8\,\text{Pa} = 1000\,\text{bar}.$$

At that pressure the melting temperature drops only by

$$\frac{1000\,\text{bar}}{135\,\text{bar}/\text{K}} \approx 7^\circ\text{C},$$

which contradicts the textbook number.

Classic claim: skaters glide because increased pressure under the skates melts the ice, forming a thin lubricating water layer.

But the melting point at the ice surface is much lower than in the bulk, so a different mechanism (surface pre-melting) actually dominates.

Phase Transformation of Mixtures

Mixing always increases entropy S, and therefore lowers Gibbs free energy: $G_{\text{mix}} < G_{\text{pure}}$.

Nitrogen liquefies at 77.4 K and oxygen at 90.2 K. If air is cooled to 90.2 K, **nothing happens**. No liquid forms until 81.6 K, and that liquid contains only 48% oxygen. The behaviour of mixtures is not a simple sum of the behaviours of its components.

Ideal Mixing

Let x be the mole fraction of B.

Unmixed system

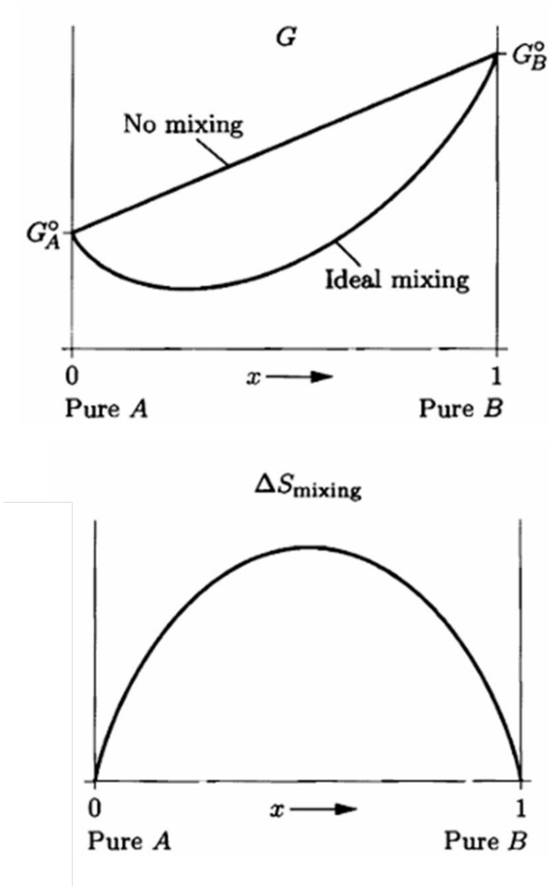
$$G_{\text{unmixed}} = (1-x)G_A + xG_B.$$

Mixed system

$$G_{\text{mixed}} = (1-x)G_A + xG_B + RT\big(x\ln x + (1-x)\ln(1-x)\big).$$

Entropy contribution

$$\Delta S_{\text{mix}} = -R\big(x\ln x + (1-x)\ln(1-x)\big).$$



Ideal-mixing free energy curve as a function of composition.

Non-Ideal Mixing

When unlike molecules mix, they may be more or less attracted to each other than like molecules – think oil and water. The energy change ΔU is then a concave-down function (like ΔS).

Recall $G = U + PV - TS$. At $T = 0$ with P, V constant, ΔG depends entirely on ΔU:

$$\Delta G \approx \Delta U \quad (T = 0).$$

So we expect concave-down behaviour of G vs. composition at $T = 0$.

When $T > 0$, there is a competition between

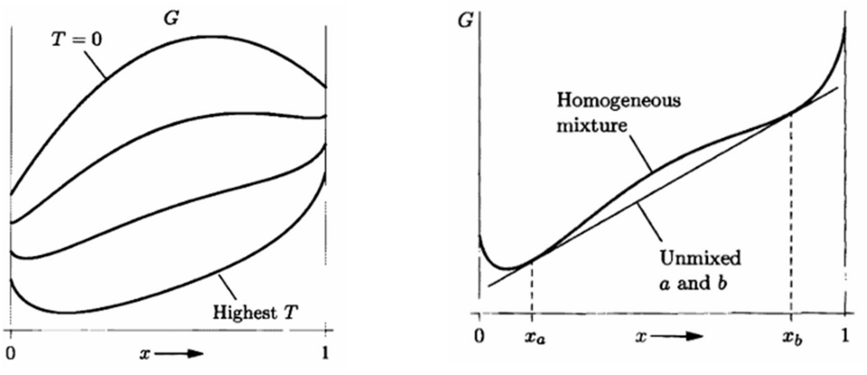
- the concave-*down* contribution from energy U, and
- the concave-*up* contribution from entropy $-T\Delta S$.

As temperature increases, the entropy contribution dominates.

