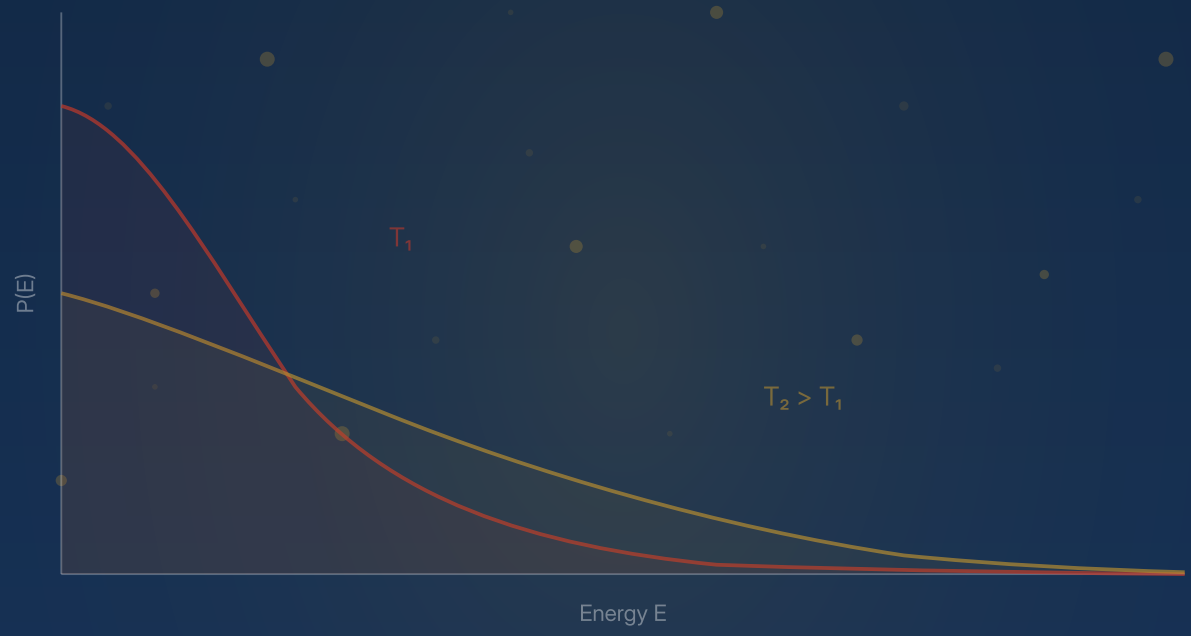
STATISTICAL PHYSICS

From Microstates to Ensembles

$$S = k_B \ln \Omega$$



GAURAV TIWARI

Statistical Physics: From Microstates to Ensembles

A Comprehensive Introduction

Gaurav Tiwari

"If you are not confused by quantum mechanics, you have not really understood it."

"The entropy of the universe tends to a maximum."

— Ludwig Boltzmann's tombstone bears the inscription $S = k \log W$

Based on articles from https://gauravtiwari.org

Compiled and expanded: February 2026

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Abstract

Statistical physics provides the bridge between the microscopic world of atoms and molecules and the macroscopic world of thermodynamics. This monograph offers a self-contained introduction to the subject, beginning with the fundamental distinction between macrostates and microstates, developing the concept of thermodynamic probability, and building systematically toward the three great ensembles of statistical mechanics: microcanonical, canonical, and grand canonical.

We present detailed derivations of the Boltzmann entropy formula $S = k_{\mathrm{B}} \ln W$, the canonical partition function and its connection to Helmholtz free energy, and the grand partition function with its role in open systems. Worked examples—including the ideal gas, quantum harmonic oscillators, two-level systems, and paramagnetic spins—illustrate each concept concretely. Throughout, we emphasise the logical structure that connects counting arguments to the full apparatus of thermodynamics.

Keywords: Statistical mechanics, macrostates, microstates, thermodynamic probability, entropy, ensembles, partition function, Boltzmann distribution, Fermi–Dirac statistics, Bose–Einstein statistics

1 Introduction to Statistical Physics

1.1 Why Statistical Methods?

A macroscopic system—a glass of water, a block of iron, or the air in a room—contains on the order of 10^{23} particles. Even if we knew the exact Hamiltonian governing every interaction, solving $\sim 10^{23}$ coupled equations of motion is utterly impossible. Statistical physics sidesteps this problem by asking not "what will each particle do?" but rather "what are the *probable* configurations of the system as a whole?"

The key insight is that macroscopic observables (pressure, temperature, magnetisation) are averages over the enormous number of microscopic configurations available to the system. Because the number of configurations is so vast, fluctuations about the average are negligibly small for large systems, and the statistical predictions become effectively deterministic. This is the fundamental reason thermodynamics—a theory that makes no reference to atoms—works so extraordinarily well.

Remark 1.1. The transition from microscopic to macroscopic is not merely a matter of convenience. It reveals *emergent* phenomena—phase transitions, spontaneous symmetry breaking, universality—that have no counterpart at the single-particle level.

1.2 Historical Overview

The development of statistical physics is one of the great intellectual achievements of the 19th and early 20th centuries. Three figures stand above all others.

1.2.1 James Clerk Maxwell (1831–1879)

Maxwell was the first to apply probability theory to physics in a systematic way. In 1860 he derived the distribution of molecular speeds in a gas—the Maxwell speed distribution:

$$f(v) = 4\pi n \left(\frac{m}{2\pi k_{\mathrm{B}} T}\right)^{3/2} v^2 \exp\!\left(-\frac{m v^2}{2 k_{\mathrm{B}} T}\right) \tag{1}$$

where n is the number density, m the molecular mass, and T the temperature. This was the first instance of a probability distribution being used to describe a physical system.

Maxwell's insight was revolutionary: he recognised that one need not track individual molecules. The distribution function contains all the information required to compute macroscopic quantities such as pressure and viscosity.

1.2.2 Ludwig Boltzmann (1844–1906)

Boltzmann elevated Maxwell's ideas into a comprehensive framework. His major contributions include:

1. The Boltzmann transport equation (1872): A kinetic equation describing the time evolution of the distribution function in phase space, including the effects of collisions.

2. The H-theorem (1872): A proof that a certain functional H (related to entropy) can only decrease over time for a gas obeying the transport equation, providing a microscopic basis for the Second Law of Thermodynamics.

3. The entropy formula $S = k_{\mathrm{B}} \ln W$ (1877): The cornerstone of statistical mechanics, relating the macroscopic concept of entropy to the microscopic count of accessible microstates W. This formula is engraved on Boltzmann's tombstone in the Zentralfriedhof, Vienna.

4. The Boltzmann distribution: The probability that a system in thermal equilibrium at temperature T occupies a microstate with energy E_i is proportional to $e^{-E_i/k_{\mathrm{B}}T}$.

Boltzmann faced fierce opposition, particularly from Ernst Mach and the energeticists who denied the reality of atoms. The attacks contributed to his declining mental health; he took his own life in 1906, tragically just a few years before experiments on Brownian motion (Einstein, 1905; Perrin, 1908) vindicated the atomic hypothesis beyond doubt.

1.2.3 Josiah Willard Gibbs (1839–1903)

Gibbs placed statistical mechanics on a rigorous mathematical foundation. His 1902 monograph *Elementary Principles in Statistical Mechanics* introduced the concept of an ensemble—an imaginary collection of copies of a system, all satisfying the same macroscopic constraints but differing in their microscopic configurations. Gibbs defined:

- The microcanonical ensemble for isolated systems (fixed E, V, N).
- The canonical ensemble for systems in thermal contact with a reservoir (fixed T, V, N).
- The grand canonical ensemble for open systems (fixed T, V, μ).

Gibbs's formulation is remarkable for its generality: it applies equally well to classical and quantum systems, and to systems with any number of degrees of freedom.

1.3 The Programme of Statistical Mechanics

The central programme of statistical mechanics can be summarised as follows:

1. Specify the system: Identify the relevant degrees of freedom and the Hamiltonian $H(q_1, \ldots, q_f; p_1, \ldots, p_f)$.
2. Choose an ensemble: Select the ensemble appropriate to the physical constraints (isolation, thermal contact, particle exchange).
3. Compute the partition function: Evaluate the relevant partition function (Ω, Z, or $\mathcal{Z}$) by summing or integrating over microstates.
4. Extract thermodynamics: Derive all thermodynamic quantities from the partition function via standard relations.

The power of this programme is that step 4 is entirely mechanical once step 3 is completed. The art lies in step 3.

2 Fundamental Concepts

2.1 Phase Space

Definition 2.1 (Phase Space). The phase space of a mechanical system with f degrees of freedom is the $2f$-dimensional space spanned by the generalised coordinates $q_1, q_2, \ldots, q_f$ and their conjugate momenta $p_1, p_2, \ldots, p_f$. A single point in phase space, called a representative point or phase point, specifies the complete microscopic state of the system at a given instant.

For a system of N point particles in three dimensions, $f = 3N$, and phase space has $6N$ dimensions. For a mole of gas ($N \approx 6 \times 10^{23}$), phase space has approximately 3.6×10^{24} dimensions—an unimaginably vast space.

Example 2.1. Consider a single particle of mass m moving in one dimension under a potential $V(q)$. The phase space is two-dimensional, with coordinates (q, p). The Hamiltonian is

$$H(q, p) = \frac{p^2}{2m} + V(q). \tag{2}$$

Trajectories in phase space are the curves of constant H (for conservative systems). For a harmonic oscillator, $V(q) = \frac{1}{2}m\omega^2 q^2$, these trajectories are ellipses.

Remark 2.1. Liouville's theorem states that the phase-space density of a Hamiltonian system is conserved along trajectories:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{H, \rho\} = 0 \tag{3}$$

where $\{\cdot, \cdot\}$ denotes the Poisson bracket. This is the classical analogue of the quantum-mechanical von Neumann equation, and it underpins the use of ensembles in statistical mechanics.

