Course Review
Statistical Mechanics[*]

Hanfeng Zhai[†]

Department of Mechanical Engineering,
Stanford University

Winter 2025

Contents

---

[*] ME 346A; Instructor: Wei Cai — TA: Myung Chul Kim

[†] E-mail: `hzhai@stanford.edu`

1 Introduction

This course summarizes key problems and definitions in statistical mechanics, bridging the gap between microscopic models and macroscopic thermodynamic properties. It emphasizes the role of ensembles, partition functions, and various models to describe real-world systems, e.g., ideal & non-ideal gas, solid, etc.

2 Useful Mathematical and Statistical Identities

2.1 Exponential and Logarithm Identities

- **Exponential of a Sum:**

  $$\exp(a+b) = \exp(a)\exp(b).$$

  Useful for factorizing Boltzmann factors when Hamiltonians split into independent parts.

- **Logarithm of a Product:**

  $$\ln(ab) = \ln a + \ln b.$$

  This is frequently used in expressing partition functions and free energies.

- **Logarithm of a Sum:**

  $$\ln(a+b) \quad \text{(no simple factorization; use approximations when one term dominates).}$$

2.2 Taylor Series Expansions

- **Exponential Function:**

  $$\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots .$$

  Used in approximating Boltzmann factors when $|x| \ll 1$.

- **Binomial Expansion:**

  $$(1+a)^n \approx 1 + na + \frac{n(n-1)}{2}a^2 + \cdots \quad (\text{for } |a| \ll 1).$$

- **Logarithmic Expansion:**

  $$\ln(1+x) \approx x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots \quad (\text{for } |x| < 1).$$

  Often used to expand the logarithm of partition functions or probabilities.

- **Geometric Series Expansion:**

  $$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots \quad (\text{for } |x| < 1).$$

  Useful for summing series, such as those encountered in partition functions of systems with equally spaced energy levels.

- **Sommerfeld Expansion (for Fermi Systems):**
  Although not a standard Taylor series, the Sommerfeld expansion is used to approximate integrals at low temperatures:

  $$\int_0^\infty f(\epsilon)\frac{d\epsilon}{e^{\beta(\epsilon-\mu)}+1} \approx \int_0^\mu f(\epsilon)d\epsilon + \frac{\pi^2}{6}(k_BT)^2 f'(\mu) + \cdots ,$$

  where $f(\epsilon)$ is a smooth function. This is particularly useful in evaluating thermodynamic quantities in Fermi systems.

2.3 Stirling's Approximation

For large N[1],

$$\ln N! \approx N \ln N - N.$$

This is crucial in statistical mechanics when counting microstates, especially for entropy calculations and deriving expressions like the Sackur-Tetrode equation for ideal gases.

2.4 Gaussian Integrals

The standard Gaussian integral is:

$$\int_{-\infty}^{\infty} \exp\left(-ax^2\right) dx = \sqrt{\frac{\pi}{a}}, \quad a > 0.$$

This identity is often used when evaluating momentum integrals or fluctuations around equilibrium in quadratic approximations.

2.5 Combinatorial Identities

- **Binomial Coefficient:**
  $$C_N^k \equiv \binom{N}{k} = \frac{N!}{k!(N-k)!}.$$
  Use this to count the number of ways to choose k objects from N; useful when deriving multiplicities in two-level systems.

- **Permutation:**
  $$A_N^k \equiv P(N,k) = \frac{N!}{(N-k)!}.$$
  counts the number of ordered arrangements of k objects chosen from a total of N.

In many cases, the choice between using $\binom{N}{k}$ (combinations) and $P(N,k)$ (permutations) depends on whether the order of selection matters. In statistical mechanics, if particles are distinguishable and order is important, use permutations; if not, combinations are more appropriate.