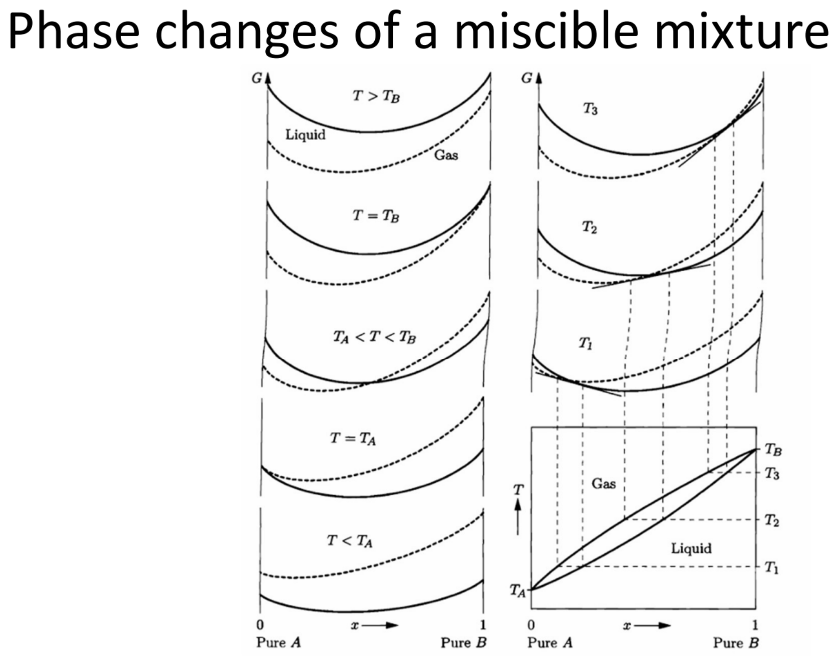
$$\Rightarrow \text{ at high } T, \text{ entropy drives mixing.}$$

Reading the curves:

- Concave down ⇒ immiscible: components prefer to be unmixed to minimise G.
- Concave up ⇒ miscible/soluble: components form a mixture.



Free-energy vs. composition for non-ideal mixing.



Phase changes of a miscible mixture

Phase behaviour of non-ideal mixtures.

1.14 Lecture 14 – Solutions, Osmosis, and Chemical Equilibrium Mar 27

Dilute Solutions and Entropy

Definition

A solution is a special kind of mixture, with a primary component (the *solvent*) and one or more secondary components (the *solutes*). A solution is *dilute* when solute molecules are much less abundant than solvent molecules. Gas mixtures and dilute solutions are entropy-driven mixing processes.

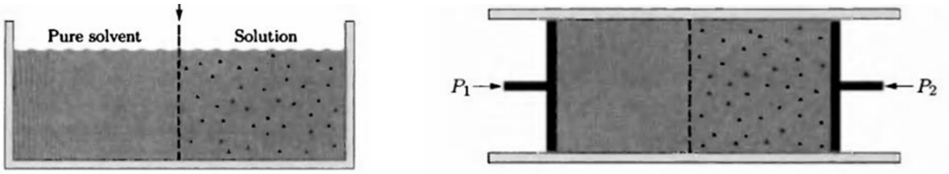
Osmotic Pressure

A solution separated from pure solvent by a semipermeable membrane allows only solvent molecules to pass.

Van 't Hoff Equation

$$\Pi = P_2 - P_1 = i\,\frac{N_B k_B T}{V} = i\,\frac{n_B RT}{V},$$

where n_B/V is the molar concentration of solute and i is the degree of dissociation.



Osmosis across a semipermeable membrane.

Example – Cell in pure water

A cell containing a 0.3 M concentration of non-dissociating sugars is placed in pure water. Calculate the pressure difference required to stop the flow of water. Repeat for 0.3 M NaCl ($i = 2$).
With $M = 0.3\,\text{mol/L} = 300\,\text{mol/m}^3$, $T = 300\,\text{K}$:
Sugar (non-dissociating, $i = 1$):

$$\Delta P = (1)(300)(8.314)(300) \approx 7.5\,\text{bar}.$$

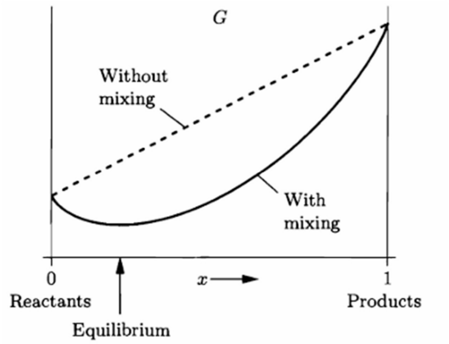
NaCl ($i = 2$):

$$\Delta P = (2)(300)(8.314)(300) \approx 15\,\text{bar}.$$

Chemical Reactions and Equilibrium

Reactions occur when molecules break apart (spontaneously or by collision) or when two reactive molecules collide. Reaction rates depend on reactant availability (concentration) and on diffusion. A reaction reaches equilibrium when the forward and backward rates are equal.

At room temperature and standard atmospheric conditions, the total Gibbs free energy is minimised at equilibrium.



Free-energy minimum at chemical equilibrium.