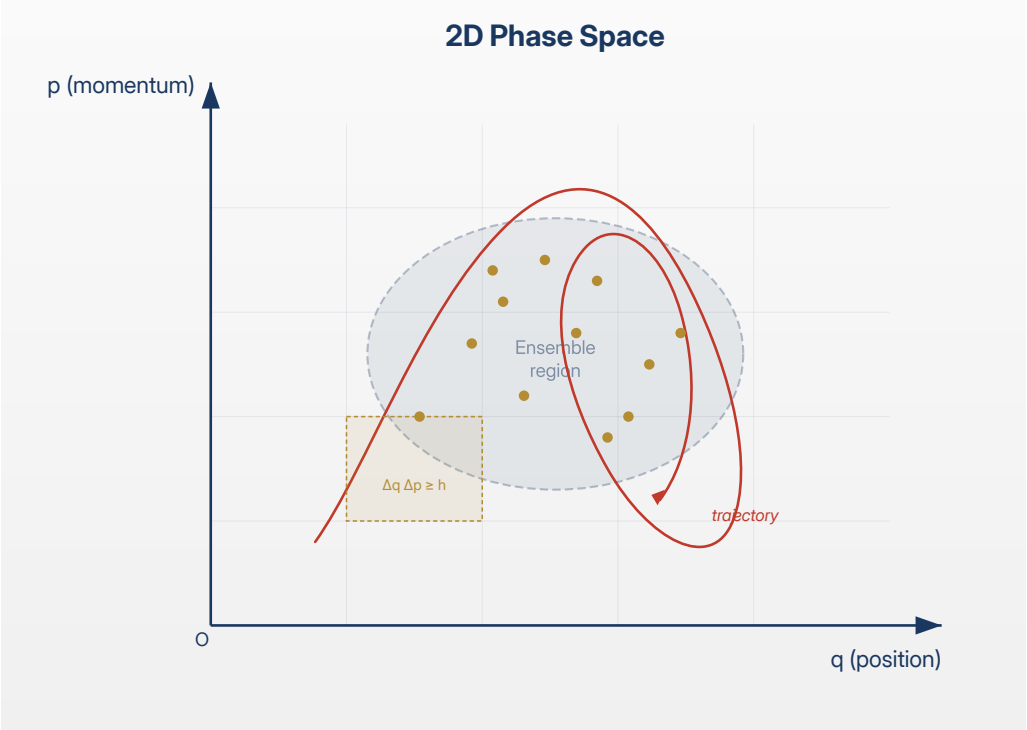

Figure 1: Two-dimensional phase space for a single particle. Each point (q, p) represents a complete microstate. For a harmonic oscillator, trajectories of constant energy form ellipses.

2.2 Degrees of Freedom and Constraints

Definition 2.2 (Degrees of Freedom). The number of degrees of freedom f of a system is the number of independent coordinates required to specify its configuration completely.

Example 2.2. 1. A single free particle in 3D: $f = 3$.

2. N free particles in 3D: $f = 3N$.

3. A rigid body: $f = 6$ (3 translational + 3 rotational).

4. A diatomic molecule (modelled as two point masses connected by a rigid rod): $f = 5$ (3 translational + 2 rotational; the third rotation about the bond axis contributes negligibly at ordinary temperatures).

5. A diatomic molecule with vibration: $f = 7$ (3 translational + 2 rotational + 1 vibrational coordinate + 1 vibrational momentum).

Constraints reduce the number of degrees of freedom. A holonomic constraint can be written as $g(q_1, \ldots, q_N, t) = 0$; each such constraint reduces f by one. For example, requiring a particle to move on a sphere ($x^2 + y^2 + z^2 = R^2$) reduces f from 3 to 2.

2.3 Accessible States and the Fundamental Postulate

Definition 2.3 (Accessible Microstate). A microstate is accessible to a system if it is consistent with the macroscopic constraints (energy, volume, particle number, etc.) imposed on the system.

> The Fundamental Postulate of Statistical Mechanics (Equal A Priori Probability):
> For an isolated system in equilibrium, all accessible microstates are equally probable.

This postulate cannot be derived from mechanics alone; it is an additional assumption justified by its consequences. From it, the entire edifice of equilibrium statistical mechanics follows.

The postulate implies that the probability of finding the system in any particular accessible microstate is

$$P_i = \frac{1}{\Omega(E, V, N)} \tag{4}$$

where $\Omega(E, V, N)$ is the total number of accessible microstates—the density of states or statistical weight.

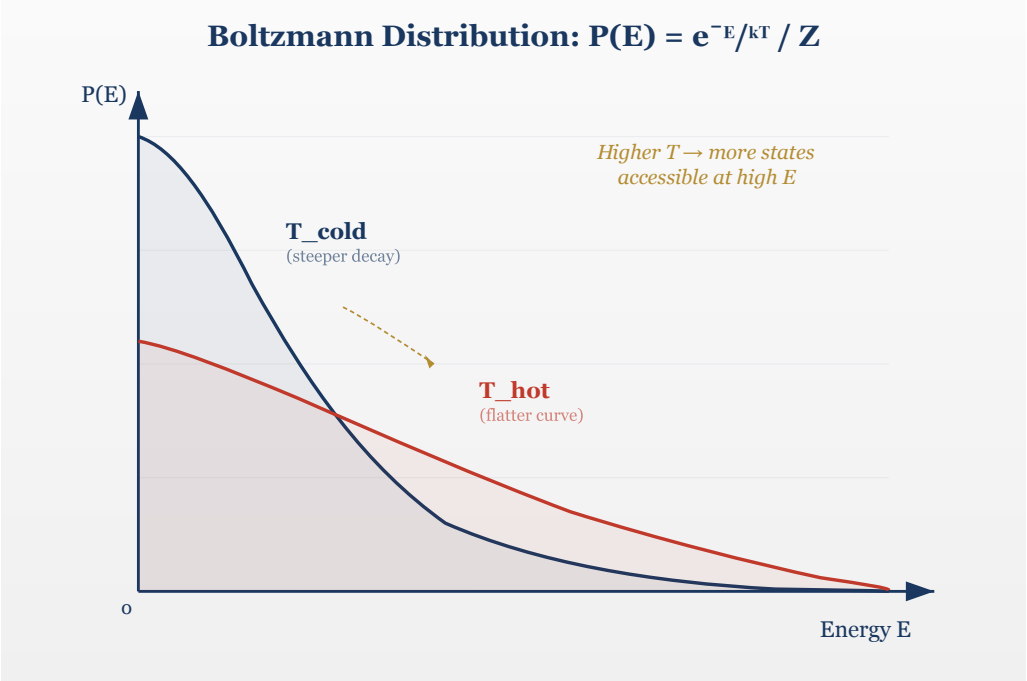

Figure 2: The Boltzmann distribution: the probability of a microstate decreases exponentially with its energy E_i. At higher temperatures the distribution broadens, populating higher-energy states more significantly.

Remark 2.2. The fundamental postulate is closely related to ergodicity: the assumption that the time average of an observable equals its ensemble average. For many systems, ergodicity can be proved rigorously; for others, it remains an assumption. In practice, the postulate is validated by the agreement between its predictions and experiment.

2.4 Quantum States and the Classical Limit

In quantum mechanics, the accessible microstates are the energy eigenstates of the Hamiltonian. For a particle in a box of volume $V = L^3$, the single-particle energy levels are

$$\epsilon_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2), \qquad n_x, n_y, n_z = 1, 2, 3, \ldots \tag{5}$$

In the classical limit (high temperature, low density), the spacing between quantum levels becomes much smaller than $k_B T$, and we can replace sums over discrete states by integrals over phase space:

$$\sum_{\text{states}} \longrightarrow \frac{1}{h^f} \int dq_1 \cdots dq_f \, dp_1 \cdots dp_f \tag{6}$$

where h is Planck's constant and the factor h^{-f} ensures the correct classical limit of quantum-mechanical counting.

For N identical particles, we must additionally divide by $N!$ to avoid overcounting permutations (the Gibbs factor):

$$\sum_{\text{states}} \longrightarrow \frac{1}{N!\, h^{3N}} \int d^{3N}q \, d^{3N}p \tag{7}$$

3 Macrostates and Microstates

3.1 Definitions

Definition 3.1 (Macrostate). A macrostate of a system is specified by a set of macroscopic variables (such as energy, volume, number of particles, magnetisation, or the distribution of particles among compartments). A macrostate describes the *overall* configuration without specifying which particular particles are where.

Definition 3.2 (Microstate). A microstate of a system is a complete specification of the state of every constituent particle. In classical mechanics, a microstate is a point in phase space; in quantum mechanics, it is a vector in Hilbert space (or, equivalently, a set of quantum numbers for all particles).

The central relationship is that *many microstates can correspond to the same macrostate*. The number of microstates corresponding to a given macrostate is the thermodynamic probability (or statistical weight) W of that macrostate.

3.2 Illustrative Example: Four Particles in Two Compartments

Consider four distinguishable particles a, b, c, d distributed into two identical compartments. Each particle independently has a 50/50 chance of being in either compartment.

3.2.1 Enumerating Macrostates

A macrostate is specified by the pair $(r, 4-r)$, where r particles are in compartment 1. There are five macrostates:

Macrostate	Distribution	Notation
1	0 in C1, 4 in C2	$(0,4)$
2	1 in C1, 3 in C2	$(1,3)$
3	2 in C1, 2 in C2	$(2,2)$
4	3 in C1, 1 in C2	$(3,1)$
5	4 in C1, 0 in C2	$(4,0)$

Table 1: Macrostates for four particles in two compartments.

Remark 3.1. For n particles in two compartments, the number of macrostates is $n+1$. More generally, for n particles in k compartments, the number of macrostates equals the number of ways to write n as an ordered sum of k non-negative integers, which is $\binom{n+k-1}{k-1}$.

3.2.2 Enumerating Microstates

Within each macrostate, we list the specific particle assignments:

Macrostate	Compartment 1	Compartment 2	Microstates W
$(0,4)$	—	$\{a,b,c,d\}$	1
$(1,3)$	$\{a\}$ or $\{b\}$ or $\{c\}$ or $\{d\}$	remaining three	4
$(2,2)$	$\{a,b\}, \{a,c\}, \{a,d\}, \{b,c\}, \{b,d\}, \{c,d\}$	remaining two	6
$(3,1)$	any three particles	remaining one	4
$(4,0)$	$\{a,b,c,d\}$	—	1

Table 2: Microstates within each macrostate.

Total microstates: $1+4+6+4+1 = 16 = 2^4$.

