

The Partition Function in Statistical Mechanics

A Comprehensive Pedagogical Treatment

Advanced Undergraduate Physics
Statistical Mechanics Course

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1 Introduction and Motivation

Statistical mechanics bridges the microscopic world of atoms and molecules with the macroscopic thermodynamic properties we observe. At the heart of this bridge lies the **partition function**, arguably the most important concept in statistical mechanics.

Key Point

The partition function Z is a generating function that encodes all thermodynamic information about a system in equilibrium. Once Z is known, every thermodynamic quantity can be calculated through appropriate derivatives.

1.1 Why Do We Need Statistical Mechanics?

Consider a macroscopic system containing $N \sim 10^{23}$ particles. Writing down and solving the equations of motion for all particles is:

- **Impossible** in practice (computational limitations)
- **Unnecessary** for our purposes (we don't care about individual particle trajectories)
- **Inappropriate** for the questions we ask (we measure averages: temperature, pressure, etc.)

Instead, statistical mechanics provides a framework where:

1. We accept that we cannot track individual particles
2. We describe the system probabilistically
3. We calculate ensemble averages that correspond to measured quantities

2 Fundamental Concepts

2.1 Microstates and Macrostates

Definition 2.1 (Microstate). A **microstate** is a complete specification of the quantum state of every particle in the system. For a system of N particles, this includes all position coordinates $\{\mathbf{r}_i\}$ and momentum coordinates $\{\mathbf{p}_i\}$ (classically), or the complete set of quantum numbers for all particles (quantum mechanically).

Definition 2.2 (Macrostate). A **macrostate** is specified by macroscopic thermodynamic variables such as:

- Number of particles N
- Volume V
- Temperature T
- Pressure P
- Internal energy U

Key Point

Many microstates correspond to the same macrostate. The fundamental postulate of statistical mechanics is that in equilibrium, all accessible microstates of an isolated system are **equally probable**.

2.2 The Canonical Ensemble

Consider a system in thermal contact with a heat reservoir (thermostat) at temperature T . The combined system (system + reservoir) is isolated with fixed total energy.

- **System:** Can exchange energy with reservoir
- **Reservoir:** So large that its temperature remains constant
- **Total:** Isolated, with fixed total energy E_{total}

This setup defines the **canonical ensemble** – the most commonly used ensemble in statistical mechanics.

3 Deriving the Boltzmann Distribution

3.1 Detailed Step-by-Step Derivation

Derivation

We now derive the probability distribution for finding the system in a particular microstate when it's in thermal equilibrium with a reservoir.

Step 1: Setup

Let the system have energy E_s when in microstate s . The reservoir then has energy:

$$E_R = E_{\text{total}} - E_s \quad (1)$$

Step 2: Apply the Fundamental Postulate

The probability of finding the system in state s is proportional to the number of microstates accessible to the reservoir:

$$P_s \propto \Omega_R(E_{\text{total}} - E_s) \quad (2)$$

where $\Omega_R(E)$ is the number of microstates of the reservoir with energy E .

Step 3: Taylor Expansion

Since the reservoir is very large ($N_R \gg N_s$), we can expand:

$$\ln \Omega_R(E_{\text{total}} - E_s) \approx \ln \Omega_R(E_{\text{total}}) - E_s \left. \frac{\partial \ln \Omega_R}{\partial E_R} \right|_{E_R=E_{\text{total}}} \quad (3)$$

Step 4: Definition of Temperature

From thermodynamics, we define temperature through entropy $S = k_B \ln \Omega$:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k_B \frac{\partial \ln \Omega}{\partial E} \quad (4)$$

Define the inverse temperature:

$$\beta \equiv \frac{1}{k_B T} \quad (5)$$

Step 5: Substitute

Therefore:

$$\ln \Omega_R(E_{\text{total}} - E_s) \approx \ln \Omega_R(E_{\text{total}}) - \beta E_s \quad (6)$$

Taking the exponential:

$$\Omega_R(E_{\text{total}} - E_s) \propto e^{-\beta E_s} \quad (7)$$

Step 6: Normalization

The probability must be normalized:

$$P_s = \frac{e^{-\beta E_s}}{\sum_j e^{-\beta E_j}} \quad (8)$$

3.2 The Partition Function Emerges

Definition 3.1 (Canonical Partition Function). The **canonical partition function** is defined as:

$$Z = \sum_s e^{-\beta E_s} = \sum_s e^{-E_s/k_B T} \quad (9)$$

where the sum runs over all accessible microstates s of the system.