Example reaction:

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}.$$

At a minimum of $G = U - TS + PV$,

$$dG = 0 = \sum_i \mu_i \, dN_i.$$

The changes in the N_i are not independent. Revisiting our water example, if a single $\mathrm{H_2O}$ molecule dissociates into $\mathrm{H^+}$ and $\mathrm{OH^-}$,

$$dN_{\mathrm{H_2O}} = -1, \quad dN_{\mathrm{H^+}} = +1, \quad dN_{\mathrm{OH^-}} = +1.$$

So

$$0 = \mu_{\mathrm{H_2O}} \, dN_{\mathrm{H_2O}} + \mu_{\mathrm{H^+}} \, dN_{\mathrm{H^+}} + \mu_{\mathrm{OH^-}} \, dN_{\mathrm{OH^-}},$$

or

$$\mu_{\mathrm{H_2O}} = \mu_{\mathrm{H^+}} + \mu_{\mathrm{OH^-}}.$$

This is the equilibrium condition.

General rule:

Equilibrium condition follows reaction stoichiometry.

For example,

$$\mathrm{N_2} + 3\mathrm{H_2} \rightleftharpoons 2\mathrm{NH_3} \implies \mu_{\mathrm{N_2}} + 3\mu_{\mathrm{H_2}} = 2\mu_{\mathrm{NH_3}}.$$

Chemical Potential and Equilibrium Constant

Chemical Potential

Key Idea

$$\mu = \mu^0 + k_B T \ln\left(\frac{P}{P^0}\right),$$

where μ^0 is the chemical potential in the standard state ($P = P^0$, usually 1 atm). This describes how μ changes with pressure or density.

Equilibrium Constant for Nitrogen Fixation

$$k_B T \ln\left(\frac{P_{\mathrm{N}_2}}{P^0}\right) + 3k_B T \ln\left(\frac{P_{\mathrm{H}_2}}{P^0}\right) - 2k_B T \ln\left(\frac{P_{\mathrm{NH}_3}}{P^0}\right) = 2\mu^0_{\mathrm{NH}_3} - \mu^0_{\mathrm{N}_2} - 3\mu^0_{\mathrm{H}_2}.$$

Multiplying by Avogadro's number converts the right-hand side to ΔG^0:

$$RT \ln\left(\frac{P_{\mathrm{N}_2}\, P^3_{\mathrm{H}_2}}{P^2_{\mathrm{NH}_3}\, (P^0)^2}\right) = \Delta G^0.$$

Exponentiating defines the equilibrium constant K (**law of mass action**):

Key Idea

$$\frac{P^2_{\mathrm{NH}_3}\, (P^0)^2}{P_{\mathrm{N}_2}\, P^3_{\mathrm{H}_2}} = e^{-\Delta G^0/(RT)} = K.$$

Le Chatelier's Principle

A system responds to disturbances so as to restore equilibrium. For example: if you double the partial pressures of both N_2 and H_2, the partial pressure of NH_3 must quadruple to maintain equilibrium.

Water Dissociation

$$\Delta G^0 = 79{,}900\,\mathrm{J}, \quad K = e^{-79{,}900/(8.31\cdot 298)} = 10^{-14}, \quad [\mathrm{H}^+] = [\mathrm{OH}^-] = 10^{-7}.$$

Dissolving Oxygen Gas in Water

The dissolution of a gas in a liquid can be treated as a chemical reaction with its own equilibrium constant. The "reaction" is

$$\mathrm{O}_2(g) \leftrightarrow \mathrm{O}_2(\mathrm{aq}), \qquad \Delta G^0 = 16.4\,\mathrm{kJ}.$$

At equilibrium $\mu_{\text{gas}} = \mu_{\text{solute}}$, i.e.

$$\mu^0_{\text{gas}} + k_B T \ln\left(\frac{P}{P^0}\right) = \mu^0_{\text{solute}} + k_B T \ln(m),$$

where m is the molality of dissolved O_2 (mol/kg of water).

Henry's Law

Key Idea

$$\frac{m}{P/P^0} = e^{-\Delta G^0/(RT)}.$$

Substituting $\Delta G^0 = 16400\,\text{J}$, $R = 8.31$, $T = 298$,

$$e^{-16400/(8.31\cdot 298)} = 0.00133 = \frac{1}{750},$$

so

$$m = \frac{1}{750}\cdot\frac{P}{P^0}.$$

Calculation of Dissolved Oxygen Volume

At atmospheric conditions $P_{O_2} \approx P^0/5$, so

$$m = \frac{1}{750}\cdot\frac{1}{5} = \frac{1}{3750}\,\text{mol/kg}.$$

Converting moles to volume (ideal gas, $1\,\text{mol} \approx 24\,\text{L}$),

$$\text{Volume} = \frac{1}{3750}\times 24 = 0.0064\,\text{L} = 6.4\,\text{cm}^3 \approx 7\,\text{cm}^3.$$

Key Idea

Each litre of water contains approximately $7\,\text{cm}^3$ of dissolved O_2.

Part II

Statistical Mechanics

CHAPTER 2

PHY294 Statistical Mechanics Notes

Part II continues the PHY294 lecture sequence, moving from thermodynamics to statistical mechanics. The central object is the **partition function** Z: once we know it, every thermodynamic property follows. We introduce the Boltzmann factor, use it to derive rotational and translational partition functions, prove the equipartition theorem, obtain the Maxwell–Boltzmann speed distribution, and close by rebuilding the thermodynamics of the ideal gas from Z alone.

