

Course Review

Statistical Mechanics*

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1 Introduction

Scope and disclaimer

These notes review the core definitions and problem-solving tools from ME 346A. They were written with the help of AI for my personal review only, to organize and consolidate course material. They are not course handouts and should not be treated as an official reference.

The course connects microscopic configurations to macroscopic thermodynamic quantities through ensembles, partition functions, and standard models such as the ideal gas, the harmonic solid, and the Ising model. The emphasis is on counting states correctly, writing Z in the right ensemble, and extracting observables from $\ln Z$.

Three-step workflow

1. Choose the ensemble that matches the fixed variables.
2. Build Z or Ω with the correct counting factors.
3. Differentiate $\ln Z$ (or use $\ln \Omega$) to get A , $\langle E \rangle$, S , C_V , and response functions.

2 Useful Mathematical and Statistical Identities

2.1 Exponential and Logarithm Identities

- **Exponential of a sum:**

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

Use this when the Hamiltonian splits into additive, statistically independent pieces.

- **Logarithm of a product:**

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

This appears when taking $\ln Z$ or $\ln \Omega$.

- **Logarithm of a sum:**

$$\ln(a + b)$$

has no simple factorization. Expand only when one term dominates, or use a saddle-point / steepest-descent argument.

2.2 Taylor Series and Useful Expansions

Expansions to recognize instantly

- $e^x = 1 + x + x^2/2! + \dots$ for $|x| \ll 1$
- $(1 + a)^n \approx 1 + na + n(n-1)a^2/2 + \dots$ for $|a| \ll 1$
- $\ln(1 + x) \approx x - x^2/2 + x^3/3 - \dots$ for $|x| < 1$
- $(1 - x)^{-1} = 1 + x + x^2 + \dots$ for $|x| < 1$
- Sommerfeld (low- T Fermi gas):

$$\int_0^\infty \frac{f(\epsilon) d\epsilon}{e^{\beta(\epsilon-\mu)} + 1} \approx \int_0^\mu f(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 f'(\mu) + \dots$$

2.3 Stirling's Approximation

For large N ,

$$\ln N! \approx N \ln N - N + \frac{1}{2} \ln(2\pi N).$$

The leading term $N \ln N - N$ is enough for most entropy estimates in the thermodynamic limit.

2.4 Gaussian Integrals

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

Generalizations to multiple dimensions appear in ideal-gas momentum integrals and quadratic fluctuation calculations.

2.5 Combinatorial Identities

- **Combinations:** $\binom{N}{k} = \frac{N!}{k!(N-k)!}$
- **Permutations:** $P(N, k) = \frac{N!}{(N-k)!}$

Particle counting traps

- **Key:** Use permutations when objects are distinguishable and assigned to distinct ordered slots.
- **Key:** Use combinations, Bose–Einstein, or Fermi–Dirac counting when particles are identical.
- **Trap:** Do not multiply by $N!$ for identical particles.
- The classical semiclassical correction is the factor $1/N!$ in the phase-space measure.

2.6 Probability, Variance, and Canonical Averages

Canonical probability and averages

For discrete microstates,

$$p_i = \frac{e^{-\beta E_i}}{Z}, \quad Z = \sum_i e^{-\beta E_i}, \quad \beta = (k_B T)^{-1}.$$

$$\langle X \rangle = \sum_i p_i X_i, \quad \text{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2.$$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}, \quad \langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial \beta^2}.$$

For continuous variables, replace the sum by $\int X p(X) dX$. If X and Y are independent, then $\langle XY \rangle = \langle X \rangle \langle Y \rangle$.