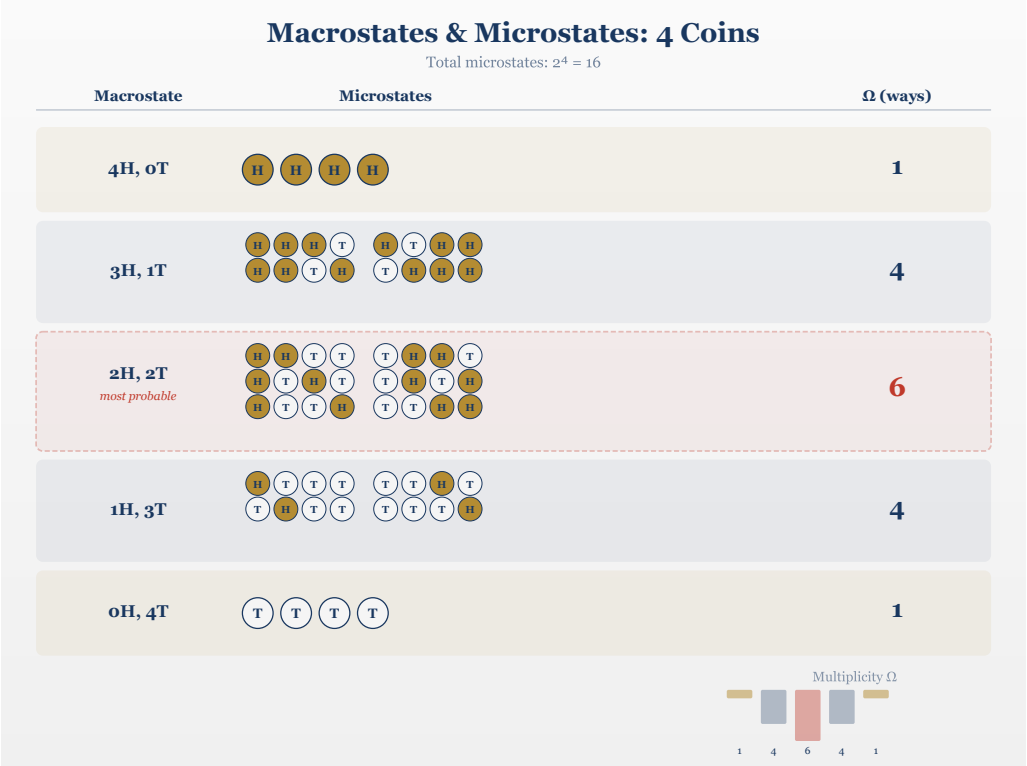

Figure 3: Macrostates and microstates illustrated with coin flips. Each macrostate (number of heads) can be realised by multiple microstates (specific arrangements), with the most balanced distribution having the greatest thermodynamic probability.

Theorem 3.1 (Total Microstates for Two Compartments). For n distinguishable particles distributed among two compartments, the total number of microstates is 2^n.

Proof. Each particle independently chooses one of two compartments, giving $\underbrace{2 \times 2 \times \cdots \times 2}_{n} = 2^n$ configurations. □

3.2.3 The Counting Formula

Theorem 3.2 (Binomial Counting). The number of microstates corresponding to macrostate $(r, n-r)$ is:

$$W(r) = \binom{n}{r} = \frac{n!}{r!(n-r)!} \tag{8}$$

Proof. We must choose which r of the n distinguishable particles go into compartment 1; the remaining $n - r$ go into compartment 2. The number of ways to make this choice is $\binom{n}{r}$. □

Example 3.1 (Verification). For $n = 4$:

$$W(0) = \binom{4}{0} = 1, \qquad W(1) = \binom{4}{1} = 4, \qquad W(2) = \binom{4}{2} = 6, \tag{9}$$

$$W(3) = \binom{4}{3} = 4, \qquad W(4) = \binom{4}{4} = 1. \tag{10}$$

Total: $1 + 4 + 6 + 4 + 1 = 16 = 2^4$. ?

This is a particular case of the binomial theorem: $\sum_{r=0}^{n} \binom{n}{r} = 2^n$.

Remark 3.2. The symmetry $\binom{n}{r} = \binom{n}{n-r}$ implies that macrostates $(r, n-r)$ and $(n-r, r)$ have the same thermodynamic probability. This reflects the physical equivalence of the two compartments.

3.3 Thermodynamic Probability

Definition 3.3 (Thermodynamic Probability). The thermodynamic probability W (also denoted Ω) of a macrostate is the number of microstates that realise it. Despite its name, W is not a probability in the mathematical sense—it is a non-negative integer that can be much greater than 1.

For the two-compartment model:

$$W_{(r,n-r)} = \binom{n}{r} = \frac{n!}{r!(n-r)!} \tag{11}$$

Example 3.2 (Dice Analogy). Roll two distinguishable dice. A "macrostate" is the sum S of the faces. There are $6^2 = 36$ microstates (ordered pairs (i, j) with $1 \le i, j \le 6$).

- $S = 2$: only $(1, 1)$, so $W = 1$.
- $S = 7$: $(1, 6), (2, 5), (3, 4), (4, 3), (5, 2), (6, 1)$, so $W = 6$.
- $S = 12$: only $(6, 6)$, so $W = 1$.

The macrostate $S = 7$ has the largest W and is therefore most probable. In a room full of gamblers, this is why seven comes up most often.

3.4 Actual Probability of a Macrostate

If all microstates are equally probable (the fundamental postulate), the probability of observing a particular macrostate is:

$$P_m = \frac{W_m}{\sum_{\text{all macrostates}} W_m} = \frac{W_m}{\Omega_{\text{total}}} \tag{12}$$

For the two-compartment model with equal-probability compartments:

$$P_{(r,n-r)} = \frac{\binom{n}{r}}{2^n} \tag{13}$$

Macrostate	W	Probability P	Percentage
$(0, 4)$	1	1/16	6.25%
$(1, 3)$	4	$4/16 = 1/4$	25%
$(2, 2)$	6	$6/16 = 3/8$	37.5%
$(3, 1)$	4	$4/16 = 1/4$	25%
$(4, 0)$	1	1/16	6.25%

Table 3: Probabilities for four particles in two compartments.

Sanity check: $1/16 + 4/16 + 6/16 + 4/16 + 1/16 = 16/16 = 1$. ?

3.5 The Most Probable Macrostate

Theorem 3.3. For n distinguishable particles in two equal compartments:

1. If n is even, the most probable macrostate is $(n/2, n/2)$ with probability

$$P_{\max} = \frac{1}{2^n}\binom{n}{n/2}. \tag{14}$$

2. If n is odd, the two most probable macrostates are $(\frac{n+1}{2}, \frac{n-1}{2})$ and $(\frac{n-1}{2}, \frac{n+1}{2})$, each with probability

$$P_{\max} = \frac{1}{2^n}\binom{n}{(n-1)/2}. \tag{15}$$

Proof. The function $\binom{n}{r}$ is maximised at $r = n/2$ (for n even) or at $r = (n \pm 1)/2$ (for n odd). This follows from examining the ratio $\binom{n}{r+1}/\binom{n}{r} = (n-r)/(r+1)$, which is greater than 1 when $r < (n-1)/2$ and less than 1 when $r > (n-1)/2$. □

3.6 The Large-n Limit and the Second Law

For small n, improbable macrostates are merely unlikely. For large n, they become essentially impossible.

Example 3.3 (Scaling with System Size). Consider the macrostate with all particles in one compartment: $W = 1$, so $P = 2^{-n}$.

- $n = 4$: $P = 1/16 = 6.25\%$ — happens occasionally.
- $n = 20$: $P \approx 10^{-6}$ — roughly one in a million.
- $n = 100$: $P \approx 10^{-30}$ — effectively never.
- $n = 10^{23}$: $P \approx 10^{-10^{22}}$ — a number so small it defies comprehension.

Meanwhile, using Stirling's approximation, the most probable macrostate $(n/2, n/2)$ has $P_{\max} \approx \sqrt{2/(\pi n)}$, which shrinks slowly. But relative to any other macrostate, the even split dominates overwhelmingly.

> Statistical Basis of the Second Law:
> Systems evolve toward macrostates with the largest thermodynamic probability W not because of any mysterious force, but because such macrostates are overwhelmingly more probable. For macroscopic systems ($n \sim 10^{23}$), the most probable macrostate is so much more probable than any alternative that deviations are never observed in practice.

3.7 Generalisation to Multiple Compartments

Theorem 3.4 (Multinomial Counting). For n distinguishable particles distributed among k compartments with n_i particles in compartment i ($\sum_{i=1}^{k} n_i = n$), the number of microstates is:

$$W = \frac{n!}{n_1!\, n_2! \cdots n_k!} = \binom{n}{n_1, n_2, \ldots, n_k} \tag{16}$$

This is the multinomial coefficient.

Proof. Choose n_1 particles for compartment 1 in $\binom{n}{n_1}$ ways, then n_2 for compartment 2 in $\binom{n-n_1}{n_2}$ ways, and so on. The product telescopes to $n!/(n_1! \cdots n_k!)$. □

Example 3.4 (Energy Distribution). Consider distributing 4 quanta of energy among 3 distinguishable oscillators. A macrostate is specified by (n_1, n_2, n_3) with $n_1 + n_2 + n_3 = 4$. Some macrostates

and their thermodynamic probabilities:

$$W(4,0,0) = \frac{4!}{4! \cdot 0! \cdot 0!} = 1 \tag{17}$$

$$W(2,1,1) = \frac{4!}{2! \cdot 1! \cdot 1!} = 12 \tag{18}$$

$$W(2,2,0) = \frac{4!}{2! \cdot 2! \cdot 0!} = 6 \tag{19}$$

$$W(1,1,2) = \frac{4!}{1! \cdot 1! \cdot 2!} = 12 \tag{20}$$

The most uniform distribution has the highest W.

4 The Boltzmann Entropy

4.1 Motivation: Why Logarithm?

Thermodynamic entropy is extensive: $S(2E, 2V, 2N) = 2S(E, V, N)$. But if we combine two independent systems, their microstates *multiply*: $W_{\text{total}} = W_1 \times W_2$. We need a function that converts a multiplicative quantity into an additive one. The logarithm is the unique continuous function (up to a multiplicative constant) satisfying $f(xy) = f(x) + f(y)$.

4.2 Boltzmann's Entropy Formula

Boltzmann's Entropy Formula:

$$S = k_{\text{B}} \ln W \tag{21}$$

where $k_{\text{B}} = 1.380649 \times 10^{-23}$ J/K is Boltzmann's constant and W is the thermodynamic probability (number of microstates) of the macrostate.

Theorem 4.1 (Derivation of $S = k_{\text{B}} \ln W$). If we require:

1. S depends only on W: $S = f(W)$.
2. S is additive for independent systems: $f(W_1 W_2) = f(W_1) + f(W_2)$.
3. S is a monotonically increasing, continuous function of W.

Then $f(W) = c \ln W$ for some positive constant c. Identifying this constant with k_{B} to match the thermodynamic definition of entropy gives $S = k_{\text{B}} \ln W$.

Proof. Condition (2) is Cauchy's functional equation for the multiplicative-to-additive case. With the continuity requirement (3), the unique solution is $f(W) = c \ln W$ for some constant $c > 0$ (where the positivity of c follows from the monotonicity requirement).

To fix $c = k_{\text{B}}$, we demand consistency with the thermodynamic relation $dS = \delta Q_{\text{rev}}/T$. For an ideal gas, explicit computation of W using the Sackur–Tetrode equation (Section 5.3) confirms that $c = k_{\text{B}}$. □

4.3 Properties of Boltzmann Entropy

Proposition 4.2. The Boltzmann entropy has the following properties:

1. Non-negativity: $S \geq 0$ since $W \geq 1$.
2. Additivity: For independent systems, $S_{\text{total}} = S_1 + S_2$.

3. Maximum at equilibrium: S is maximised when W is maximised, which corresponds to the equilibrium macrostate.
4. Monotonicity: If $W_A > W_B$, then $S_A > S_B$.
5. Vanishing at absolute zero: If $W = 1$ (unique ground state), $S = 0$. This is the Third Law of Thermodynamics (Nernst's theorem).