2.1 Lecture 15 – Boltzmann Factors and the Partition Function Mar 30

Can We Calculate All Thermodynamic Quantities from First Principles?

In Part I we derived thermodynamics from multiplicity in special cases (Einstein solid, ideal gas). The goal now is a *general* recipe: given the energy levels of a system in contact with a heat bath, compute every thermodynamic quantity directly. The central object will be the **partition function** Z.

Boltzmann Statistics = Hot Topic

Demo. Burning calories. How much is 25 calories anyway?

Combustion of Glucose and Boltzmann Factors

$$\mathrm{C_6H_{12}O_6}(s) + 6\,\mathrm{O_2}(g) \;\rightarrow\; 6\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(l).$$

Standard enthalpies of formation:

$$\Delta H_f^\circ[\mathrm{C_6H_{12}O_6}(s)] \approx -1273\,\mathrm{kJ/mol}, \quad \Delta H_f^\circ[\mathrm{CO_2}(g)] = -393.5\,\mathrm{kJ/mol},$$

$$\Delta H_f^\circ[\mathrm{H_2O}(l)] = -285.8\,\mathrm{kJ/mol}, \quad \Delta H_f^\circ[\mathrm{O_2}(g)] = 0 \;\; \text{(standard state)}.$$

The enthalpy of combustion of glucose is $\approx -2800\,\mathrm{kJ/mol}$ or $\approx 700\,\mathrm{kcal/mol}$ ($\approx 700\,\mathrm{Cal}$ on the food scale) – strongly exothermic, a substantial free-energy driving force. One gummi bear is about $25\,\mathrm{Cal} \approx 100\,\mathrm{kJ}$: a huge amount of energy for a small sweet.

Mechanism: Boltzmann Factors

A catalyst lowers the activation barrier so that the thermal population of oxidation pathways along C–C and C–H bonds is non-negligible. Complicated chains of radical formation eventually lead to decarboxylation. **Everything in action depends on Boltzmann weighting factors**, i.e. the probability for a transition to occur.

Direct combustion of sugar requires very high temperatures to overcome the activation barrier in a single step. Cells instead use catalysts (enzymes) to split the oxidation into many small steps with activation energies comparable to $k_B T$ at body temperature, storing some of the released free energy in carrier molecules (ATP, NADH) rather than dumping it as heat.

Key Idea

The probability of any microscopic process occurring is governed by Boltzmann factors of the form $e^{-\Delta E/k_B T}$.

Boltzmann Factors: Probability of a Specific Microstate

Consider an atom in thermal equilibrium with a reservoir of energy U_R at temperature T. The microstates of the atom correspond to its energy levels (e.g. the hydrogen-atom levels $-13.6, -3.4, -1.5, \dots$ eV). Microstates with the same energy share the same probability (degeneracy).

Question. How do we find the most probable energy state when the atom is in contact with a reservoir?

Consider two microstates s_1 and s_2 with energies E_1 and E_2 and probabilities P_1 and P_2.

Combined System is Isolated

For an isolated system, all accessible microstates are equally probable. The atom alone is *not* isolated, but the **[atom + reservoir]** system is. So the fundamental postulate applies to the combined system, not the atom on its own.

We don't care about the specific microscopic arrangements of the reservoir particles. The reservoir has a huge number of equally probable accessible states. What matters is how many states are available to the reservoir (Ω_R) – and this depends on the microstate of the atom, because conserving total energy ties them together.

Denote by $\Omega_R(s_1)$ and $\Omega_R(s_2)$ the multiplicity of the reservoir when the atom sits in s_1 and s_2 respectively. If $E_2 > E_1$, the reservoir has less energy when the atom is in s_2, so $\Omega_R(s_2) < \Omega_R(s_1)$.

Ratio of Probabilities

If $\Omega_R(s_1) = 2\,\Omega_R(s_2)$, there are twice as many accessible combined microstates when the atom is in s_1. Since all combined microstates are equally probable, $P_1 = 2P_2$.

More generally,

$$\frac{P_2}{P_1} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}.$$

Using $S = k_B \ln \Omega \Rightarrow \Omega = e^{S/k_B}$,

$$\frac{P_2}{P_1} = e^{\,(S_R(s_2) - S_R(s_1))/k_B} = e^{\,\Delta S_R/k_B},$$

where ΔS_R is the change in reservoir entropy when the atom transitions from s_1 to s_2.

Evaluating ΔS_R

Because the atom is much smaller than the reservoir, the change is infinitesimal and we use the thermodynamic identity

$$dS_R = \frac{1}{T}(dU_R + P\,dV_R - \mu\,dN_R)\,.$$

The dN term vanishes (no particle exchange) and the dV term is negligible (the volume change of an atom during a transition is tiny compared to its energy change). Hence

$$dS_R = \frac{1}{T}\, dU_R.$$

Energy conservation gives $U_R(s_2) - U_R(s_1) = -[E(s_2) - E(s_1)]$, so

$$\Delta S_R = \frac{1}{T}\left[U_R(s_2) - U_R(s_1)\right] = -\frac{1}{T}\left[E(s_2) - E(s_1)\right].$$

The Boltzmann Factor

Therefore

$$\frac{P_2}{P_1} = e^{-\left(E(s_2)-E(s_1)\right)/k_BT} = \frac{e^{-E(s_2)/k_BT}}{e^{-E(s_1)/k_BT}}.$$

The quantity $e^{-E(s)/k_BT}$ is called the **Boltzmann factor**.