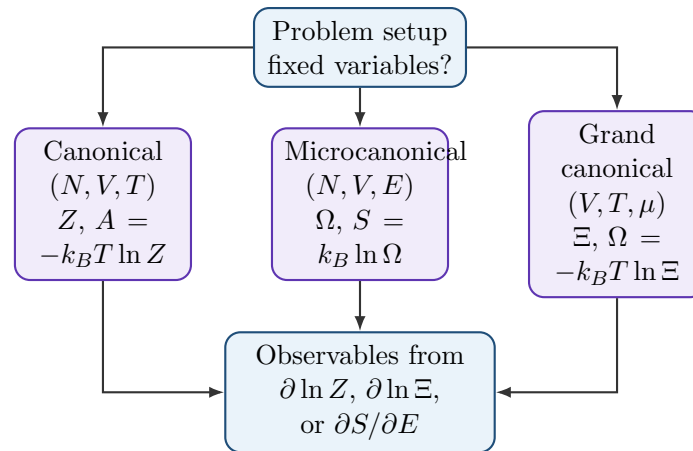
2.7 Standard Sums

- **Finite geometric:** $\sum_{n=0}^{N-1} ar^n = a \frac{1 - r^N}{1 - r}, \quad r \neq 1$
- **Infinite geometric:** $\sum_{n=0}^{\infty} ar^n = \frac{a}{1 - r}, \quad |r| < 1$
- **Exponential series:** $e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$
- **Logarithmic series:** $\ln(1 - x) = -\sum_{n=1}^{\infty} \frac{x^n}{n}, \quad |x| < 1$

3 Fundamental Concepts

3.1 Microstates, Macrostates, and Ensembles

- **Microstate:** a complete microscopic specification of the system.
- **Macrostate:** specified by a small set of macroscopic variables such as T , p , or M .
- **Ensemble:** a statistical distribution over microstates consistent with the chosen macroscopic constraints.



Key: Pick the ensemble that matches the physical control knobs of the problem.

3.2 Partition Functions and Thermodynamic Potentials

3.2.1 Canonical Ensemble

Canonical hub (memorize this block)

The canonical partition function is

$$Z = \sum_i e^{-\beta E_i} \quad \text{or} \quad Z = \int \frac{d^N q d^N p}{N! h^{3N}} e^{-\beta H(\mathbf{q}, \mathbf{p})}.$$

The factor $1/N!$ removes overcounting of identical particles. The factor h^{3N} converts the phase-space integral to a sum over quantum states.

From Z ,

$$A = -k_B T \ln Z, \quad \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta},$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = k_B (\ln Z + \beta \langle E \rangle),$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}, \quad C_V = k_B \beta^2 (\langle E^2 \rangle - \langle E \rangle^2).$$

3.2.2 Microcanonical Ensemble

For an isolated system,

$$\Omega(E, V, N) = \text{microstates with } E \leq E' < E + \delta E, \quad S = k_B \ln \Omega, \quad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}.$$

The microcanonical ensemble is the starting point for Boltzmann entropy. The canonical and grand-canonical ensembles follow from coupling the system to a bath.

3.2.3 Workflow in the Canonical Ensemble

Canonical recipe

1. Write H and identify the degrees of freedom.
2. Construct Z with the correct symmetry factors ($1/N!$, Bose/Fermi occupation, etc.).
3. Compute $A = -k_B T \ln Z$.
4. Differentiate to obtain $\langle E \rangle$, S , p , and C_V .
5. Check limiting cases ($T \rightarrow 0$, $T \rightarrow \infty$, noninteracting limit).