2.6 Probability and Expectation

- **Definition of Expectation:**
  $$\langle X \rangle = \sum_i p_i X_i \quad \text{or} \quad \langle X \rangle = \int X\, p(X)\, dX.$$

- **Linearity of Expectation:**
  $$\langle X + Y \rangle = \langle X \rangle + \langle Y \rangle.$$

---

[1] i.e., $\to \infty$

- **Expectation for Independent Variables:**
$$\langle XY \rangle = \langle X \rangle \langle Y \rangle \quad \text{(if } X \text{ and } Y \text{ are independent).}$$
- **Standard Deviation:** For a random variable X,
$$\sigma_X = \sqrt{\langle (X - \langle X \rangle)^2 \rangle} = \sqrt{\langle X^2 \rangle - \langle X \rangle^2}.$$
- **Variance:** Denoted as $\mathrm{Var}(X) = \sigma_X^2$.
- **Energy Expectation in the Canonical Ensemble:**
$$\langle E \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{\partial \ln Z}{\partial \beta}.$$
This is a key relation used to compute the average energy of a system.

2.7 Useful Sums and Series

- **Geometric Series:**
  - **Infinite Geometric Series:**
  $$\sum_{n=0}^{\infty} ar^n = \frac{a}{1-r}, \quad \text{for } |r| < 1.$$
  Useful when summing Boltzmann factors in discrete energy level systems.
  - **Finite Geometric Series:**
  $$\sum_{n=0}^{N-1} ar^n = a\frac{1-r^N}{1-r}, \quad \text{for } r \neq 1.$$
  Applicable when considering a finite number of terms, such as systems with a limited number of energy levels.
- **Exponential Series:**
$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}.$$
Essential for deriving the partition function in systems with quantized energy levels.
- **Binomial Series:**
$$(1+x)^n = \sum_{k=0}^{\infty} \binom{n}{k} x^k.$$
Useful in expanding expressions involving probabilities and partition functions.
- **Logarithmic Series:**
$$\ln(1-x) = -\sum_{n=1}^{\infty} \frac{x^n}{n}, \quad \text{for } |x| < 1.$$
Appears in the calculation of entropy and free energy expressions.

When to Use These Identities: These mathematical tools and approximations are essential in various stages of a statistical mechanics calculation:

- *Exponential and logarithm identities* simplify the manipulation of partition functions and free energy expressions.
- *Taylor series and Stirling's approximation* are invaluable when evaluating asymptotic behavior or approximating functions in the thermodynamic limit.
- *Gaussian integrals* appear in the evaluation of integrals in momentum space or in the analysis of fluctuations.
- *Combinatorial identities* help in counting microstates[2] and in the derivation of entropy.
- *Probability rules and expectations* are used throughout to derive macroscopic observables from microscopic distributions.

2.8 Probability, Mean, and Standard Deviation

In statistical mechanics, the probability p_i that the system is in a microstate i with energy E_i is given by the Boltzmann distribution:

$$p_i = \frac{e^{-\beta E_i}}{Z},$$

where the partition function is

$$Z = \sum_i e^{-\beta E_i},$$

and $\beta = \frac{1}{k_B T}$.

The expectation (or mean) value of any observable X is computed as:

$$\langle X \rangle = \sum_i p_i X_i.$$

For a continuous variable X, this generalizes to:

$$\langle X \rangle = \int X \, p(X) \, dX.$$

The variance of X is defined by:

$$\mathrm{Var}(X) = \langle (X - \langle X \rangle)^2 \rangle = \langle X^2 \rangle - \langle X \rangle^2,$$

and the standard deviation is:

$$\sigma_X = \sqrt{\langle X^2 \rangle - \langle X \rangle^2}.$$

These definitions allow you to estimate the average behavior of observables (such as energy, magnetization, etc.) and their fluctuations, which are key to solving problems in statistical mechanics.

---

[2] and derive degeneracy

3 Fundamental Concepts

3.1 Microstates, Macrostates, and Ensembles

- **Microstate:** A complete specification of the system at the microscopic level.
- **Macrostate:** Characterized by macroscopic variables (e.g., temperature, pressure, magnetization) and can correspond to many microstates.
- **Ensembles:**
  - **Microcanonical:** Fixed energy, volume, and particle number. (N, V, E)
  - **Canonical:** Fixed temperature, volume, and particle number. (N, V, T)
  - **Grand Canonical:** Fixed temperature, volume, and chemical potential.