Equivalently,

$$\frac{P_2}{e^{-E(s_2)/k_BT}} = \frac{P_1}{e^{-E(s_1)/k_BT}} = \text{constant} \equiv \frac{1}{Z}.$$

Key Idea

The Boltzmann distribution. For any microstate s of a system at temperature T,

$$\boxed{P(s) = \frac{1}{Z}\, e^{-E(s)/k_BT}.}$$

Normalisation: The Partition Function

Probabilities must sum to unity:

$$\sum_s P(s) = 1 = \frac{1}{Z}\sum_s e^{-E(s)/k_BT},$$

so

$$\boxed{Z = \sum_s e^{-E(s)/k_BT} = \text{sum of all Boltzmann factors.}}$$

Z is the **partition function**.

Z as a State Counter

Set $E_0 = 0$. The ground-state Boltzmann factor is $e^0 = 1$; every excited state gets a factor < 1. So Z counts the ground state fully and adds a fractional count for each excited state proportional to its accessibility. It tells us how many states the system is effectively using at temperature T:

- **Low** T ($k_BT \ll \Delta E$): Boltzmann factors ≈ 0, so $Z \approx 1$ – only the ground state is effectively accessible.

- **High** T ($k_BT \gg \Delta E$): many factors ≈ 1, so Z approaches the total number of states – many states are effectively accessible.

At absolute zero, $Z = 1$; as we heat the system, more states become "affordable" and Z grows.

Only Relative Energy Matters

If we shift all energies by a constant, $E'_s = E_s + E_0$, then

$$Z_{\text{new}} = Z \cdot e^{-E_0/k_BT},$$

and the extra factor cancels from every probability:

$$P_s = \frac{e^{-E'_s/k_BT}}{Z_{\text{new}}} = \frac{e^{-E_s/k_BT} \cdot e^{-E_0/k_BT}}{Z \cdot e^{-E_0/k_BT}} = \frac{1}{Z}\, e^{-E_s/k_BT}.$$

Nature doesn't care where we set the zero of energy. Only relative differences matter.

Example: Thermal Population of H_2O Bending Modes

Example – Water bending mode at room temperature

Assume the bend is harmonic with frequency $\nu = 4.8 \times 10^{13}\,\mathrm{s}^{-1}$. The harmonic levels are $E_n = (n + \frac{1}{2})h\nu$, so the partition function is

$$Z = e^{-h\nu/2k_BT} + e^{-3h\nu/2k_BT} + e^{-5h\nu/2k_BT} + \cdots$$

At $T = 300\,\mathrm{K}$, $h\nu/k_BT = 7.68$, so

$$Z = e^{-3.83} + e^{-11.52} + e^{-19.20} + \cdots = 0.0215 + 9.9 \times 10^{-6} + 4.6 \times 10^{-9} \approx 0.0215.$$

The populations of the first three levels are

$$P_0 \approx 1, \qquad P_1 = \frac{9.9 \times 10^{-6}}{0.0215} \approx 0.00046, \qquad P_2 = \frac{4.6 \times 10^{-9}}{0.0215} \approx 2.1 \times 10^{-7}.$$

Nearly all population sits in the ground state – zero-point motion. This is the enormous effect of Boltzmann factors on level populations, controlled entirely by $\Delta E/k_BT$.

Average Values

The average (expected) energy of a system is

$$\bar{E} = \sum_s E(s)\,P(s) = \frac{1}{Z}\sum_s E(s)\,e^{-E(s)/k_BT}.$$

If a larger system consists of N identical atoms each with average energy $\bar{E}$, the average total energy is

$$U = N\bar{E}.$$

Problem 6.15 – Ten Atoms of Weberium

Example – Ten weberium atoms

Suppose you have 10 atoms of weberium: 4 with energy $0\,\mathrm{eV}$, 3 with $1\,\mathrm{eV}$, 2 with $4\,\mathrm{eV}$, and 1 with $6\,\mathrm{eV}$.

(a) Direct average,

$$\bar{E} = \frac{4\cdot 0 + 3\cdot 1 + 2\cdot 4 + 1\cdot 6}{10} = 1.7\,\mathrm{eV}.$$

(b) The probability that a randomly chosen atom has a given energy:

$$P(0\,\mathrm{eV}) = \tfrac{4}{10}, \quad P(1\,\mathrm{eV}) = \tfrac{3}{10}, \quad P(4\,\mathrm{eV}) = \tfrac{2}{10}, \quad P(6\,\mathrm{eV}) = \tfrac{1}{10}.$$

(c) Using $\bar{E} = \sum_s E(s)P(s)$,

$$\bar{E} = (0)\tfrac{4}{10} + (1)\tfrac{3}{10} + (4)\tfrac{2}{10} + (6)\tfrac{1}{10} = 1.7\,\mathrm{eV},$$

consistent with part (a).