Example 4.1 (Entropy of the Two-Compartment System). For the macrostate $(2, 2)$ with $W = 6$:

$$S = k_{\mathrm{B}} \ln 6 \approx 1.79\, k_{\mathrm{B}} \approx 2.47 \times 10^{-23}\ \mathrm{J/K} \tag{22}$$

For the macrostate $(4, 0)$ with $W = 1$:

$$S = k_{\mathrm{B}} \ln 1 = 0 \tag{23}$$

The perfectly ordered state (all particles in one compartment) has zero entropy.

4.4 Connection to Thermodynamic Entropy

Definition 4.1 (Temperature from Entropy). The thermodynamic temperature is defined by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = k_{\mathrm{B}} \left(\frac{\partial \ln W}{\partial E}\right)_{V,N} \tag{24}$$

This provides the bridge between the statistical definition of entropy and the thermodynamic definition. Equilibrium between two systems in thermal contact is reached when their temperatures are equal, which is equivalent to the total W being maximised.

Theorem 4.3 (Equilibrium Condition). Two systems in thermal contact reach equilibrium when

$$\left(\frac{\partial \ln W_1}{\partial E_1}\right)_{V_1,N_1} = \left(\frac{\partial \ln W_2}{\partial E_2}\right)_{V_2,N_2} \tag{25}$$

i.e., when $T_1 = T_2$.

Proof. The total number of microstates is $W = W_1(E_1) \cdot W_2(E_2)$ with $E_1 + E_2 = E_{\mathrm{total}} = \text{const}$. Maximising $\ln W = \ln W_1 + \ln W_2$ subject to this constraint:

$$\frac{\partial \ln W_1}{\partial E_1} - \frac{\partial \ln W_2}{\partial E_2} = 0 \implies \frac{1}{k_{\mathrm{B}} T_1} = \frac{1}{k_{\mathrm{B}} T_2} \implies T_1 = T_2. \tag{26}$$

□

4.5 Boltzmann's H-Theorem: An Overview

In 1872, Boltzmann proved the H-theorem, which provides a kinetic-theory derivation of the approach to equilibrium.

Definition 4.2 (H-functional). For a gas with velocity distribution function $f(\mathrm{v}, t)$, define

$$H(t) = \int f(\mathrm{v}, t) \ln f(\mathrm{v}, t)\, d^3 v \tag{27}$$

Theorem 4.4 (H-Theorem). Under the assumptions of the Boltzmann transport equation (molecular chaos, binary collisions), $dH/dt \leq 0$, with equality if and only if f is the Maxwell–Boltzmann equilibrium distribution.

The connection to entropy is $S = -N k_{\mathrm{B}} H + \text{const}$, so the H-theorem implies that entropy increases monotonically toward its equilibrium value—a microscopic derivation of the Second Law.

Remark 4.1 (Loschmidt's Paradox). Loschmidt objected: the microscopic equations of motion are time-reversible, so how can H decrease monotonically? The resolution is that the "molecular chaos" assumption (*Stoßzahlansatz*) implicitly introduces a time asymmetry. The H-theorem is a statistical statement, not a mechanical one.

5 The Microcanonical Ensemble

5.1 Definition and Setup

Definition 5.1 (Microcanonical Ensemble). The microcanonical ensemble describes an isolated system with fixed energy E (within a small tolerance δE), fixed volume V, and fixed particle number N. The systems constituting the ensemble are separated by rigid, impermeable, and insulating walls.

In the microcanonical ensemble, the fundamental postulate asserts that all microstates with energy in $[E, E + \delta E]$ are equally probable. The probability of microstate i is:

$$P_i = \begin{cases} 1/\Omega(E, V, N) & \text{if } E \leq E_i \leq E + \delta E \\ 0 & \text{otherwise} \end{cases} \tag{28}$$

where $\Omega(E, V, N)$ is the number of accessible microstates.

5.2 Density of States

Definition 5.2 (Density of States). The density of states $g(E)$ is defined such that $g(E)\,\delta E$ equals the number of microstates with energy between E and $E + \delta E$. Then $\Omega = g(E)\,\delta E$.

For a classical system:

$$\Omega(E) = \frac{1}{N!\,h^{3N}} \int_{E \leq H \leq E+\delta E} d^{3N}q\, d^{3N}p \tag{29}$$

5.3 Application: Ideal Gas

Example 5.1 (Ideal Gas in the Microcanonical Ensemble). For N non-interacting point particles of mass m in a box of volume V:

$$H = \sum_{i=1}^{N} \frac{\mathrm{p}_i^2}{2m} \tag{30}$$

The phase-space volume with energy less than E is:

$$\Phi(E) = \frac{V^N}{N!\,h^{3N}} \cdot \frac{(2\pi m E)^{3N/2}}{(3N/2)!} \tag{31}$$

The spatial integral gives V^N (particles move freely in volume V). The momentum integral is the volume of a $3N$-dimensional sphere of radius $\sqrt{2mE}$:

$$\int_{|\mathrm{p}|^2 \leq 2mE} d^{3N}p = \frac{(2\pi m E)^{3N/2}}{\Gamma(3N/2 + 1)} \tag{32}$$

The density of states is $g(E) = d\Phi/dE$, and the entropy is:

$$S = k_{\mathrm{B}} \ln \Omega \approx k_{\mathrm{B}} \ln g(E) + k_{\mathrm{B}} \ln \delta E \tag{33}$$

Since $\ln \delta E$ is negligible compared to $\ln g(E)$ for large N, we obtain the Sackur–Tetrode equation:

Sackur–Tetrode Equation:

$$S = N k_{\mathrm{B}} \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{34}$$

This formula was derived independently by Otto Sackur and Hugo Tetrode in 1912. It provides the correct entropy of an ideal gas, including the $N!$ Gibbs factor that resolves the Gibbs paradox.

Remark 5.1 (Gibbs Paradox). Without the $N!$ factor, the entropy of mixing two identical gases at the same temperature and pressure would be non-zero, contradicting experiment. The resolution is that identical particles are indistinguishable, and permutations of identical particles do not generate new microstates. This is a fundamentally quantum-mechanical effect, even though it appears in the classical formula.

5.4 Entropy of Mixing

Theorem 5.1 (Entropy of Mixing). When two ideal gases (species A and B, with N_A and N_B particles respectively) initially in separate containers of volumes V_A and V_B are allowed to mix at constant total energy, the entropy change is:

$$\Delta S_{\text{mix}} = -k_{\text{B}} \left(N_A \ln \frac{V_A}{V_A + V_B} + N_B \ln \frac{V_B}{V_A + V_B} \right) \tag{35}$$

Since $V_A < V_A + V_B$ and $V_B < V_A + V_B$, both logarithms are negative, so $\Delta S_{\text{mix}} > 0$.

If $V_A = V_B = V$ and $N_A = N_B = N$:

$$\Delta S_{\text{mix}} = 2Nk_{\text{B}} \ln 2 \tag{36}$$

If the two gases are identical ($A = B$), then $\Delta S_{\text{mix}} = 0$—there is no entropy of mixing. This is the resolution of the Gibbs paradox.

6 The Canonical Ensemble

6.1 Systems in Thermal Contact

Definition 6.1 (Canonical Ensemble). The canonical ensemble describes a system in thermal equilibrium with a heat reservoir at temperature T. The system has fixed volume V and particle number N, but its energy can fluctuate due to exchange with the reservoir. The systems are separated by rigid, impermeable, but thermally *conducting* walls.

The canonical ensemble is the workhorse of statistical mechanics: most real experiments are performed at constant temperature rather than constant energy.

6.2 Derivation of the Boltzmann Distribution

Theorem 6.1 (Boltzmann Distribution). In the canonical ensemble, the probability of the system being in microstate i with energy E_i is:

$$P_i = \frac{e^{-\beta E_i}}{Z} \tag{37}$$

where $\beta = 1/(k_{\text{B}}T)$ and Z is the partition function.

Proof. Consider the system ($\mathcal{S}$) plus reservoir ($\mathcal{R}$) as an isolated supersystem with total energy $E_{\text{tot}} = E_i + E_R$. By the fundamental postulate, all microstates of the supersystem are equally probable. The probability of the system being in microstate i is proportional to the number of microstates available to the reservoir:

$$P_i \propto \Omega_R(E_{\text{tot}} - E_i) \tag{38}$$

Taking the logarithm and expanding for $E_i \ll E_{\text{tot}}$:

$$\ln \Omega_R(E_{\text{tot}} - E_i) \approx \ln \Omega_R(E_{\text{tot}}) - E_i \frac{\partial \ln \Omega_R}{\partial E_R}\bigg|_{E_R = E_{\text{tot}}} \tag{39}$$

Since $\frac{\partial \ln \Omega_R}{\partial E_R} = \frac{1}{k_B T} = \beta$ (definition of temperature), we obtain:

$$\Omega_R(E_{\text{tot}} - E_i) \propto e^{-\beta E_i} \tag{40}$$

Normalising: $P_i = e^{-\beta E_i}/Z$, where $Z = \sum_i e^{-\beta E_i}$. □

6.3 The Partition Function

Definition 6.2 (Canonical Partition Function). The canonical partition function is:

$$Z(T, V, N) = \sum_i e^{-\beta E_i} = \sum_i e^{-E_i/k_B T} \tag{41}$$

where the sum runs over all microstates i.

The partition function is the single most important quantity in statistical mechanics: once Z is known, all thermodynamic properties follow.

Thermodynamic Relations from the Partition Function:

$$F = -k_B T \ln Z \qquad \text{(Helmholtz free energy)} \tag{42}$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = k_B \ln Z + k_B T \left.\frac{\partial \ln Z}{\partial T}\right|_{V,N} \qquad \text{(Entropy)} \tag{43}$$

$$\langle E \rangle = -\left.\frac{\partial \ln Z}{\partial \beta}\right|_{V,N} = k_B T^2 \left.\frac{\partial \ln Z}{\partial T}\right|_{V,N} \qquad \text{(Average energy)} \tag{44}$$

$$P = k_B T \left.\frac{\partial \ln Z}{\partial V}\right|_{T,N} \qquad \text{(Pressure)} \tag{45}$$

$$C_V = \left.\frac{\partial \langle E \rangle}{\partial T}\right|_{V,N} = k_B \beta^2 \left.\frac{\partial^2 \ln Z}{\partial \beta^2}\right|_{V,N} \qquad \text{(Heat capacity)} \tag{46}$$

Derivation of $F = -k_B T \ln Z$. The average energy is $\langle E \rangle = \sum_i P_i E_i = -\partial \ln Z/\partial \beta$. The entropy is

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i P_i(-\beta E_i - \ln Z) = k_B \beta \langle E \rangle + k_B \ln Z \tag{47}$$

Therefore $F = \langle E \rangle - TS = \langle E \rangle - T(k_B \beta \langle E \rangle + k_B \ln Z) = \langle E \rangle - \langle E \rangle - k_B T \ln Z = -k_B T \ln Z$. □

6.4 Energy Fluctuations

Theorem 6.2 (Energy Fluctuations in the Canonical Ensemble). The variance of the energy is:

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 C_V \tag{48}$$

where C_V is the heat capacity at constant volume.