The Boltzmann distribution can now be written compactly:

$$P_s = \frac{e^{-\beta E_s}}{Z} = \frac{1}{Z} e^{-\beta E_s} \quad (10)$$

Key Point

The partition function Z is the normalization constant that ensures probabilities sum to unity. But it contains far more information than just normalization – it encodes the complete thermodynamic behavior of the system.

4 Physical Interpretation

4.1 What Does the Partition Function Mean?

The partition function can be interpreted in several ways:

4.1.1 As a Sum Over States

Z literally counts the number of accessible states, weighted by their Boltzmann factors $e^{-\beta E_s}$:

- States with low energy ($E_s \ll k_B T$) contribute factors ≈ 1
- States with high energy ($E_s \gg k_B T$) contribute factors ≈ 0
- States with $E_s \approx k_B T$ contribute factors $\approx e^{-1} \approx 0.37$

4.1.2 As an Effective Number of States

At temperature T , only states within energy $\sim k_B T$ of the ground state are significantly populated. Thus Z roughly counts the "effective number" of thermally accessible states.

4.1.3 Temperature Dependence

- **Low temperature** ($T \rightarrow 0, \beta \rightarrow \infty$): Only the ground state contributes, $Z \rightarrow e^{-\beta E_0}$
- **High temperature** ($T \rightarrow \infty, \beta \rightarrow 0$): All states contribute equally, $Z \rightarrow \Omega$ (total number of states)

5 Thermodynamic Relations from the Partition Function

Once we know Z , we can calculate any thermodynamic quantity. Here we derive the fundamental relationships.

5.1 Internal Energy

Derivation

The average (internal) energy is:

$$U = \langle E \rangle = \sum_s P_s E_s = \frac{1}{Z} \sum_s E_s e^{-\beta E_s} \quad (11)$$

Notice that:

$$\frac{\partial Z}{\partial \beta} = \frac{\partial}{\partial \beta} \sum_s e^{-\beta E_s} = - \sum_s E_s e^{-\beta E_s} \quad (12)$$

Therefore:

$$U = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial \beta} \quad (13)$$

Alternatively, using $\beta = 1/k_B T$:

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T} \quad (14)$$

5.2 Helmholtz Free Energy

Theorem 5.1 (Helmholtz Free Energy from Partition Function). The Helmholtz free energy is directly related to the partition function by:

$$F = -k_B T \ln Z \quad (15)$$

Proof. Start with the thermodynamic definition:

$$F = U - TS \quad (16)$$

From statistical mechanics, entropy is:

$$S = -k_B \sum_s P_s \ln P_s \quad (17)$$

Substitute $P_s = \frac{e^{-\beta E_s}}{Z}$:

$$S = -k_B \sum_s \frac{e^{-\beta E_s}}{Z} \ln \left(\frac{e^{-\beta E_s}}{Z} \right) \quad (18)$$

$$= -k_B \sum_s \frac{e^{-\beta E_s}}{Z} (-\beta E_s - \ln Z) \quad (19)$$

$$= k_B \beta \sum_s P_s E_s + k_B \ln Z \sum_s P_s \quad (20)$$

$$= k_B \beta U + k_B \ln Z \quad (21)$$

Therefore:

$$F = U - TS \quad (22)$$

$$= U - T(k_B \beta U + k_B \ln Z) \quad (23)$$

$$= U - U - k_B T \ln Z \quad (24)$$

$$= -k_B T \ln Z \quad (25)$$

□

Key Point

This is perhaps the most important relationship: the partition function is essentially the exponential of the free energy (up to factors of $k_B T$). Since F is a thermodynamic potential, all other quantities can be derived from it.