3.2 Partition Functions and Thermodynamic Properties

3.2.1 Canonical Ensemble

The canonical partition function is defined as[3]:

$$Z = \sum_{\text{states}} e^{-\beta E} \quad \text{or, for continuous degrees of freedom,} \quad Z = \int d\Gamma\, e^{-\beta H(\boldsymbol{q},\boldsymbol{p})},$$

where $\beta \equiv \frac{1}{k_B T}$. For a system of N particles, if the particles are indistinguishable and quantum effects are important, the partition function should include the appropriate normalization:

$$Z = \frac{1}{N!\, h^{3N}} \sum_{\text{states}} e^{-\beta E} \quad \text{or} \quad Z = \frac{1}{N!\, h^{3N}} \int d\Gamma\, e^{-\beta H(\boldsymbol{q},\boldsymbol{p})}.$$

Here, the $1/N!$ factor avoids overcounting due to indistinguishability, and the factor h^{3N} provides the quantum mechanical correction by normalizing the phase space.

Once Z is determined, key thermodynamic quantities can be calculated:

- **Helmholtz Free Energy:**
$$A = -k_B T \ln Z.$$
- **Internal Energy:**
$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}.$$
- **Entropy:**
$$S = k_B(\ln Z + \beta \langle E \rangle) \quad \text{or equivalently} \quad S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}.$$

---

[3] For a system in thermal contact with a heat bath.

- **Specific Heat (at constant volume):**

$$C_V = k_B \beta^2 \left(\langle E^2 \rangle - \langle E \rangle^2 \right) = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V .$$

- **Pressure:** For systems where volume V is a variable,

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

The above relations allow one to derive all thermodynamic properties once the partition function is known.

3.2.2 Microcanonical Ensemble

In the microcanonical ensemble, the system is isolated with fixed energy E, volume V, and number of particles N. The key quantity here is the number of microstates $\Omega(E, V, N)$ accessible to the system:

$$\Omega(E, V, N) = \text{number of states with energy between } E \text{ and } E + \Delta E.$$

The entropy is then defined by Boltzmann's relation:

$$S = k_B \ln \Omega(E, V, N).$$

The microcanonical ensemble is often used as a starting point to derive other ensembles via a Legendre transform. For example, the temperature is defined by:

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

and the Helmholtz free energy in the canonical ensemble can be obtained via:

$$A = E - TS.$$

Although direct calculations in the microcanonical ensemble can be challenging, it provides the fundamental connection between microscopic state counting and thermodynamic entropy.

3.2.3 When to Use $N!$ and h^{3N}

- **Indistinguishability:** In a system of N identical particles, without the $1/N!$ factor, the same physical state would be overcounted. This factor is essential for obtaining the correct entropy and free energy.

- **Quantum Correction:** The factor h^{3N} arises when converting a sum over quantum states to an integral over phase space. It ensures consistency with the Heisenberg uncertainty principle by providing the correct quantum of phase space volume.

3.2.4 Calculating Thermodynamic Quantities in the Canonical Ensemble

1. **Compute the Partition Function Z:** Include the appropriate corrections for indistinguishability and quantum effects if dealing with a system of identical particles.
2. **Determine the Free Energy A:** Use the relation:
$$A = -k_B T \ln Z.$$
3. **Find the Internal Energy $\langle E \rangle$:** Differentiate $\ln Z$ with respect to β:
$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}.$$
4. **Calculate the Entropy S:** This can be done either by using:
$$S = k_B(\ln Z + \beta \langle E \rangle),$$
or by differentiating the free energy:
$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}.$$
5. **Obtain the Specific Heat C_V:** Differentiate the internal energy with respect to temperature:
$$C_V = \frac{\partial \langle E \rangle}{\partial T},$$
or compute it directly from the fluctuations in energy:
$$C_V = k_B \beta^2 \left(\langle E^2 \rangle - \langle E \rangle^2 \right).$$

These steps form the basis for extracting macroscopic properties from the canonical partition function.

3.3 Degeneracy in Partition Function

Key Points:

- **Overlap Allowed** means multiple particles can occupy the same quantum state (e.g. bosons).
- **Overlap Forbidden** means each state can hold at most one particle (e.g. Pauli exclusion for fermions, or physically limited seats).
- **Distinguishable** particles are labeled (e.g. each particle has a unique identity).
- **Indistinguishable** particles are identical; permuting them does not yield a new physical state.