Proof.

$$\langle E^2 \rangle = \frac{1}{Z} \sum_i E_i^2 e^{-\beta E_i} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \tag{49}$$

$$\langle E \rangle^2 = \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta}\right)^2 = \left(\frac{\partial \ln Z}{\partial \beta}\right)^2 \tag{50}$$

Therefore:

$$\sigma_E^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial \langle E \rangle}{\partial \beta} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T} = k_B T^2 C_V \tag{51}$$

□

Corollary 6.3. The relative fluctuation is:

$$\frac{\sigma_E}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \tag{52}$$

For macroscopic systems ($N \sim 10^{23}$), the relative fluctuation is $\sim 10^{-12}$, utterly negligible. This is why the canonical and microcanonical ensembles give the same results for large systems.

6.5 The Equipartition Theorem

Equipartition Theorem:
For a classical system in thermal equilibrium at temperature T, each quadratic term in the Hamiltonian contributes $\frac{1}{2}k_{\mathrm{B}}T$ to the average energy.

Theorem 6.4 (Equipartition). If the Hamiltonian contains a term of the form αx_i^2 (where x_i is a generalised coordinate or momentum and α is a constant), then

$$\langle \alpha x_i^2 \rangle = \frac{1}{2}k_{\mathrm{B}}T \tag{53}$$

Proof. Consider the contribution of the variable x_i to the partition function:

$$\int_{-\infty}^{\infty} e^{-\beta\alpha x_i^2} dx_i = \sqrt{\frac{\pi}{\beta\alpha}} \tag{54}$$

The average:

$$\langle \alpha x_i^2 \rangle = \frac{\int \alpha x_i^2 e^{-\beta\alpha x_i^2} dx_i}{\int e^{-\beta\alpha x_i^2} dx_i} = -\frac{\partial}{\partial\beta} \ln \sqrt{\frac{\pi}{\beta\alpha}} = \frac{1}{2\beta} = \frac{1}{2}k_{\mathrm{B}}T \tag{55}$$

□

Example 6.1 (Applications of Equipartition). 1. Monatomic ideal gas: $H = \sum_{i=1}^{N} \frac{p_{xi}^2 + p_{yi}^2 + p_{zi}^2}{2m}$. Three quadratic terms per particle, so $\langle E \rangle = \frac{3}{2}Nk_{\mathrm{B}}T$ and $C_V = \frac{3}{2}Nk_{\mathrm{B}}$.

2. Diatomic gas (classical): 3 translational + 2 rotational + 1 vibrational kinetic + 1 vibrational potential = 7 quadratic terms, giving $\langle E \rangle = \frac{7}{2}Nk_{\mathrm{B}}T$.

3. Harmonic solid (3D): Each atom has 3 kinetic + 3 potential quadratic terms, giving $\langle E \rangle = 3Nk_{\mathrm{B}}T$ and $C_V = 3Nk_{\mathrm{B}}$ (the Dulong–Petit law).

4. Classical harmonic oscillator: $H = p^2/(2m) + \frac{1}{2}m\omega^2 q^2$. Two quadratic terms: $\langle E \rangle = k_{\mathrm{B}}T$.

Remark 6.1. The equipartition theorem is purely classical. At low temperatures, quantum effects "freeze out" degrees of freedom, and the theorem fails. For example, the heat capacity of a diatomic gas at room temperature is $\frac{5}{2}Nk_{\mathrm{B}}$ (not $\frac{7}{2}$) because the vibrational mode is frozen out. A proper treatment requires the quantum partition function.

6.6 Examples of Partition Functions

6.6.1 Ideal Gas

Example 6.2 (Classical Ideal Gas Partition Function). For N identical non-interacting particles in volume V:

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \tag{56}$$

where $\lambda = \sqrt{2\pi\hbar^2/(mk_{\mathrm{B}}T)}$ is the thermal de Broglie wavelength.

Proof. The single-particle partition function is:

$$Z_1 = \frac{1}{h^3}\int d^3q \int d^3p\, e^{-\beta p^2/(2m)} = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} = \frac{V}{\lambda^3} \tag{57}$$

For N identical particles: $Z = Z_1^N/N!$ (Gibbs factor for indistinguishability). □

From $F = -k_{\mathrm{B}}T\ln Z$, using Stirling's approximation $\ln N! \approx N\ln N - N$:

$$F = -k_{\mathrm{B}}T\left[N\ln\frac{V}{\lambda^3} - N\ln N + N\right] = -Nk_{\mathrm{B}}T\left[\ln\frac{V}{N\lambda^3} + 1\right] \tag{58}$$

The pressure follows:

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{Nk_{\mathrm{B}}T}{V} \tag{59}$$

recovering the ideal gas law $PV = Nk_{\mathrm{B}}T$.

6.6.2 Quantum Harmonic Oscillator

Example 6.3 (Quantum Harmonic Oscillator). A single quantum harmonic oscillator with frequency ω has energy levels $E_n = \hbar\omega(n + 1/2)$, $n = 0, 1, 2, \ldots$

The partition function is:

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\beta\hbar\omega/2)} \tag{60}$$

The average energy is:

$$\langle E\rangle = -\frac{\partial \ln Z_1}{\partial\beta} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/k_{\mathrm{B}}T} - 1}\right) \tag{61}$$

The second term is the Planck distribution function (the average number of quanta).

Limiting cases:

- High temperature ($k_{\mathrm{B}}T \gg \hbar\omega$): $\langle E\rangle \approx k_{\mathrm{B}}T$ (classical equipartition).
- Low temperature ($k_{\mathrm{B}}T \ll \hbar\omega$): $\langle E\rangle \approx \frac{1}{2}\hbar\omega + \hbar\omega e^{-\hbar\omega/k_{\mathrm{B}}T}$ (ground state dominates).

The heat capacity is:

$$C_V = k_{\mathrm{B}}(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \tag{62}$$

This goes to k_{B} at high T (Dulong–Petit) and to zero exponentially at low T (quantum freeze-out).

6.6.3 Two-Level System

Example 6.4 (Two-Level System). Consider a system with two states: a ground state with energy 0 and an excited state with energy ϵ.

The partition function is:

$$Z = 1 + e^{-\beta\epsilon} \tag{63}$$

The average energy:

$$\langle E \rangle = \frac{\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \frac{\epsilon}{e^{\beta\epsilon} + 1} \tag{64}$$

The probability of being in the excited state:

$$P_{\text{excited}} = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \tag{65}$$

At $T = 0$: $P_{\text{excited}} = 0$ (system in ground state).
At $T \to \infty$: $P_{\text{excited}} = 1/2$ (equal population).
At $k_B T = \epsilon$: $P_{\text{excited}} = 1/(e + 1) \approx 0.269$.

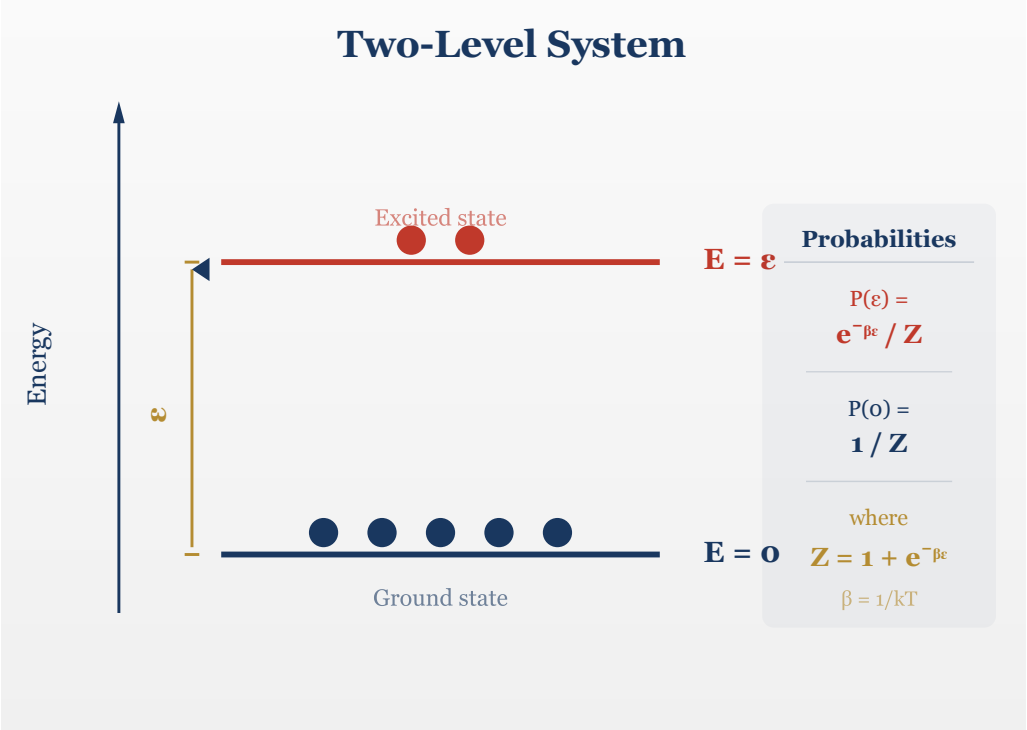

Figure 4: Energy levels of a two-state system with ground state energy 0 and excited state energy ϵ. The occupation probabilities are governed by the Boltzmann factor $e^{-\beta\epsilon}$.

The heat capacity is:

$$C_V = k_B(\beta\epsilon)^2 \frac{e^{\beta\epsilon}}{(e^{\beta\epsilon} + 1)^2} \tag{66}$$

This exhibits a characteristic Schottky anomaly: C_V is zero at $T = 0$, rises to a maximum near $k_B T \approx 0.42\epsilon$, then decreases as T^{-2} at high temperatures.