5.3 Entropy

From $F = -k_B T \ln Z$ and $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$:

$$S = k_B \ln Z + k_B T \frac{\partial \ln Z}{\partial T} = k_B \ln Z + \frac{U}{T} \quad (26)$$

Alternatively:

$$S = k_B (\ln Z + \beta U) \quad (27)$$

5.4 Pressure

From $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$:

$$P = k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N} \quad (28)$$

Note 5.1. Pressure arises from the volume dependence of energy levels. For a particle in a box, energy levels $\propto 1/L^2 \propto 1/V^{2/3}$, leading to the familiar ideal gas law.

5.5 Heat Capacity

The heat capacity at constant volume is:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = k_B \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2} \quad (29)$$

Equivalently, using energy fluctuations:

$$C_V = \frac{1}{k_B T^2} (\langle E^2 \rangle - \langle E \rangle^2) = \frac{1}{k_B T^2} \text{Var}(E) \quad (30)$$

Key Point

Heat capacity measures energy fluctuations. Larger fluctuations mean the system can absorb/release more energy for a given temperature change.

5.6 Summary Table

Quantity	Formula
Probability	$P_s = \frac{e^{-\beta E_s}}{Z}$
Helmholtz Free Energy	$F = -k_B T \ln Z$
Internal Energy	$U = -\frac{\partial \ln Z}{\partial \beta}$
Entropy	$S = k_B (\ln Z + \beta U)$
Pressure	$P = k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N}$
Heat Capacity	$C_V = k_B \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2}$
Chemical Potential	$\mu = -k_B T \left(\frac{\partial \ln Z}{\partial N} \right)_{T,V}$

Table 1: Thermodynamic quantities from the partition function

6 Calculating Partition Functions: Examples

6.1 Two-Level System

Example 6.1 (Two-Level System). Consider a system with only two energy levels: ground state with energy $E_0 = 0$ and excited state with energy $E_1 = \epsilon$.

Step 1: Write the partition function

$$Z = e^{-\beta \cdot 0} + e^{-\beta \epsilon} = 1 + e^{-\beta \epsilon} \quad (31)$$

Step 2: Calculate probabilities

$$P_0 = \frac{1}{Z} = \frac{1}{1 + e^{-\beta \epsilon}} \quad (32)$$

$$P_1 = \frac{e^{-\beta \epsilon}}{Z} = \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \quad (33)$$

Step 3: Average energy

$$U = 0 \cdot P_0 + \epsilon \cdot P_1 = \frac{\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \frac{\epsilon}{e^{\beta\epsilon} + 1} \quad (34)$$

Step 4: Limiting behavior

- Low temperature ($T \rightarrow 0, \beta \rightarrow \infty$): $U \rightarrow 0$ (all in ground state)
- High temperature ($T \rightarrow \infty, \beta \rightarrow 0$): $U \rightarrow \epsilon/2$ (equal population)

Step 5: Heat capacity

$$C_V = \frac{\partial U}{\partial T} = k_B \left(\frac{\epsilon}{k_B T} \right)^2 \frac{e^{\epsilon/k_B T}}{(e^{\epsilon/k_B T} + 1)^2} \quad (35)$$

This exhibits the **Schottky anomaly**: a peak in C_V at temperature $T \sim \epsilon/k_B$.

Figure 1: Heat capacity vs. temperature for two-level system showing Schottky anomaly

6.2 Quantum Harmonic Oscillator

Example 6.2 (1D Quantum Harmonic Oscillator). Energy levels are:

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots \quad (36)$$

Step 1: Write partition function

$$Z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} \quad (37)$$

$$= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \quad (38)$$

$$= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n \quad (39)$$

This is a geometric series with ratio $r = e^{-\beta\hbar\omega}$:

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2 \sinh(\beta\hbar\omega/2)} \quad (40)$$

Step 2: Average energy

$$U = -\frac{\partial \ln Z}{\partial \beta} \quad (41)$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \quad (42)$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \quad (43)$$

The first term is the **zero-point energy** (quantum mechanical, no classical analog). The second term is the **Planck distribution** for the average number of quanta.