	Overlap Allowed	**Overlap Forbidden**
Distinguishable	**Case 1:** • Particles are labeled. • Multiple occupancy of a single state is allowed. • Example: Classical spins on different sites. • Number of microstates $\sim n^N$ if each of N particles can occupy n states independently. • Partition function factorizes easily, $Z = z^N$.	**Case 3:** • Particles are labeled. • Only one particle per state (no overlap). • Example: N distinct seats, each seat can hold only one person. • Number of microstates $\sim P(n, N) = \frac{n!}{(n-N)!}$. • Partition function may involve permutations of distinct states.
Indistinguishable	**Case 2:** • Particles are identical. • Multiple occupancy allowed (e.g. bosons). • Example: Photons in a cavity (Bose-Einstein). • State counting uses Bose-Einstein combinatorics or $N!$ factors in partition function may be replaced by bosonic distribution. • If classical, factor $\frac{1}{N!}$ in Z for indistinguishability.	**Case 4:** • Particles are identical. • Single occupancy per state (Pauli exclusion). • Example: Electrons (fermions). • State counting uses Fermi-Dirac statistics (occupancy 0 or 1). • Partition function construction: product over states with occupancy constraints. $\sim \binom{n}{N} = \frac{n!}{N!(n-N)!}$

Table 1: Overview of four degeneracy cases based on overlap (multiple occupancy) and distinguishability.

Usage in Partition Functions: When constructing a partition function, the degeneracy factor $g(E)$ (number of states with energy E) appears as a multiplicative factor:

$$Z = \sum_E g(E)\, e^{-\beta E}.$$

Depending on the nature of the particles and the occupancy rules, $g(E)$ will be computed differently according to the four cases outlined above. For example, in a classical ideal gas (indistinguishable particles, overlap allowed), the partition function includes the factor $\frac{1}{N!}$ to account for indistinguishability and h^{3N} as a quantum correction:

$$Z = \frac{1}{N!\, h^{3N}} \int d\Gamma\, e^{-\beta H(\Gamma)}.$$

This systematic approach to degeneracy is fundamental in statistical mechanics, as it ensures that the partition function correctly reflects the physical counting of microstates.

4 Analytical Techniques and Approximations

4.1 Derivatives of the Partition Function

- Use of $\frac{\partial \ln Z}{\partial \beta}$ and $\frac{\partial \ln Z}{\partial h}$ to compute energy and magnetization.

4.2 Limits and Approximations

- **Low-Temperature Limit:** Approximations that focus on ground state properties.
- **High-Temperature Limit:** Series expansions and simplification to ideal behavior.
- **Asymptotic Analysis:** Behavior of functions like $g(E)$ in extreme limits.

4.3 Transfer Matrix Method

- Construction and diagonalization of the transfer matrix to handle 1D systems.
- Extraction of the largest eigenvalue to determine the free energy per spin in the thermodynamic limit.

4.4 Fluctuation Analysis

- Calculation of standard deviations and other moments to understand thermal fluctuations.

5 The Ising Model

5.1 1D Ising Model

- **Hamiltonian:** For N spins with nearest-neighbor interactions,

$$H = -J \sum_{i=1}^{N-1} s_i s_{i+1} - h \sum_{i=1}^{N} s_i, \quad s_i = \pm 1.$$

- **Transfer Matrix Method:** This technique provides an exact solution in 1D.

  1. **Constructing the Transfer Matrix:**
     Define a 2×2 matrix P with elements given by

     $$P(s, s') = \exp\left[\beta(J s s' + \tfrac{h}{2}(s + s'))\right],$$

     where $s, s' \in \{+1, -1\}$.
  2. **Partition Function:**
     The partition function can then be written as

     $$Z = \sum_{\{s_i\}} \prod_{i=1}^{N-1} P(s_i, s_{i+1}) = \mathrm{Tr}(P^{N-1}).$$

3. **Diagonalization:**
   Find the eigenvalues λ_+ and λ_- of P. For large N, the partition function is dominated by the largest eigenvalue,
   $$Z \approx \lambda_+^{N-1}.$$
4. **Example Calculation:**
   For instance, with $h = 0$ the matrix simplifies to
   $$P = \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix}.$$
   Its eigenvalues are
   $$\lambda_+ = e^{\beta J} + e^{-\beta J} = 2\cosh(\beta J), \quad \lambda_- = e^{\beta J} - e^{-\beta J} = 2\sinh(\beta J).$$
   Therefore, for large N (and when $h = 0$),
   $$Z \approx (2\cosh(\beta J))^{N-1}.$$

- **Key Results:**
  - Free energy density:
    $$a = -k_B T \ln \lambda_+.$$
  - Magnetization (in a nonzero field) can be computed via
    $$M = \frac{1}{\beta}\frac{\partial \ln Z}{\partial h}.$$
  - In 1D, there is no phase transition at $T > 0$.