2.2 Lecture 16 – Rotational Partition Function and Free Energy Apr 2

Boltzmann Factors: Rotation of a Diatomic Molecule

Rotational energy is quantised. For a diatomic molecule made of two different atoms,

$$E(j) = j(j+1)\,\varepsilon,$$

where j is a non-negative integer and ε is a constant inversely proportional to the moment of inertia.

QM convention:

$$E_J = B\,J(J+1), \qquad B = \frac{h^2}{8\pi^2 I}, \qquad I = \mu r^2, \qquad \mu = \frac{m_1 m_2}{m_1 + m_2},$$

so $\varepsilon = h^2/(8\pi^2 I)$. Examples include CO, HCl, O_2, NO, N_2.

Degeneracy of Rotational Levels

The number of degenerate states at level j is

$$g_j = 2j + 1.$$

Levels are at energies $0, 2\varepsilon, 6\varepsilon, 12\varepsilon, \ldots$ with degeneracies $1, 3, 5, 7, \ldots$.

Partition Function of the Rotational Energy

Including the degeneracy,

$$Z_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1)\, e^{-E(j)/k_B T} = \sum_{j=0}^{\infty} (2j+1)\, e^{-j(j+1)\varepsilon/k_B T}.$$

For $k_B T \gg \varepsilon$ the levels are closely spaced compared to $k_B T$ and we can replace the sum by an integral,

$$Z_{\text{rot}} \approx \int_0^{\infty} (2j+1)\, e^{-j(j+1)\varepsilon/k_B T}\, dj = \frac{k_B T}{\varepsilon}.$$

Takeaways.

- Z_{rot} increases linearly with temperature.
- The average rotational energy is $\overline{E_{\text{rot}}} = -\frac{1}{Z}\,\partial Z/\partial\beta$ with $\beta = 1/k_B T$, giving

$$\overline{E_{\text{rot}}} = k_B T.$$

This matches equipartition for two rotational degrees of freedom, $\frac{1}{2}k_B T + \frac{1}{2}k_B T$ (see Lecture 2).

Diatomic Molecules of Identical Atoms

For homonuclear diatomics such as O_2 or N_2, rotating the molecule by 180° does not produce a new configuration. In the high-temperature limit we must divide by 2:

$$Z_{\text{rot}} \approx \frac{k_B T}{2\varepsilon}, \qquad \overline{E_{\text{rot}}} = k_B T.$$

The factor of $1/2$ cancels in the derivative that gives the average energy. The same reasoning applies to symmetric linear molecules such as CO_2 (see problem 6.25).

Example – Rotational partition function of CO

For CO, $\varepsilon \approx 0.00024\,\text{eV}$. Compute Z_{rot} at room temperature two ways.

(a) Exact sum (truncated at $j = 30$):

$$\sum_{j=0}^{30} (2j+1)\, e^{-j(j+1)\varepsilon/k_B T} \approx 108.07.$$

(b) Integral approximation:

$$Z_{\text{rot}} \approx \frac{k_B T}{\varepsilon} \approx 107.8.$$

Proving the Equipartition Theorem with Boltzmann Factors

Suppose the energy takes the quadratic form

$$E = cq^2,$$

where c is a constant and q is a coordinate or momentum. For translational motion, $E_k = \frac{1}{2}mv^2$ with $c = \frac{1}{2}m$.

We have been treating states discretely, but q is continuous. Count states by spacing them by a small Δq:

$$Z = \sum e^{-\beta c q^2} = \frac{1}{\Delta q} \sum e^{-\beta c q^2}\, \Delta q.$$

As $\Delta q \to 0$ the Riemann sum becomes

$$Z = \frac{1}{\Delta q} \int e^{-\beta c q^2}\, dq.$$

Change variables $x = q\sqrt{\beta c}$, $dx = \sqrt{\beta c}\, dq$:

$$Z = \frac{1}{\Delta q \sqrt{\beta c}} \int e^{-x^2}\, dx = \frac{1}{\Delta q} \sqrt{\frac{\pi}{\beta c}},$$

using $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$.

Deriving the Average Energy

$$\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}.$$

Take the log,

$$\ln Z = \ln\left(\frac{1}{\Delta q}\sqrt{\frac{\pi}{c}}\right) + \ln(\beta^{-1/2}) = \text{const} - \tfrac{1}{2}\ln\beta,$$

so

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2\beta} = \tfrac{1}{2}k_B T.$$

Key Idea

The constants c and Δq drop out: this is why equipartition is universal. It doesn't matter how stiff the spring is or how heavy the particle – the average energy of each quadratic degree of freedom depends only on T.