Step 3: High temperature limit When $k_B T \gg \hbar\omega$:

$$e^{\hbar\omega/k_B T} \approx 1 + \frac{\hbar\omega}{k_B T} + \dots \quad (44)$$

Therefore:

$$U \approx \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\hbar\omega/k_B T} = \frac{\hbar\omega}{2} + k_B T \quad (45)$$

At high T , this gives $C_V \rightarrow k_B$ (classical equipartition: $k_B T/2$ per quadratic degree of freedom, and we have kinetic + potential energy).

Step 4: Low temperature limit When $k_B T \ll \hbar\omega$:

$$U \approx \frac{\hbar\omega}{2} + \hbar\omega e^{-\hbar\omega/k_B T} \quad (46)$$

The excited states are "frozen out" exponentially.

6.3 Classical Ideal Gas

Example 6.3 (Monatomic Ideal Gas). For a classical gas, we must use the classical partition function and account for indistinguishability.

Step 1: Single particle partition function

The single-particle quantum states for a particle in a box of volume $V = L^3$ have energies:

$$\epsilon_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (47)$$

In the classical limit (high T , large V), we can replace the sum by an integral:

$$z_1 = \sum_{\text{states}} e^{-\beta\epsilon} \rightarrow \frac{V}{\lambda_T^3} \quad (48)$$

where the **thermal de Broglie wavelength** is:

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad (49)$$

Step 2: Account for indistinguishability

For N indistinguishable particles:

$$Z_N = \frac{z_1^N}{N!} = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N \quad (50)$$

The $1/N!$ factor corrects for overcounting (Gibbs paradox resolution).

Step 3: Take logarithm (using Stirling)

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

$$\ln Z = N \ln \left(\frac{V}{\lambda_T^3} \right) - \ln N! \quad (51)$$

$$\approx N \ln \left(\frac{V}{\lambda_T^3} \right) - N \ln N + N \quad (52)$$

$$= N \ln \left(\frac{V}{N \lambda_T^3} \right) + N \quad (53)$$

Step 4: Thermodynamic quantities*Free energy:*

$$F = -k_B T \ln Z = -Nk_B T \left[\ln \left(\frac{V}{N\lambda_T^3} \right) + 1 \right] \quad (54)$$

Pressure:

$$P = k_B T \frac{\partial \ln Z}{\partial V} = \frac{Nk_B T}{V} \quad (55)$$

This is the **ideal gas law**: $PV = Nk_B T$.*Internal energy:*

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} Nk_B T \quad (56)$$

This confirms equipartition: $\frac{1}{2}k_B T$ per translational degree of freedom.*Entropy (Sackur-Tetrode equation):*

$$S = Nk_B \left[\ln \left(\frac{V}{N\lambda_T^3} \right) + \frac{5}{2} \right] \quad (57)$$

6.4 Paramagnetism: Spin-1/2 System**Example 6.4** (Non-interacting Spins in Magnetic Field). Consider N non-interacting spin- $\frac{1}{2}$ particles in an external magnetic field B .**Step 1: Single spin partition function**Each spin can be up ($\uparrow$) or down ($\downarrow$) with energies:

$$E_{\uparrow} = -\mu B, \quad E_{\downarrow} = +\mu B \quad (58)$$

where μ is the magnetic moment.

Single spin partition function:

$$z = e^{\beta\mu B} + e^{-\beta\mu B} = 2 \cosh(\beta\mu B) \quad (59)$$

Step 2: Total partition functionFor N independent spins:

$$Z = z^N = [2 \cosh(\beta\mu B)]^N \quad (60)$$

Step 3: Magnetization

The magnetization is:

$$M = -\frac{\partial F}{\partial B} = Nk_B T \frac{\partial \ln Z}{\partial B} = N\mu \tanh(\beta\mu B) \quad (61)$$

Step 4: Limiting cases*High temperature or weak field* ($\mu B \ll k_B T$):

$$M \approx N\mu \cdot \frac{\mu B}{k_B T} = \frac{N\mu^2 B}{k_B T} \quad (62)$$

This is **Curie's law**: $M \propto B/T$.*Low temperature or strong field* ($\mu B \gg k_B T$):

$$M \rightarrow N\mu \quad (63)$$

All spins align with the field (saturation).