3.3 Degeneracy and State Counting

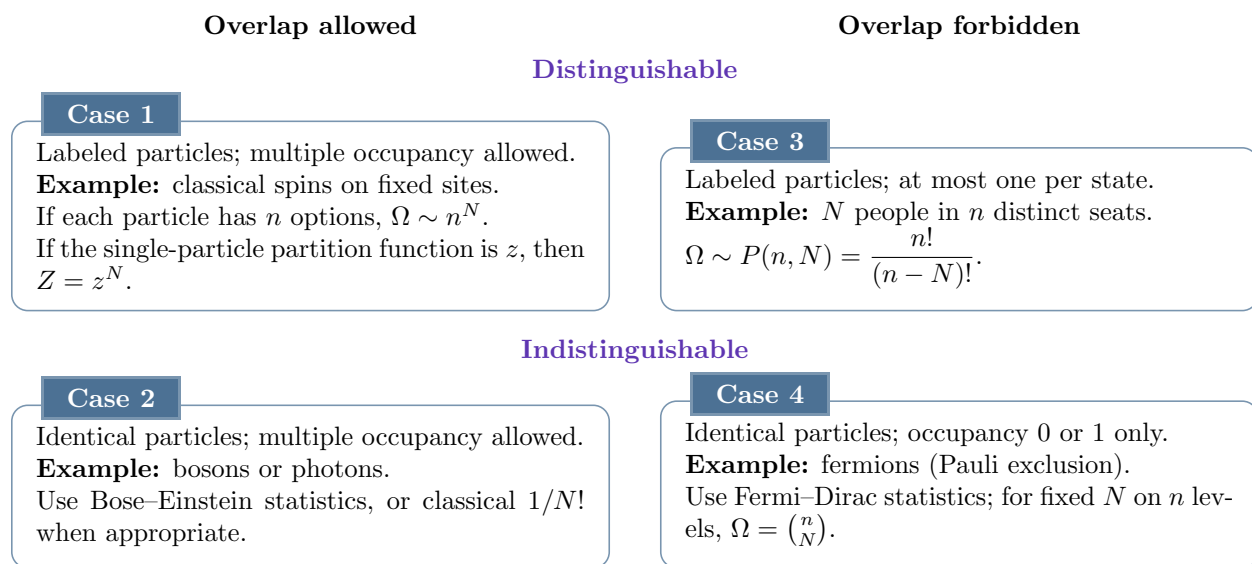


Figure 1: Four counting regimes determined by distinguishability and occupancy rules.

When level degeneracy $g(E)$ is known,

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

The choice of $g(E)$ must match the particle statistics and the allowed occupancies.

4 Analytical Techniques and Approximations

4.1 Derivatives of $\ln Z$

Thermodynamics from $\ln Z$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}, \quad \langle M \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial h},$$

$$\chi = \beta (\langle M^2 \rangle - \langle M \rangle^2), \quad C_V = k_B \beta^2 (\langle E^2 \rangle - \langle E \rangle^2).$$

4.2 Limiting Cases

- **Low T :** only the ground state and low-lying excitations matter.
- **High T :** expand Boltzmann weights to first order in β and recover classical or noninteracting behavior.
- **Large N :** use Stirling's approximation, saddle-point methods, or the largest eigenvalue of a transfer matrix.

4.3 Transfer Matrix Method (1D)

For a chain Hamiltonian written as a sum of nearest-neighbor bonds,

$$H = \sum_{i=1}^{N-1} \phi(s_i, s_{i+1}) + (\text{local fields}), \quad P(s, s') = \exp[-\beta \phi_{\text{bond}}(s, s')].$$

Open vs. periodic chain

Open chain:

$$Z = \mathbf{1}^T P^{N-1} \mathbf{1}, \quad Z \approx \lambda_+^{N-1} c \quad (N \rightarrow \infty).$$

Periodic chain:

$$Z = \text{Tr}(P^N), \quad Z \approx \lambda_+^N \quad \text{if } \lambda_+ \gg \lambda_-.$$

Free energy per site: $F/N \approx -k_B T \ln \lambda_+$.

5 The Ising Model

5.1 1D Ising Model

For spins $s_i = \pm 1$ on a chain,

$$H = -J \sum_{i=1}^{N-1} s_i s_{i+1} - h \sum_{i=1}^N s_i, \quad P(s, s') = \exp[\beta (J s s' + \frac{h}{2}(s + s'))].$$

Zero field ($h = 0$): transfer matrix

$$P = \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix}, \quad \lambda_{\pm} = 2 \cosh(\beta J), \quad 2 \sinh(\beta J), \quad Z \approx (2 \cosh \beta J)^{N-1}.$$

1D Ising: common pitfalls

- Free energy per spin: $f \approx -k_B T \ln(2 \cosh \beta J)$ in the open-chain, large- N limit.
- Magnetization with field: $M = \frac{1}{\beta N} \frac{\partial \ln Z}{\partial h}$.
- **Trap:** There is **no** spontaneous magnetization at $T > 0$ in one dimension.