Example: Partition Function for H_2O Vibrations

Example – H_2O bending mode, revisited

Water bend mode $\nu = 4.8\times 10^{13}$ Hz; relative occupation at room temperature?
With $h\nu/k_BT = 7.68$ at 300 K,

$$Z = e^{-3.84} + e^{-11.52} + e^{-19.20} + \cdots = 0.0215 + 9.9\times 10^{-6} + 4.6\times 10^{-9} + \cdots \approx 0.0215,$$

$$P_1 = \frac{9.9\times 10^{-6}}{0.0215} = 0.00046, \qquad P_2 = \frac{4.6\times 10^{-9}}{0.0215} = 2.1\times 10^{-7}.$$

More precisely $P_0 = 1 - P_1 \approx 0.99954$ – nearly all population sits in the zero-point ($n = 0$) level.

Partition Functions and Free Energy

Isolated system (fixed U)	**System at fixed T (reservoir)**
Multiplicity Ω is the number of accessible states; maximise it.	Partition function Z is the *effective* number of accessible states.
Entropy S tends to **increase**.	Helmholtz free energy F tends to **decrease**.

The log of multiplicity is entropy. What is the log of Z? We now establish $F = -k_BT\ln Z$.

Proof 1 (Gibbs entropy)

Recall the Gibbs entropy formula and the Boltzmann probability,

$$S = -k_B\sum_s P(s)\ln[P(s)], \qquad P(s) = \frac{1}{Z}e^{-\beta E_s}.$$

Then

$$S = -k_B \sum_s P(s) \ln\left(\frac{1}{Z}\, e^{-\beta E_s}\right).$$

Using $\ln(a/b) = \ln a - \ln b$ and distributing the sum,

$$S = k_B \beta \sum_s P(s)\, E_s + k_B \ln Z \sum_s P(s).$$

Since $\sum_s P(s) E_s = U$, $\sum_s P(s) = 1$, and $\beta = 1/k_B T$,

$$TS = U + k_B T \ln Z \iff -k_B T \ln Z = U - TS = F.$$

Key Idea

$$\boxed{F = -k_B T \ln Z.}$$

Practical use: calculate S for gases without a heat-engine cycle.

Proof 2 (Schroeder)

Recall $F = U - TS$ and $(\partial F/\partial T)_{V,N} = -S$. Together these give

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F - U}{T}.$$

Show that $F = -k_B T \ln Z$ satisfies this relation.

$$\frac{\partial(-k_B T \ln Z)}{\partial T} = -k_B \ln Z - k_B T \,\frac{\partial \ln Z}{\partial T}.$$

By the chain rule with $\beta = 1/k_B T$ (so $\partial\beta/\partial T = -1/(k_B T^2)$),

$$\frac{\partial \ln Z}{\partial T} = \frac{\partial \beta}{\partial T}\,\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{k_B T^2}\,\frac{1}{Z}\,\frac{\partial Z}{\partial \beta} = \frac{U}{k_B T^2},$$

using $\bar{E} = -(1/Z)\,\partial Z/\partial\beta$, with U the average energy. Then

$$\frac{\partial(-k_B T \ln Z)}{\partial T} = -k_B \ln Z - k_B T \cdot \frac{U}{k_B T^2} = -\frac{k_B T \ln Z}{T} - \frac{U}{T} = \frac{F - U}{T},$$

as required.

Thermodynamic Properties From Z

Once we have Z, every thermodynamic property follows:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}, \qquad F = -k_B T \ln Z.$$

Partition Function of Composite Systems

Two Non-Interacting Distinguishable Particles

Let s_1 be the state of particle A and s_2 the state of particle B, with total energy $E = E_A(s_1) + E_B(s_2)$. The system's states are all pairs (s_1, s_2), so

$$Z_{\text{total}} = \sum_{s_1} \sum_{s_2} e^{-\beta E_A(s_1)}\, e^{-\beta E_B(s_2)} = Z_A\, Z_B.$$

Two Non-Interacting Indistinguishable Particles

Swapping A and B produces the same physical state, so each configuration is counted twice:

$$Z_{\text{total}} = \tfrac{1}{2}\, Z_A\, Z_B.$$

Generalisation to N Particles

Key Idea

Non-interacting distinguishable particles:

$$Z_{\text{total}} = Z_A\, Z_B\, Z_C \cdots Z_N.$$

Non-interacting indistinguishable particles:

$$Z_{\text{total}} = \frac{1}{N!}\, Z_A^N.$$

2.3 Lecture 17 – Maxwell–Boltzmann Distribution and the Ideal Gas Revisited

Apr 6

Velocity Distribution

From the kinetic theory,

$$v_{\text{RMS}} = \sqrt{\frac{3k_BT}{m}}.$$

But we want the full *distribution* of molecular speeds, not just the RMS.

The probability that a molecule occupies the microstate with velocity vector (v_x, v_y, v_z) is given by the Boltzmann factor

$$P(\vec{v}) \propto e^{-E(s)/k_BT},$$

with $E = \frac{1}{2}mv^2$ and $v = |\vec{v}|$. So

$$P(\vec{v}) \propto e^{-mv^2/2k_BT}.$$

This peaks at $\vec{v} = 0$: the most probable *velocity vector* is the zero vector. How do we reconcile this with the intuition that molecules move at high speeds at room temperature?