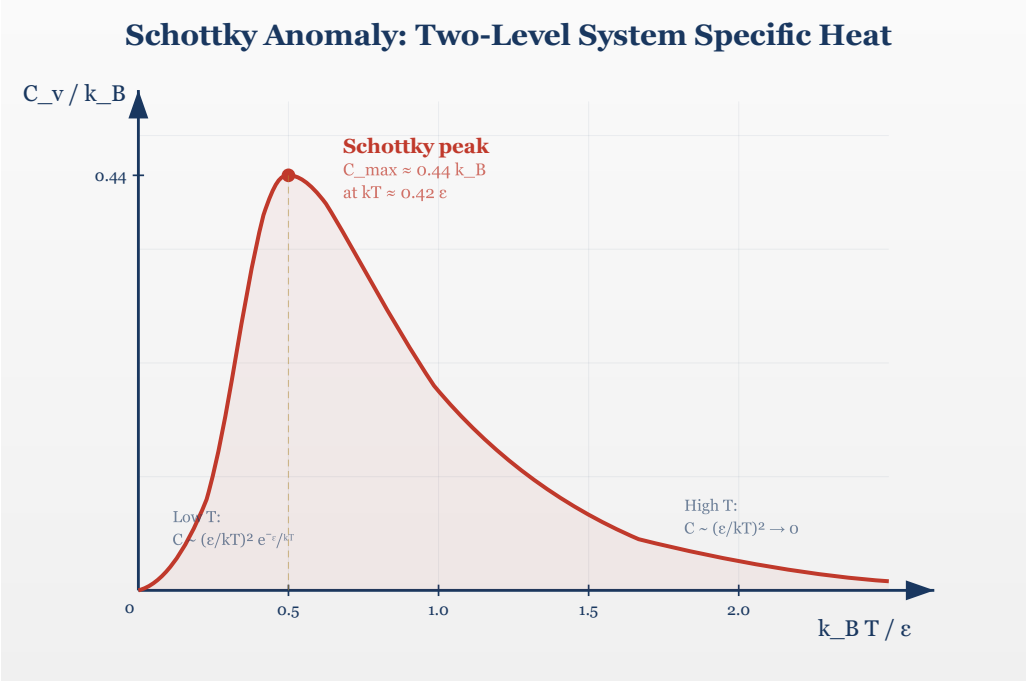

Figure 5: The Schottky anomaly in the heat capacity of a two-level system. The heat capacity vanishes at both low and high temperatures, with a characteristic peak near $k_{\mathrm{B}}T \approx 0.42\,\epsilon$.

6.6.4 Paramagnetism

Example 6.5 (Classical Paramagnetism). Consider N non-interacting magnetic moments μ in an external field $\mathrm{B} = B\hat{z}$. For spin-$\frac{1}{2}$ particles, each moment can be either parallel ($\uparrow$, energy $-\mu B$) or antiparallel ($\downarrow$, energy $+\mu B$).

This is a two-level system with $\epsilon = 2\mu B$ and a shift: $E_\uparrow = -\mu B$, $E_\downarrow = +\mu B$.

The single-spin partition function:

$$z = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B) \tag{67}$$

The N-spin partition function: $Z = z^N = [2\cosh(\beta\mu B)]^N$.

The average magnetisation:

$$\langle M\rangle = N\mu\tanh(\beta\mu B) \tag{68}$$

Limiting cases:

- High temperature ($k_{\mathrm{B}}T \gg \mu B$): $\langle M\rangle \approx N\mu^2 B/(k_{\mathrm{B}}T)$ — Curie's law, $\chi = C/T$.
- Low temperature ($k_{\mathrm{B}}T \ll \mu B$): $\langle M\rangle \approx N\mu$ — complete alignment (saturation).

The magnetic susceptibility $\chi = \partial\langle M\rangle/\partial B|_{B\to 0}$ gives the Curie constant $C = N\mu^2/k_{\mathrm{B}}$.

Remark 6.2 (Spin-J Generalisation). For a spin-J particle with $2J+1$ states ($m = -J, -J+1, \ldots, J$) and energies $E_m = -mg\mu_B B$, the partition function is:

$$z = \sum_{m=-J}^{J} e^{m\beta g\mu_B B} = \frac{\sinh\!\left[(2J+1)x/2\right]}{\sinh(x/2)}, \qquad x = \beta g\mu_B B \tag{69}$$

The magnetisation is $\langle M\rangle = Ng\mu_B J\, B_J(Jx)$, where B_J is the Brillouin function.

7 The Grand Canonical Ensemble

7.1 Open Systems and Chemical Potential

Definition 7.1 (Grand Canonical Ensemble). The grand canonical ensemble describes a system in thermal and diffusive equilibrium with a reservoir. The system has fixed volume V, but both energy and particle number can fluctuate. The reservoir is characterised by temperature T and chemical potential μ.

The chemical potential μ governs particle exchange just as temperature governs energy exchange:

$$\mu = -k_B T \left(\frac{\partial \ln W}{\partial N}\right)_{E,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{70}$$

Systems in diffusive equilibrium have equal chemical potentials, just as systems in thermal equilibrium have equal temperatures.

7.2 The Grand Partition Function

Definition 7.2 (Grand Partition Function). The grand partition function (or grand canonical partition function) is:

$$\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} \sum_{i} e^{-\beta(E_i^{(N)} - \mu N)} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,V,N) \tag{71}$$

where $Z(T,V,N)$ is the canonical partition function for N particles and the double sum runs over all particle numbers and all microstates for each N.

The fugacity $z = e^{\beta\mu}$ is often used, so $\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z(T,V,N)$.

Thermodynamic Relations from the Grand Partition Function:

$$\Phi = -k_B T \ln \mathcal{Z} \qquad \text{(Grand potential, } \Phi = F - \mu N = -PV\text{)} \tag{72}$$

$$\langle N \rangle = k_B T \left.\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right|_{T,V} = z \left.\frac{\partial \ln \mathcal{Z}}{\partial z}\right|_{T,V} \qquad \text{(Average particle number)} \tag{73}$$

$$P = k_B T \frac{\ln \mathcal{Z}}{V} \qquad \text{(Pressure)} \tag{74}$$

$$S = k_B \ln \mathcal{Z} + k_B T \left.\frac{\partial \ln \mathcal{Z}}{\partial T}\right|_{V,\mu} - \frac{\mu}{T}\langle N \rangle \qquad \text{(Entropy)} \tag{75}$$

7.3 Particle Number Fluctuations

Theorem 7.1 (Particle Number Fluctuations). In the grand canonical ensemble:

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = k_B T \left.\frac{\partial \langle N \rangle}{\partial \mu}\right|_{T,V} \tag{76}$$

Proof.

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu}, \qquad \langle N^2 \rangle = \frac{1}{\beta^2}\frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \tag{77}$$

Computing $\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2}\frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} = \frac{1}{\beta}\frac{\partial \langle N \rangle}{\partial \mu}$. □

For an ideal gas, one can show that $\sigma_N^2 = \langle N \rangle$, so $\sigma_N / \langle N \rangle = 1/\sqrt{\langle N \rangle}$, which is negligible for macroscopic systems.

7.4 Quantum Statistics: Fermi–Dirac and Bose–Einstein

The grand canonical ensemble is the natural framework for quantum statistics, where the number of particles is not fixed.

Definition 7.3 (Occupation Numbers). For a system of identical particles, a microstate is specified by the set of occupation numbers $\{n_k\}$, where n_k is the number of particles in single-particle state k with energy ϵ_k.

The constraints on n_k depend on the nature of the particles:

- Fermions (half-integer spin): $n_k = 0$ or 1 (Pauli exclusion principle).
- Bosons (integer spin): $n_k = 0, 1, 2, 3, \ldots$ (no restriction).

Theorem 7.2 (Fermi–Dirac Distribution). For a system of non-interacting fermions, the average occupation number of state k is:

$$\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} \tag{78}$$

This is the Fermi–Dirac distribution.

Proof. For a single fermion level k with $n_k \in \{0, 1\}$:

$$\mathcal{Z}_k = \sum_{n_k=0}^{1} e^{-\beta(\epsilon_k - \mu)n_k} = 1 + e^{-\beta(\epsilon_k - \mu)} \tag{79}$$

The average occupation:

$$\langle n_k \rangle = \frac{0 \cdot 1 + 1 \cdot e^{-\beta(\epsilon_k - \mu)}}{1 + e^{-\beta(\epsilon_k - \mu)}} = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} \tag{80}$$

□

Theorem 7.3 (Bose–Einstein Distribution). For a system of non-interacting bosons, the average occupation number is:

$$\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} \tag{81}$$

This is the Bose–Einstein distribution.

Proof. For a single boson level k with $n_k \in \{0, 1, 2, \ldots\}$:

$$\mathcal{Z}_k = \sum_{n_k=0}^{\infty} e^{-\beta(\epsilon_k - \mu)n_k} = \frac{1}{1 - e^{-\beta(\epsilon_k - \mu)}} \qquad (\text{for } \epsilon_k > \mu) \tag{82}$$

Then:

$$\langle n_k \rangle = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_k}{\partial \epsilon_k} = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} \tag{83}$$

□

Remark 7.1. In the classical limit $e^{\beta(\epsilon_k - \mu)} \gg 1$, both distributions reduce to the Maxwell–Boltzmann distribution:

$$\langle n_k \rangle \approx e^{-\beta(\epsilon_k - \mu)} \tag{84}$$

This occurs when the average occupation numbers are much less than 1 (dilute, high-temperature limit).

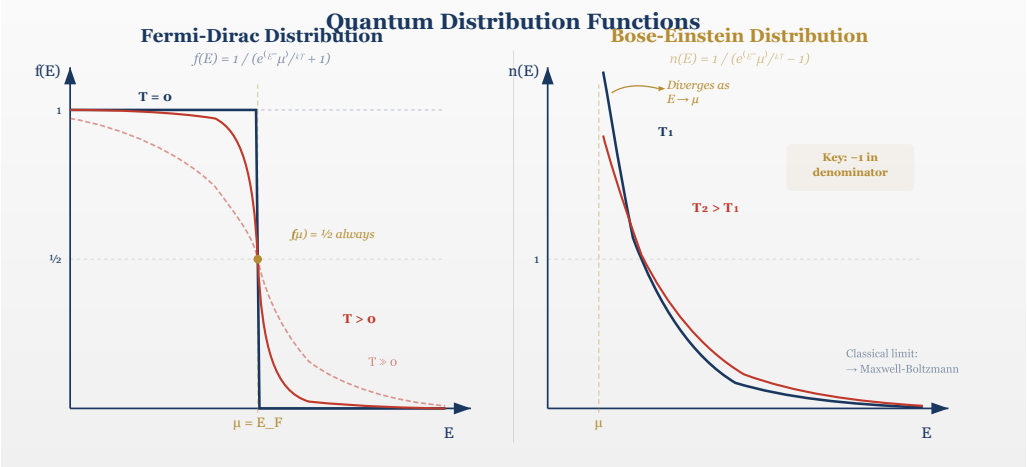

Figure 6: Comparison of the three quantum statistics. The Fermi–Dirac distribution (fermions) is bounded by $0 \leq \langle n \rangle \leq 1$, while the Bose–Einstein distribution (bosons) diverges as $\epsilon \to \mu$. Both approach the classical Maxwell–Boltzmann distribution in the high-energy (dilute) limit.