5.2 Example: Three-Spin Periodic Chain**Periodic chain with $N = 3$ spins**

$$H = -J(s_1 s_2 + s_2 s_3 + s_3 s_1) - h(s_1 + s_2 + s_3),$$

$$P = \begin{pmatrix} e^{\beta(J+h)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-h)} \end{pmatrix}, \quad Z = \text{Tr}(P^3) = \lambda_+^3 + \lambda_-^3.$$

5.3 Beyond Nearest Neighbors

If interactions extend beyond nearest neighbors, enlarge the local state space. Example: for $H = -J_1 \sum_i s_i s_{i+1} - J_2 \sum_i s_i s_{i+2}$, group consecutive spins into blocks and build a larger transfer matrix. The method is unchanged in principle:

1. Write the Boltzmann weight as a product of local factors.
2. Build the transfer matrix on the enlarged state space.
3. Diagonalize and keep the largest eigenvalue in the thermodynamic limit.

5.4 2D Ising Model (Overview)**2D Ising highlights**

Critical temperature (Onsager):

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

Below T_c : spontaneous magnetization. Near T_c : $\chi \sim |T - T_c|^{-\gamma}$, $\xi \sim |T - T_c|^{-\nu}$.

Metropolis Monte Carlo (sketch)

1. Initialize a spin configuration.
2. Propose a single-spin flip and compute ΔE .
3. Accept if $\Delta E \leq 0$; otherwise accept with probability $e^{-\beta \Delta E}$.
4. Measure observables after equilibration.

6 Density of States

The density of states $g(E)$ is the number of quantum states per unit energy:

$$g(E) dE = \text{number of states with } E \leq E' < E + dE.$$

6.1 General k -space counting

Master DOS formula

In volume V ,

$$dN = \frac{V}{(2\pi)^3} 4\pi k^2 dk, \quad g(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \frac{k^2}{v_g}, \quad v_g = \frac{dE}{dk}.$$

System	Dispersion	DOS $g(E)$
Free electrons (3D)	$E = \hbar^2 k^2 / (2m)$	$\frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$
Acoustic phonons (3D)	$E = \hbar c_s k$	$\frac{V}{2\pi^2} \frac{E^2}{\hbar^3 c_s^3}$
Photons (3D cavity)	$E = \hbar c k$	$\frac{V}{2\pi^2} \frac{E^2}{\hbar^3 c^3}$

Table 1: DOS results from the same k -space counting argument once $E(k)$ is specified.

Spin degeneracy multiplies the electron result by 2 when both spin projections are included. Bose statistics with $\mu = 0$ are essential for the photon gas.

7 General Problem-Solving Strategy

Problem-solving checklist

1. **Define the system.** List degrees of freedom and fixed constraints.
2. **Choose the ensemble.** Match (N, V, E) , (N, V, T) , or (V, T, μ) to the problem.
3. **Write Z or Ω .** Include counting factors before any sum or integral.
4. **Extract observables.** Use $\ln Z$, its derivatives, and fluctuation formulas.
5. **Take limits.** Check $T \rightarrow 0$, $T \rightarrow \infty$, and noninteracting limits.
6. **Pick the tool.** Transfer matrix in 1D; mean field or numerics otherwise.
7. **State assumptions.** Stirling, semiclassical integration, mean-field decoupling, etc.

8 Conclusion

Quick recap

These notes collect the identities, ensemble formulas, counting rules, and standard models used throughout ME 346A. The recurring workflow is to choose the correct ensemble, construct Z with the right symmetry factors, and reduce the problem to derivatives of $\ln Z$. The one-dimensional Ising model and the transfer-matrix method are the main exact tools for interacting chains. The density-of-states examples show how the same k -space counting argument carries over to electrons, phonons, and photons once the dispersion relation is specified.