6.5 Einstein Solid

Example 6.5 (Einstein Model of a Solid). Model a crystalline solid as N atoms, each oscillating independently as a 3D quantum harmonic oscillator with frequency ω_E .

Step 1: Single atom partition function

Each atom has 3 independent oscillators (x, y, z directions):

$$z_{\text{atom}} = z_{\text{osc}}^3 = \left[\frac{e^{-\beta\hbar\omega_E/2}}{1 - e^{-\beta\hbar\omega_E}} \right]^3 \quad (64)$$

Step 2: Total partition function

$$Z = z_{\text{atom}}^N = \left[\frac{e^{-\beta\hbar\omega_E/2}}{1 - e^{-\beta\hbar\omega_E}} \right]^{3N} \quad (65)$$

Step 3: Internal energy

$$U = 3N \left[\frac{\hbar\omega_E}{2} + \frac{\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1} \right] \quad (66)$$

Step 4: Heat capacity

Define the **Einstein temperature**: $\Theta_E = \hbar\omega_E/k_B$.

$$C_V = 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \quad (67)$$

High temperature ($T \gg \Theta_E$): $C_V \rightarrow 3Nk_B$ (Dulong-Petit law)

Low temperature ($T \ll \Theta_E$): $C_V \propto e^{-\Theta_E/T}$ (exponential suppression)

Note 6.1. The Einstein model qualitatively captures heat capacity behavior but fails quantitatively at low T . The Debye model (which accounts for phonon dispersion) gives $C_V \propto T^3$ at low temperatures, in better agreement with experiment.

7 Advanced Topics and Extensions

7.1 Grand Canonical Ensemble

When both energy and particle number can fluctuate (e.g., system in contact with particle reservoir):

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N = \sum_{N=0}^{\infty} \sum_s e^{\beta(\mu N - E_s)} \quad (68)$$

where μ is the chemical potential. The grand potential is:

$$\Phi = -k_B T \ln \mathcal{Z} = F - \mu N \quad (69)$$

This ensemble is crucial for:

- Quantum gases (Bose-Einstein, Fermi-Dirac statistics)
- Chemical reactions
- Adsorption phenomena

7.2 Quantum Statistics

For identical quantum particles, the partition function must account for quantum statistics:

Bosons (integer spin, symmetric wavefunctions):

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \quad (\text{Bose-Einstein}) \quad (70)$$

Fermions (half-integer spin, antisymmetric wavefunctions):

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1} \quad (\text{Fermi-Dirac}) \quad (71)$$

These distributions arise naturally when constructing the grand partition function with appropriate symmetry constraints.

7.3 Interacting Systems

For systems with interactions, the partition function becomes:

$$Z = \sum_{\text{configs}} e^{-\beta E_{\text{total}}(\text{config})} \quad (72)$$

where E_{total} includes interaction terms. Examples:

- **Ising model:** $E = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i$
- **Van der Waals gas:** Includes attractive/repulsive interactions
- **Molecular systems:** Intermolecular potentials

Exact solutions are rare; approximations (mean field theory, series expansions, Monte Carlo) are typically needed.

8 Practical Strategies for Calculating Z

8.1 General Procedure

1. **Identify energy levels:** Determine E_s for all microstates s
2. **Check for factorization:** If subsystems are independent, $Z = \prod_i z_i$
3. **Handle degeneracy:** If energy E_n has degeneracy g_n , then $Z = \sum_n g_n e^{-\beta E_n}$
4. **Sum or integrate:**
 - Discrete levels: Direct summation
 - Continuous/quasicontinuous: Convert to integral using density of states
5. **Account for indistinguishability:** For identical particles, divide by $N!$ (classical) or use proper quantum statistics
6. **Take logarithm:** Usually $\ln Z$ appears in formulas; take log early to simplify
7. **Extract thermodynamics:** Use standard formulas from Section 4

8.2 When to Use Sum vs. Integral

Use summation when:

- Energy levels are discrete and countable
- Level spacing is comparable to or larger than $k_B T$
- Number of levels is small

Use integration when:

- Classical limit ($\lambda_T \ll$ system size)
- Level spacing $\ll k_B T$ (quasicontinuum)
- Need density of states $g(E)$: $Z = \int g(E) e^{-\beta E} dE$

8.3 Common Sums and Integrals

Sum/Integral	Result
$\sum_{n=0}^{\infty} x^n$	$\frac{1}{1-x} \quad (x < 1)$
$\sum_{n=0}^{\infty} n x^n$	$\frac{x}{(1-x)^2} \quad (x < 1)$
$\int_0^{\infty} x^n e^{-ax} dx$	$\frac{n!}{a^{n+1}}$
$\int_{-\infty}^{\infty} e^{-ax^2} dx$	$\sqrt{\frac{\pi}{a}}$
$\int_0^{\infty} x^{1/2} e^{-ax} dx$	$\frac{\sqrt{\pi}}{2a^{3/2}}$

Table 2: Useful mathematical results for partition function calculations

9 Common Mistakes and How to Avoid Them

Common Mistake

Mistake 1: Forgetting the $1/N!$ factor

For indistinguishable classical particles, the correct partition function is:

$$Z = \frac{z_1^N}{N!} \quad (73)$$

Why? Without this, entropy is not extensive (Gibbs paradox). The factor accounts for overcounting identical configurations.

Common Mistake**Mistake 2: Confusing β and T**

Remember: $\beta = 1/(k_B T)$. When taking derivatives:

$$\frac{\partial}{\partial T} = -\beta^2 k_B \frac{\partial}{\partial \beta} \quad (74)$$

Always check units and signs!

Common Mistake**Mistake 3: Not checking if subsystems are independent**

The factorization $Z = z_1 \cdot z_2 \cdots$ only works if subsystems don't interact. For interacting systems, you must sum over joint configurations.

Common Mistake**Mistake 4: Ignoring zero-point energy**

In quantum systems, don't forget terms like $\hbar\omega/2$. While they don't affect heat capacity or other derivatives, they matter for absolute values of F , S , and chemical equilibrium calculations.

Common Mistake**Mistake 5: Wrong reference for energy**

The choice of zero energy is arbitrary, but must be consistent. A shift $E_s \rightarrow E_s + E_0$ gives $Z \rightarrow e^{-\beta E_0} Z$, which cancels in probabilities but affects $F = -k_B T \ln Z$.

10 Worked Problems

10.1 Problem 1: Diatomic Molecule Rotation

Problem: Calculate the rotational partition function of a diatomic molecule at temperature T .

Solution:

The rotational energy levels are:

$$E_J = \frac{\hbar^2}{2I} J(J+1) = B_{\text{rot}} J(J+1) \quad (75)$$

where $J = 0, 1, 2, \dots$ and each level has degeneracy $g_J = 2J + 1$.

Step 1: Write partition function

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta B_{\text{rot}} J(J+1)} \quad (76)$$

Step 2: High temperature approximation

When $k_B T \gg B_{\text{rot}}$, we can replace the sum by an integral. Let $x = J(J+1)$, then $dx \approx 2J dJ$:

$$Z_{\text{rot}} \approx \int_0^\infty (2J+1)e^{-\beta B_{\text{rot}} J(J+1)} dJ \quad (77)$$

$$\approx \int_0^\infty e^{-\beta B_{\text{rot}} x} dx \quad (78)$$

$$= \frac{1}{\beta B_{\text{rot}}} = \frac{k_B T}{B_{\text{rot}}} \quad (79)$$

Step 3: Average energy

$$U_{\text{rot}} = -\frac{\partial \ln Z_{\text{rot}}}{\partial \beta} = k_B T \quad (80)$$

This confirms equipartition: $k_B T/2$ per rotational degree of freedom (there are 2 for a linear molecule).

10.2 Problem 2: Adsorption on Surface

Problem: M molecules can adsorb on N surface sites ($M \leq N$). Each adsorbed molecule has energy $-\epsilon$ (binding energy). Calculate the partition function and average number of adsorbed molecules.

Solution:

Step 1: Counting configurations

The number of ways to place M molecules on N sites is:

$$\Omega(M) = \binom{N}{M} = \frac{N!}{M!(N-M)!} \quad (81)$$

Total energy when M molecules are adsorbed: $E(M) = -M\epsilon$.