Speed vs. Velocity

We don't care about the *direction* of motion, only the *speed*,

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}.$$

There are many more combinations of (v_x, v_y, v_z) producing a high speed than a low speed. The volume of velocity-space between v and $v + dv$ is a spherical shell,

$$dV = 4\pi v^2\, dv,$$

which acts as a geometric degeneracy factor:

$$P(v)\, dv = (\text{Boltzmann factor}) \times (\text{degeneracy factor}).$$

Normalisation

We require $\int_0^\infty P(v)\, dv = 1$:

$$\int_0^\infty A \cdot 4\pi v^2 e^{-mv^2/2k_BT}\, dv = 1.$$

Using standard Gaussian integrals,

$$A = \left(\frac{m}{2\pi k_BT}\right)^{3/2}.$$

Key Idea

Maxwell–Boltzmann speed distribution:

$$\boxed{P(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \, e^{-mv^2/2k_B T}.}$$

Three Characteristic Speeds

The distribution is parabolic at small v and dies exponentially at large v.

Most probable speed. Set $dP(v)/dv = 0$:

$$v_p = \sqrt{\frac{2k_B T}{m}}.$$

Average speed. $\bar{v} = \int_0^\infty v \, P(v) \, dv$:

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}.$$

RMS speed.

$$v_{\text{RMS}} = \sqrt{\frac{3k_B T}{m}}.$$

These satisfy $v_p < \bar{v} < v_{\text{RMS}}$.

Revisiting the Ideal Gas

With the machinery of the partition function in hand, we can now derive *all* the thermodynamic properties of a monatomic ideal gas starting only from Z. Start with the simplest system: a single atom in a box of volume V.

Single-Atom Partition Function

For a particle in a 3D box of side L, the energy levels are

$$E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right).$$

Approximating the sum by an integral,

$$Z_1 = \int_0^\infty \int_0^\infty \int_0^\infty dn_x \, dn_y \, dn_z \, e^{-\beta \frac{h^2}{8mL^2}(n_x^2+n_y^2+n_z^2)} = \left[\sqrt{\frac{2\pi m k_B T}{h^2}}\, L\right]^3.$$

Quantum Volume

Define the **quantum volume**

$$v_q = \left(\sqrt{\frac{h^2}{2\pi m k_B T}}\right)^3 = \left(\frac{h^2}{2\pi m k_B T}\right)^{3/2},$$

so that

$$Z_1 = \frac{V}{v_q}.$$

Key Idea

v_q is the threshold at which classical physics breaks down: it is the volume of a cube whose side is the thermal de Broglie wavelength of a particle with kinetic energy $k_B T$. The translational partition function Z_1 counts how many such quantum cubes fit inside the box.

Extending to N Atoms

Atoms of a single species are indistinguishable, so

$$Z_N = \frac{1}{N!}\,(Z_1)^N = \frac{1}{N!}\left(\frac{V}{v_q}\right)^N.$$

This is the **Boltzmann limit**; it holds when $V/N \gg v_q$ (the gas is dilute). Once atoms start to overlap, quantum statistics (Bose–Einstein or Fermi–Dirac) take over.

Extending to N Molecules

The preceding formula is for monatomic gases, for which there are no internal degrees of freedom. For polyatomic gases like N_2, include an extra factor Z_{int} for rotation, vibration, etc.:

$$Z_N = \frac{1}{N!}\left(\frac{V\,Z_{\text{int}}}{v_q}\right)^N.$$

Thermodynamics From the Partition Function

Internal energy

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}.$$

Substituting and differentiating,

$$U = -N\frac{\partial \ln Z_{\text{int}}}{\partial \beta} + N\,\frac{1}{v_q}\,\frac{\partial v_q}{\partial \beta} = N\,\overline{E_{\text{int}}} + \tfrac{3}{2}\,N k_B T = U_{\text{int}} + \tfrac{3}{2}\,N k_B T.$$

Here $\overline{E_{\text{int}}}$ is the average internal energy of a molecule, and the translational contribution is $\frac{3}{2}k_B T$ per atom – exactly equipartition.

Heat capacity at constant volume

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial U_{\text{int}}}{\partial T} + \tfrac{3}{2} N k_B.$$

Helmholtz free energy

$$F = -k_B T \ln Z = -N k_B T \left[\ln V - \ln N - \ln v_q + 1\right] + F_{\text{int}},$$

where $F_{\text{int}} = -N k_B T \ln Z_{\text{int}}$ is the internal-degree contribution.

Pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V} \qquad \Longrightarrow \qquad PV = N k_B T.$$

We recover the ideal gas law directly from the partition function.

Entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = N k_B \left[\ln\left(\frac{V}{N v_q}\right) + \tfrac{5}{2}\right] - \frac{\partial F_{\text{int}}}{\partial T}.$$

This is the Sackur–Tetrode formula (plus internal-mode corrections).

Chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \ln\left(\frac{V Z_{\text{int}}}{N v_q}\right).$$

Key Idea

Knowing $Z(T, V, N)$ is equivalent to knowing all of thermodynamics. One expression – the partition function – yields the equation of state, entropy, heat capacity, chemical potential, and free energies.

End of the Course

FINIS – Good luck in the partition functions of life. It's a probability, after all.