5.2 Example Problem: Constructing the Transfer Matrix for a 1D Chain

Problem: Consider a 1D Ising chain of 3 spins with periodic boundary conditions, $s_1, s_2, s_3 \in \{+1, -1\}$ and Hamiltonian
$$H = -J(s_1 s_2 + s_2 s_3 + s_3 s_1) - h(s_1 + s_2 + s_3).$$

Solution:

1. Write the Boltzmann factor for a single nearest-neighbor interaction:
   $$w(s, s') = e^{\beta(Jss' + \frac{h}{2}(s+s'))}.$$
2. The transfer matrix P is then
   $$P = \begin{pmatrix} e^{\beta(J+h)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-h)} \end{pmatrix}.$$
3. The partition function is
   $$Z = \mathrm{Tr}(P^3).$$
4. Diagonalize P to find its eigenvalues λ_+ and λ_-, then express
   $$Z = \lambda_+^3 + \lambda_-^3.$$

5.3 Generalization: Constructing the Transfer Matrix in More Complex Cases

In many models, the Hamiltonian may include additional interactions or more complex dependencies that require a modified approach to constructing the transfer matrix. The following outlines a general strategy:

1. Factorization of the Boltzmann Factor: Begin by writing the partition function as a sum over configurations:

$$Z = \sum_{\{s_i\}} \exp\left[-\beta H(\{s_i\})\right].$$

For Hamiltonians that can be written as a sum over bonds (or interactions), such as

$$H = \sum_i \phi(s_i, s_{i+1}, \ldots),$$

attempt to factorize the Boltzmann factor into a product over local contributions.

2. Identifying Local Contributions: Even if the Hamiltonian involves more than nearest-neighbor interactions (for example, next-nearest-neighbor terms or multi-spin interactions), try to rewrite the exponential as:

$$\exp\left[-\beta H\right] = \prod_i W(s_i, s_{i+1}, \ldots),$$

where W is the local weight that may depend on several spins. For extra terms such as an external field, it is common to split the contribution equally between adjacent bonds.

3. Defining an Enlarged State Space: For interactions beyond nearest-neighbor, it is often necessary to *enlarge the state space*. For example, if the Hamiltonian includes both nearest-neighbor and next-nearest-neighbor interactions,

$$H = -J_1 \sum_i s_i s_{i+1} - J_2 \sum_i s_i s_{i+2},$$

one approach is to define a block variable (e.g., the state of a pair of consecutive spins) and then construct a transfer matrix T whose indices represent these block states. In this case, each matrix element takes the form:

$$T\Big((s_i, s_{i+1}), (s_{i+1}, s_{i+2})\Big) = \exp\Big[-\beta\, \psi(s_i, s_{i+1}, s_{i+2})\Big],$$

where ψ collects all interaction terms involving spins s_i, s_{i+1}, and s_{i+2}.

4. Handling Anisotropy or Multi-Spin Interactions: For models with anisotropic interactions or other “weird” features (e.g., additional directional couplings), the key is to appropriately partition the Hamiltonian so that each term is assigned to a bond (or a block) in a consistent manner. Often, the idea is to write:

$$Z = \mathrm{Tr}\left(T^N\right),$$

where the transfer matrix T is defined such that its matrix elements capture the contributions from all the interactions between adjacent blocks.