Step 2: Canonical partition function (fixed M)

If M is fixed:

$$Z(N, M) = \binom{N}{M} e^{\beta M \epsilon} \quad (82)$$

Step 3: Grand canonical partition function

If M fluctuates (molecule reservoir with chemical potential μ):

$$\mathcal{Z} = \sum_{M=0}^N e^{\beta \mu M} \binom{N}{M} e^{\beta M \epsilon} \quad (83)$$

$$= \sum_{M=0}^N \binom{N}{M} e^{\beta M(\mu+\epsilon)} \quad (84)$$

$$= (1 + e^{\beta(\mu+\epsilon)})^N \quad (85)$$

using the binomial theorem.

Step 4: Average occupancy

$$\langle M \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \frac{N e^{\beta(\mu+\epsilon)}}{1 + e^{\beta(\mu+\epsilon)}} = \frac{N}{1 + e^{-\beta(\mu+\epsilon)}} \quad (86)$$

Coverage fraction: $\theta = \langle M \rangle / N$:

$$\boxed{\theta = \frac{1}{1 + e^{-\beta(\mu+\epsilon)}}} \quad (87)$$

This is the **Langmuir adsorption isotherm**.

11 Connections to Other Areas of Physics

11.1 Quantum Field Theory

The partition function in QFT (Euclidean path integral) has form:

$$Z = \int \mathcal{D}\phi e^{-S_E[\phi]/\hbar} \quad (88)$$

where S_E is the Euclidean action. This connects statistical mechanics directly to quantum field theory (thermal field theory).

11.2 Information Theory

The partition function is related to the **Shannon entropy**:

$$S_{\text{Shannon}} = - \sum_s P_s \ln P_s = k_B \ln Z + \beta U \quad (89)$$

Maximizing entropy subject to fixed average energy yields the Boltzmann distribution – a deep connection between thermodynamics and information theory.

11.3 Machine Learning

Partition functions appear in probabilistic models:

- **Boltzmann machines**: Energy-based models where $P(\text{state}) \propto e^{-E(\text{state})}$
- **Restricted Boltzmann machines (RBMs)**: Used in deep learning
- **Markov Random Fields**: Graphical models with energy functions

The challenge: computing Z is often intractable (NP-hard), requiring Monte Carlo or variational methods.

12 Summary and Key Takeaways

Key Point

What is the partition function?

The partition function $Z = \sum_s e^{-\beta E_s}$ is the fundamental object in statistical mechanics that:

- Normalizes the Boltzmann distribution
- Encodes all thermodynamic information
- Connects microscopic (energy levels) to macroscopic (temperature, pressure, etc.)

Key Point**How do we derive it?**

Starting from:

1. Fundamental postulate (equal a priori probabilities)
2. System in thermal contact with reservoir
3. Taylor expansion for large reservoir
4. Definition of temperature from entropy

We arrive at $P_s = e^{-\beta E_s}/Z$.

Key Point**What can we calculate from it?**

Every thermodynamic quantity:

- Free energy: $F = -k_B T \ln Z$
- Internal energy: $U = -\partial \ln Z / \partial \beta$
- Entropy: $S = k_B (\ln Z + \beta U)$
- Pressure, heat capacity, chemical potential, etc.

Key Point**How do we calculate it?**

1. Identify energy levels E_s
2. Check for factorization (independent subsystems)
3. Sum (discrete) or integrate (continuous)
4. Account for degeneracy and indistinguishability
5. Extract thermodynamics via derivatives

13 Further Reading

Textbooks:

- Pathria & Beale, *Statistical Mechanics* (comprehensive, graduate level)
- Kardar, *Statistical Physics of Particles* (modern, field-theoretic perspective)
- Schroeder, *An Introduction to Thermal Physics* (excellent undergraduate introduction)

- Landau & Lifshitz, *Statistical Physics Part 1* (classic, concise, elegant)

Online Resources:

- MIT OCW 8.044 (Statistical Physics I)
- David Tong's lecture notes: <http://www.damtp.cam.ac.uk/user/tong/statphys.html>