Example 7.1 (Ideal Fermi Gas at $T = 0$). At absolute zero, the Fermi–Dirac distribution becomes a step function:

$$\langle n_k \rangle = \begin{cases} 1 & \text{if } \epsilon_k < \mu_0 \equiv E_F \\ 0 & \text{if } \epsilon_k > E_F \end{cases} \tag{85}$$

where E_F is the Fermi energy. All states below E_F are occupied; all above are empty. The Fermi energy is determined by the total particle number:

$$N = \int_0^{E_F} g(\epsilon)\, d\epsilon \tag{86}$$

For free electrons in 3D with density of states $g(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}$:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \tag{87}$$

For copper, $E_F \approx 7\,\text{eV}$, corresponding to a Fermi temperature $T_F = E_F/k_\text{B} \approx 80{,}000\,\text{K}$. Since room temperature ($\sim 300\,\text{K}$) is far below T_F, the electron gas in metals is deeply degenerate.

Example 7.2 (Ideal Bose Gas and Bose–Einstein Condensation). For bosons, the chemical potential must satisfy $\mu \leq \epsilon_0$ (the ground state energy). As T decreases at fixed N, μ increases toward ϵ_0. When $\mu = \epsilon_0$, a macroscopic fraction of particles condenses into the ground state. This occurs below the critical temperature:

$$T_\text{BEC} = \frac{2\pi\hbar^2}{m k_\text{B}}\left(\frac{n}{\zeta(3/2)}\right)^{2/3} \tag{88}$$

where $\zeta(3/2) \approx 2.612$ is the Riemann zeta function. Below T_BEC, the fraction of particles in the ground state is:

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_\text{BEC}}\right)^{3/2} \tag{89}$$

Bose–Einstein condensation was experimentally achieved in dilute atomic gases in 1995 by Cornell, Wieman (rubidium-87) and Ketterle (sodium-23), earning them the 2001 Nobel Prize in Physics.

7.5 Comparison of the Three Ensembles

	Microcanonical	Canonical	Grand Can
Fixed quantities	E, V, N	T, V, N	$T, V,$
Wall type	Rigid, insulating, impermeable	Rigid, conducting, impermeable	Rigid, conductin
Partition function	$\Omega(E, V, N)$	$Z(T, V, N)$	$\mathcal{Z}(T, V,$
Thermodynamic potential	$S = k_B \ln \Omega$	$F = -k_B T \ln Z$	$\Phi = -k_B T$
Fluctuating quantity	None	E	E and

Table 4: Comparison of the three ensembles.

For macroscopic systems, all three ensembles give identical results for thermodynamic quantities. They differ only for small systems or near phase transitions.

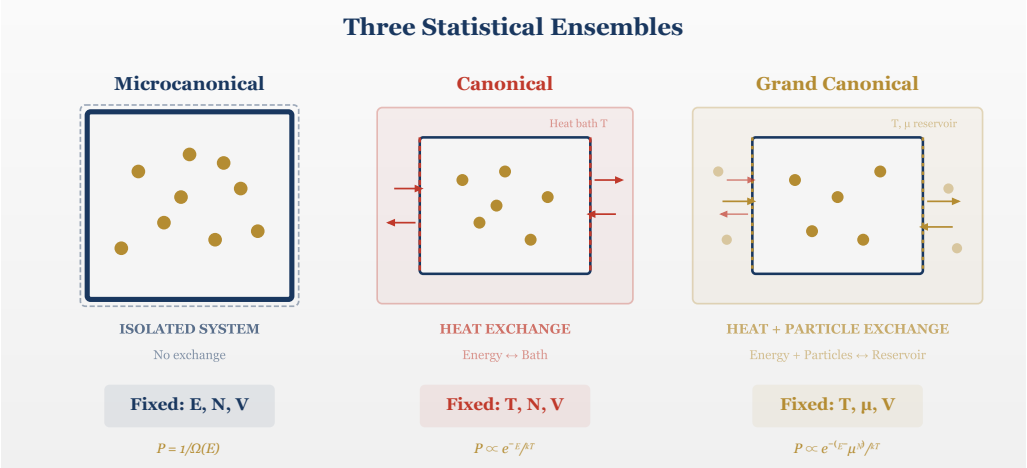

Figure 7: Comparison of the three statistical ensembles. The microcanonical ensemble describes an isolated system; the canonical ensemble allows energy exchange with a heat bath at temperature T; the grand canonical ensemble additionally permits particle exchange at chemical potential μ.

8 Applications and Connections

8.1 Ideal Gas: Complete Treatment

We have already derived the ideal gas law from the canonical partition function. Let us collect the complete thermodynamic description.

Theorem 8.1 (Ideal Gas Thermodynamics). For N non-interacting identical particles of mass m in

volume V at temperature T, with $\lambda = \sqrt{2\pi\hbar^2/(mk_{\mathrm{B}}T)}$:

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \tag{90}$$

$$F = -Nk_{\mathrm{B}}T\left[\ln\frac{V}{N\lambda^3} + 1\right] \tag{91}$$

$$S = Nk_{\mathrm{B}}\left[\ln\frac{V}{N\lambda^3} + \frac{5}{2}\right] \qquad \text{(Sackur–Tetrode)} \tag{92}$$

$$P = \frac{Nk_{\mathrm{B}}T}{V} \tag{93}$$

$$\langle E\rangle = \frac{3}{2}Nk_{\mathrm{B}}T \tag{94}$$

$$C_V = \frac{3}{2}Nk_{\mathrm{B}} \tag{95}$$

$$\mu = k_{\mathrm{B}}T\ln\frac{N\lambda^3}{V} = k_{\mathrm{B}}T\ln(n\lambda^3) \tag{96}$$

where $n = N/V$ is the number density.

Remark 8.1. The condition for classical behaviour is $n\lambda^3 \ll 1$, i.e., the average inter-particle spacing is much larger than the thermal de Broglie wavelength. When $n\lambda^3 \sim 1$, quantum effects (Bose–Einstein condensation, Fermi degeneracy) become important.

8.2 Einstein Model of a Solid

Example 8.1 (Einstein Solid). Model a solid as N atoms, each vibrating independently as a 3D quantum harmonic oscillator with frequency ω_E (the Einstein frequency). The partition function is:

$$Z = \left[\frac{1}{2\sinh(\beta\hbar\omega_E/2)}\right]^{3N} \tag{97}$$

The average energy and heat capacity:

$$\langle E\rangle = 3N\hbar\omega_E\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_E} - 1}\right) \tag{98}$$

$$C_V = 3Nk_{\mathrm{B}}\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \tag{99}$$

where $\Theta_E = \hbar\omega_E/k_{\mathrm{B}}$ is the Einstein temperature.

At high T ($T \gg \Theta_E$): $C_V \to 3Nk_{\mathrm{B}}$ (Dulong–Petit law).
At low T ($T \ll \Theta_E$): $C_V \to 3Nk_{\mathrm{B}}(\Theta_E/T)^2 e^{-\Theta_E/T} \to 0$ exponentially.

The exponential vanishing at low T is qualitatively correct but quantitatively too fast; the Debye model (which uses a distribution of frequencies rather than a single frequency) gives the correct T^3 dependence at low temperatures.

8.3 Connections to Classical Thermodynamics

Statistical mechanics reproduces all of classical thermodynamics and provides a microscopic interpretation:

Thermodynamic Concept	Statistical Interpretation
Temperature T	Measure of average kinetic energy per degree of freedom
Entropy S	Logarithm of number of microstates: $S = k_B \ln W$
Pressure P	Average rate of momentum transfer per unit area
Free energy F	$-k_B T \ln Z$ (logarithm of partition function)
Chemical potential μ	Free energy cost of adding one particle
Second Law	Systems evolve toward macrostates with higher W
Third Law	Unique ground state $\Rightarrow W = 1 \Rightarrow S = 0$
Equilibrium	Maximum of total entropy (maximum W)

Table 5: Correspondence between thermodynamics and statistical mechanics.

The Power of Statistical Mechanics:
Classical thermodynamics tells us *what* happens (e.g., heat flows from hot to cold). Statistical mechanics tells us *why*: the overwhelmingly larger number of microstates corresponding to the equilibrium macrostate makes any other outcome astronomically improbable.

9 Further Topics

9.1 Quantum Statistical Mechanics: Overview

In quantum mechanics, the state of a system is described by a density matrix $\hat{\rho}$ rather than a phase-space distribution. The ensemble average of an observable $\hat{A}$ is:

$$\langle A \rangle = \mathrm{Tr}(\hat{\rho}\hat{A}) \tag{100}$$

The density matrices for the three ensembles are:

1. Microcanonical: $\hat{\rho} = \frac{1}{\Omega} \sum_{E_i \in [E, E+\delta E]} |i\rangle\langle i|$
2. Canonical: $\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z}$, where $Z = \mathrm{Tr}(e^{-\beta \hat{H}})$
3. Grand canonical: $\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\mathcal{Z}}$, where $\mathcal{Z} = \mathrm{Tr}(e^{-\beta(\hat{H} - \mu \hat{N})})$

The quantum formulation is essential for understanding low-temperature phenomena: superfluidity (bosons), superconductivity (fermion pairs), Bose–Einstein condensation, and the behaviour of electrons in metals (Fermi gas).

9.2 Phase Transitions: A Preview

Phase transitions—the dramatic changes in material properties at critical points—are among the most striking phenomena in statistical physics.

Definition 9.1 (Phase Transition). A phase transition occurs when a thermodynamic potential (or its derivatives) exhibits a non-analytic dependence on a control parameter (temperature, pressure, magnetic field).

- First-order transitions: The first derivative of the free energy is discontinuous (e.g., boiling, melting). Characterised by latent heat and coexistence of phases.

- Continuous (second-order) transitions: The first derivative is continuous but the second derivative diverges (e.g., the ferromagnetic–paramagnetic transition at the Curie temperature). Characterised by power-law singularities and critical exponents.

The simplest model exhibiting a phase transition is the Ising model: N spins on a lattice with nearest-neighbour interactions. The Hamiltonian is

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i \tag{101}$$

where $s_i = \pm 1$, J is the coupling constant, and h is the external field.

In one dimension, the Ising model has no phase transition (at $T > 0$). In two dimensions, Onsager's exact solution (1944) shows a transition at $k_{\mathrm{B}} T_c / J = 2/\ln(1+\sqrt{2}) \approx 2.269$. In three dimensions, no exact solution is known, but the transition is well-established numerically and experimentally.

9.3 Information Theory and Entropy

There is a profound connection between statistical mechanical entropy and the information-theoretic entropy introduced by Claude Shannon in 1948.

Definition 9.2 (Shannon Entropy). For a discrete probability distribution $\{p_i\}$, the Shannon entropy is:

$$H = -\sum_i p_i \ln p_i \tag{102}$$

The Gibbs entropy formula in statistical mechanics is:

$$S = -k_{\mathrm{B}} \sum_i P_i \ln P_i \tag{103}$$

which is precisely k_{B} times the Shannon entropy of the microstate probability distribution.