5. Diagonalization and Extraction of Thermodynamic Quantities: Once the transfer matrix T is constructed, the next steps are similar to the standard case:

1. Diagonalize T to find its eigenvalues $\lambda_1, \lambda_2, \ldots$.
2. In the thermodynamic limit, the largest eigenvalue $\lambda_{\max}$ dominates:

$$Z \approx \lambda_{\max}^N.$$

3. The free energy per block is then given by:

$$a = -k_B T \ln \lambda_{\max}.$$

Example of a “Weirder” Case: Consider a 1D chain where each spin interacts with both its nearest and next-nearest neighbors. The Hamiltonian might be:

$$H = -J_1 \sum_i s_i s_{i+1} - J_2 \sum_i s_i s_{i+2} - h \sum_i s_i.$$

To handle the next-nearest-neighbor interaction, define a block of two consecutive spins, say $\sigma_i = (s_i, s_{i+1})$. Then, rewrite the Hamiltonian in terms of overlapping blocks and construct a transfer matrix $T(\sigma_i, \sigma_{i+1})$ that includes the interaction energies shared between blocks. Although this increases the matrix size (from 2×2 to 4×4 in this case), it allows the same method to be applied.

Summary: The transfer matrix method is versatile and can be adapted to more complex models by:

- Expressing the partition function as a product of local weights.
- Distributing interaction terms (e.g., external fields) appropriately between neighboring sites.
- Enlarging the state space when interactions extend beyond nearest neighbors.
- Constructing the transfer matrix such that its elements represent the Boltzmann weights of transitions between block states.

By following these steps, you can derive a suitable transfer matrix even for “weird” cases, and proceed to extract thermodynamic properties from its largest eigenvalue.

5.4 2D Ising Model (Overview)

- **Phase Transition:** Onsager's solution reveals a critical temperature

$$k_B T_c = \frac{2J}{\ln(1+\sqrt{2})} \approx 2.269J.$$

- **Key Features:**
  - Spontaneous magnetization for $T < T_c$.
  - Diverging susceptibility $\chi \sim |T - T_c|^{-\gamma}$.
  - Correlation length $\xi \sim |T - T_c|^{-\nu}$.
- **Monte Carlo Simulation:** For numerical studies, the Metropolis algorithm is used:
  1. Initialize a random spin configuration.
  2. Randomly select a spin and compute the energy change ΔE.
  3. Flip the spin if $\Delta E < 0$ or with probability $e^{-\beta \Delta E}$.
  4. Measure observables after equilibration.

6 Counting Number of States and Density of States

6.1 Density of States in the Energy Shell

The density of states (DOS), $g(E)$, represents the number of quantum states per unit energy at a given energy E. It is crucial for determining the statistical properties of systems in condensed matter physics, such as electrons in solids, phonons, and photons.

6.1.1 General Derivation

Consider a system where particles are confined in a volume V. The number of quantum states with wave vectors between $\mathbf{k}$ and $\mathbf{k} + d\mathbf{k}$ is given by:

$$dN = \frac{V}{(2\pi)^3} d^3\mathbf{k}$$

For isotropic systems, this can be expressed in spherical coordinates:

$$dN = \frac{V}{(2\pi)^3} 4\pi k^2 dk$$

The energy E is related to the wave vector k by the dispersion relation $E = E(k)$. The density of states $g(E)$ is then:

$$g(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \frac{k^2}{v_g}$$

where $v_g = \frac{dE}{dk}$ is the group velocity of the particles.

6.2 Examples

6.2.1 Electrons in a 3D Free Electron Gas

For free electrons, the energy dispersion relation is:

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

Solving for k:

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

The group velocity v_g is:

$$v_g = \frac{dE}{dk} = \frac{\hbar^2 k}{m} = \frac{\hbar}{m}\sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2E}{m}}$$

Substituting into the DOS expression:

$$g(E) = \frac{V}{2\pi^2}\frac{\left(\frac{2mE}{\hbar^2}\right)}{\sqrt{\frac{2E}{m}}} = \frac{V}{2\pi^2}\frac{2mE}{\hbar^2}\sqrt{\frac{m}{2E}} = \frac{V}{2\pi^2}\frac{2m^{3/2}\sqrt{E}}{\hbar^3\sqrt{2}} = \frac{V}{2\pi^2}\frac{m^{3/2}\sqrt{2E}}{\hbar^3}$$

Simplifying:

$$g(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$

6.2.2 Phonons in a 3D Solid

For acoustic phonons, the dispersion relation is linear:

$$E = \hbar\omega = \hbar c_s k$$

where c_s is the speed of sound in the material. Solving for k:

$$k = \frac{E}{\hbar c_s}$$

The group velocity v_g is:

$$v_g = \frac{dE}{dk} = \hbar c_s$$

Substituting into the DOS expression:

$$g(E) = \frac{V}{2\pi^2}\frac{\left(\frac{E}{\hbar c_s}\right)^2}{c_s} = \frac{V}{2\pi^2}\frac{E^2}{\hbar^3 c_s^3}$$