Remark 9.1. E.T. Jaynes (1957) proposed that statistical mechanics should be understood as a form of statistical inference. The equilibrium distribution (Boltzmann, Fermi–Dirac, Bose–Einstein) is the one that *maximises* the Shannon entropy subject to the known constraints (average energy, particle number, etc.). This "Maximum Entropy" principle provides a unified derivation of all equilibrium distributions and connects statistical physics directly to information theory and Bayesian probability.

Theorem 9.1 (Maximum Entropy Principle). Among all probability distributions $\{P_i\}$ satisfying:

1. Normalisation: $\sum_i P_i = 1$
2. Average energy: $\sum_i P_i E_i = \langle E \rangle$

the one that maximises $S = -k_{\mathrm{B}} \sum_i P_i \ln P_i$ is the Boltzmann distribution $P_i = e^{-\beta E_i}/Z$.

Proof. Use the method of Lagrange multipliers. Maximise

$$\mathcal{L} = -k_{\mathrm{B}} \sum_i P_i \ln P_i - \alpha \left(\sum_i P_i - 1 \right) - \beta' \left(\sum_i P_i E_i - \langle E \rangle \right) \tag{104}$$

Setting $\partial \mathcal{L} / \partial P_i = 0$:

$$-k_{\mathrm{B}}(\ln P_i + 1) - \alpha - \beta' E_i = 0 \implies P_i = e^{-(\alpha/k_{\mathrm{B}}+1)} \cdot e^{-(\beta'/k_{\mathrm{B}})E_i} \tag{105}$$

Identifying $\beta'/k_{\mathrm{B}} = \beta = 1/(k_{\mathrm{B}}T)$ and using normalisation to fix the prefactor gives $P_i = e^{-\beta E_i}/Z$. □

9.4 Landau Free Energy and Mean-Field Theory

The Landau theory of phase transitions provides a phenomenological framework that complements the microscopic statistical mechanical approach. Near a continuous phase transition, we expand the free energy as a function of an order parameter ϕ (e.g., magnetisation for a ferromagnet):

$$F(\phi, T) = F_0(T) + a(T)\phi^2 + b\phi^4 + \cdots \tag{106}$$

where $b > 0$ for stability. The coefficient $a(T) = a_0(T - T_c)$ changes sign at the critical temperature T_c.

- For $T > T_c$: $a > 0$, minimum at $\phi = 0$ (disordered phase).
- For $T < T_c$: $a < 0$, minima at $\phi = \pm\sqrt{-a/(2b)} \propto (T_c - T)^{1/2}$ (ordered phase with spontaneous symmetry breaking).

The critical exponent $\beta = 1/2$ (mean-field value) differs from the exact value in $d < 4$ dimensions due to fluctuations. Renormalisation group theory, developed by Kenneth Wilson in the 1970s, provides a systematic framework for computing the correct exponents and explains the phenomenon of *universality*—the remarkable observation that systems with very different microscopic details can exhibit identical critical behaviour.

Example 9.1 (Mean-Field Ising Model). In the mean-field approximation, each spin s_i interacts with the average magnetisation $m = \langle s \rangle$ rather than with its actual neighbours. The self-consistency equation is:

$$m = \tanh\left(\frac{JZ_{\text{nn}}m + h}{k_{\text{B}}T}\right) \tag{107}$$

where Z_{nn} is the number of nearest neighbours. For $h = 0$, this equation has a non-trivial solution $m \neq 0$ below $T_c = JZ_{\text{nn}}/k_{\text{B}}$.

9.5 The Arrow of Time

The fundamental laws of physics are time-reversible (Newton's equations, Schrödinger's equation, even the standard model Lagrangian is CPT-invariant). Yet the Second Law of Thermodynamics defines a clear "arrow of time": entropy increases.

Statistical mechanics resolves this apparent paradox. The Second Law is not a fundamental law but a statistical statement: systems evolve from less probable to more probable macrostates. Given the enormous number of particles in macroscopic systems, the probability of entropy decreasing by a measurable amount is so incredibly small as to be unobservable.

Remark 9.2 (Fluctuation Theorems). Modern research has quantified this precisely. The Jarzynski equality (1997) and Crooks fluctuation theorem (1999) provide exact relations between equilibrium free energy differences and the statistics of non-equilibrium work processes. These results extend the Second Law to small systems where fluctuations matter.

Conclusion

Statistical physics provides the fundamental connection between the microscopic world of atoms and the macroscopic world of thermodynamics. The key ideas developed in this monograph are:

1. Macrostates and microstates: Many microscopic configurations correspond to the same macroscopic description. The number of such configurations—the thermodynamic probability W—determines which macrostates are observed.

2. Boltzmann entropy: $S = k_{\mathrm{B}} \ln W$ connects the microscopic count of microstates to the macroscopic concept of entropy, providing a statistical foundation for the Second Law.

3. The microcanonical ensemble: For isolated systems, all accessible microstates are equally probable. The entropy is $S = k_{\mathrm{B}} \ln \Omega$.

4. The canonical ensemble: For systems at fixed temperature, the Boltzmann distribution $P_i \propto e^{-\beta E_i}$ governs the probabilities, and the partition function Z encodes all thermodynamics via $F = -k_{\mathrm{B}} T \ln Z$.

5. The grand canonical ensemble: For open systems, the grand partition function $\mathcal{Z}$ accounts for particle exchange and leads naturally to Fermi–Dirac and Bose–Einstein statistics.

6. Applications: The formalism yields concrete results for ideal gases, harmonic oscillators, two-level systems, and paramagnets, demonstrating the power and universality of the statistical approach.

The subject continues to evolve, with modern developments in non-equilibrium statistical mechanics, quantum information, and the statistical physics of complex systems opening new frontiers of research.

References

[1] Boltzmann, L. *Vorlesungen über Gastheorie*. J.A. Barth, Leipzig, 1896–1898. English translation: *Lectures on Gas Theory*, Dover, 1995.

[2] Gibbs, J.W. *Elementary Principles in Statistical Mechanics*. Yale University Press, 1902. Reprinted by Dover, 2014.

[3] Reif, F. *Fundamentals of Statistical and Thermal Physics*. McGraw-Hill, 1965. A classic comprehensive textbook.

[4] Pathria, R.K. and Beale, P.D. *Statistical Mechanics*, 4th ed. Academic Press, 2021.

[5] Kittel, C. and Kroemer, H. *Thermal Physics*, 2nd ed. W.H. Freeman, 1980.

[6] Huang, K. *Statistical Mechanics*, 2nd ed. John Wiley & Sons, 1987.

[7] Schroeder, D.V. *An Introduction to Thermal Physics*. Addison-Wesley, 2000. Excellent for building intuition.

[8] Jaynes, E.T. "Information Theory and Statistical Mechanics." *Physical Review* 106 (1957): 620–630.

[9] Shannon, C.E. "A Mathematical Theory of Communication." *Bell System Technical Journal* 27 (1948): 379–423, 623–656.

[10] Chandler, D. *Introduction to Modern Statistical Mechanics*. Oxford University Press, 1987.

[11] Mandl, F. *Statistical Physics*, 2nd ed. John Wiley & Sons, 1988.

[12] Sethna, J.P. *Statistical Mechanics: Entropy, Order Parameters, and Complexity*, 2nd ed. Oxford University Press, 2021.

A Useful Thermodynamic Identities

The four thermodynamic potentials and their natural variables:

$$dU = T\,dS - P\,dV + \mu\,dN \qquad \text{(Internal energy)} \tag{108}$$

$$dF = -S\,dT - P\,dV + \mu\,dN \qquad \text{(Helmholtz free energy, } F = U - TS\text{)} \tag{109}$$

$$dG = -S\,dT + V\,dP + \mu\,dN \qquad \text{(Gibbs free energy, } G = U - TS + PV\text{)} \tag{110}$$

$$d\Phi = -S\,dT - P\,dV - N\,d\mu \qquad \text{(Grand potential, } \Phi = U - TS - \mu N\text{)} \tag{111}$$

Maxwell relations (from equality of mixed partial derivatives):

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V \qquad \left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P \tag{112}$$

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V \qquad \left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P \tag{113}$$

B Stirling's Approximation

For large n:

$$\ln n! \approx n\ln n - n + \frac{1}{2}\ln(2\pi n) \tag{114}$$

For most purposes in statistical mechanics, the simpler form suffices:

$$\ln n! \approx n\ln n - n \tag{115}$$

Derivation.

$$\ln n! = \sum_{k=1}^{n} \ln k \approx \int_1^n \ln x\,dx = [x\ln x - x]_1^n = n\ln n - n + 1 \approx n\ln n - n \tag{116}$$

The more precise form follows from the Euler–Maclaurin formula or the method of steepest descent applied to $n! = \int_0^\infty t^n e^{-t}dt$. □

C Gaussian Integrals

The fundamental Gaussian integral:

$$\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}, \qquad a > 0 \tag{117}$$

Higher moments:

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a^3}} \tag{118}$$

$$\int_{-\infty}^{\infty} x^{2n} e^{-ax^2}dx = \frac{(2n)!}{n!\,4^n}\sqrt{\frac{\pi}{a^{2n+1}}} \tag{119}$$

The n-dimensional generalisation:

$$\int_{\mathbb{R}^n} e^{-\frac{1}{2}\mathbf{x}^T A\mathbf{x}}d^n x = \frac{(2\pi)^{n/2}}{(\det A)^{1/2}} \tag{120}$$

where A is a positive-definite symmetric matrix.

D Summary of Key Formulas

Quantity	Formula
Boltzmann entropy	$S = k_{\mathrm{B}} \ln W$
Boltzmann distribution	$P_i = e^{-\beta E_i}/Z$
Canonical partition function	$Z = \sum_i e^{-\beta E_i}$
Helmholtz free energy	$F = -k_{\mathrm{B}} T \ln Z$
Average energy	$\langle E \rangle = -\partial \ln Z / \partial \beta$
Energy fluctuations	$\sigma_E^2 = k_{\mathrm{B}} T^2 C_V$
Grand partition function	$\mathcal{Z} = \sum_N e^{\beta \mu N} Z_N$
Grand potential	$\Phi = -k_{\mathrm{B}} T \ln \mathcal{Z}$
Fermi–Dirac distribution	$\langle n_k \rangle = [e^{\beta(\epsilon_k - \mu)} + 1]^{-1}$
Bose–Einstein distribution	$\langle n_k \rangle = [e^{\beta(\epsilon_k - \mu)} - 1]^{-1}$
Ideal gas law	$PV = N k_{\mathrm{B}} T$
Equipartition	$\langle \frac{1}{2} \alpha x^2 \rangle = \frac{1}{2} k_{\mathrm{B}} T$ per quadratic term

Table 6: Summary of key formulas in statistical physics.

Document typeset in LaTeX using STIX Two fonts.

February 2026

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