6.2.3 Photons in a 3D Cavity

Photons also have a linear dispersion relation:

$$E = \hbar\omega = \hbar c k$$

where c is the speed of light. Following a similar derivation as for phonons:

$$g(E) = \frac{V}{2\pi^2}\frac{E^2}{\hbar^3 c^3}$$

6.3 Summary

The density of states is a fundamental concept in statistical mechanics and condensed matter physics, providing insight into the distribution of available quantum states at each energy level. Its calculation varies depending on the dispersion relation of the particles in the system, as demonstrated in the examples above.

7 General Problem-Solving Strategies

When approaching problems in statistical mechanics, the following steps provide a systematic framework:

7.1 Define the System and Identify Degrees of Freedom

- Clearly specify the microscopic variables (positions, momenta, spins, etc.) and the constraints of the system.
- Decide on the relevant ensemble (e.g., microcanonical, canonical, or grand canonical) based on the physical situation.

7.2 Construct the Partition Function

- Write the partition function in its general form:

  $$Z = \sum_{\text{states}} e^{-\beta E} \quad \text{or} \quad Z = \int d\Gamma\, e^{-\beta H(\Gamma)},$$

  where $\beta = 1/(k_B T)$.
- Factorize the partition function when possible. For systems with independent or weakly interacting components, express Z as a product over contributions.
- For systems with interactions, consider techniques such as the transfer matrix method, mean-field approximations, or cluster expansions.

7.3 Derive Thermodynamic Quantities

- Extract macroscopic observables using derivatives of $\ln Z$:

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}, \quad C_V = k_B T^2 \frac{\partial^2 \ln Z}{\partial \beta^2}.$$

- Compute other quantities such as magnetization, entropy, and free energies via appropriate Legendre transforms:

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

7.4 Use Approximation Methods Where Necessary

- **Low/High-Temperature Limits:** Evaluate series expansions or asymptotic forms in the limits $T \to 0$ or $T \to \infty$.

- **Saddle-Point/Steepest-Descent:** Use these techniques for evaluating integrals in the thermodynamic limit when N is large.

- **Perturbation Theory:** For weakly interacting systems, treat interactions as perturbations to the ideal case.

7.5 Using Advanced Methods for Interacting Systems

- **Transfer Matrix Method:** For 1D systems or systems reducible to 1D-like chains, construct a matrix whose largest eigenvalue gives the dominant contribution to Z.

- **Renormalization Group:** For critical phenomena and phase transitions, use renormalization methods to study scale-dependent behavior.

- **Monte Carlo Simulations:** In cases where analytic solutions are intractable, apply numerical techniques (e.g., the Metropolis algorithm) to sample configurations.

7.6 Verify Consistency and Check Limits

- Confirm that results reduce to known expressions in appropriate limits (e.g., non-interacting or high-temperature limits).

- Check dimensional consistency and the behavior of extensive versus intensive quantities.

- Validate that fluctuations vanish in the thermodynamic limit (ensemble equivalence).

7.7 Interpret Physical Significance

- Relate the derived thermodynamic quantities to experimental observables.
- Analyze critical behavior by studying divergences (e.g., in susceptibility or correlation length) and extracting critical exponents.
- Understand the impact of symmetry and conservation laws on the solution.

7.8 Document Assumptions and Approximations

- Clearly state any assumptions (e.g., neglecting interactions, ideal behavior) and justify their validity.
- Discuss potential corrections or limitations of the approximations used.

This systematic approach provides a robust framework to tackle a broad spectrum of problems in statistical mechanics, ensuring that you can move from the microscopic description to macroscopic predictions while maintaining consistency with fundamental physical principles.

8 Conclusion

Here's a quick recap of the key points and problem-solving methods covered in the class. We delved deeper into the Ising model, with hands-on examples on building and working out the transfer matrix, which sets you up nicely for handling all sorts of problems in statistical mechanics. Grasping these ideas is essential for nailing the final exam.