Complete Statistical Mechanics

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Contents

1 The Statistical Basis of Thermodynamics

1.1 Core ideas

Statistical mechanics explains thermodynamics from microscopic states. Entropy counts compatible microstates, equilibrium is overwhelmingly probable, and macroscopic laws emerge from averages over many degrees of freedom. Temperature and chemical potential are derivatives of entropy.

For review, be able to derive thermodynamic variables from entropy, distinguish microstate and macrostate, and explain why equilibrium is statistical. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

1.2 Mathematical spine

$$S = k_B \ln \Omega, \qquad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \qquad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

Section summary Thermodynamics is the large-number limit of microscopic statistics.

2 Elements of Ensemble Theory

2.1 Core ideas

An ensemble is a probability distribution over microstates representing given macroscopic information. Microcanonical, canonical, and grand canonical ensembles differ by what is held fixed and what can be exchanged with a reservoir.

For review, be able to choose the right ensemble, compute averages, relate fluctuations to response, and understand equivalence of ensembles in the thermodynamic limit. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

2.2 Mathematical spine

$$\langle A \rangle = \sum_s p_s A_s, \qquad p_s \geq 0, \qquad \sum_s p_s = 1$$

Section summary Ensembles turn incomplete microscopic information into predictions.

3 The Canonical Ensemble

3.1 Core ideas

The canonical ensemble describes systems exchanging energy with a heat bath at fixed temperature. The partition function normalizes probabilities and generates energy, entropy, heat capacity, and free energy.

For review, be able to compute Z, derive F, U, S, and heat capacity, and use factorization for independent degrees of freedom. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

3.2 Mathematical spine

$$Z = \sum_s e^{-\beta E_s}, \qquad F = -k_B T \ln Z, \qquad U = -\partial_\beta \ln Z$$

Section summary The canonical partition function is the engine of fixed-temperature statistical mechanics.

4 The Grand Canonical Ensemble

4.1 Core ideas

The grand canonical ensemble allows both energy and particles to fluctuate. It is natural for gases, quantum many-particle systems, adsorption, and reactions. The grand potential controls pressure and particle number.

For review, be able to compute $\mathcal{Z}$, obtain $\langle N \rangle$, relate Ω to pressure, and use fugacity. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

4.2 Mathematical spine

$$\mathcal{Z} = \sum_{N,s} e^{-\beta(E_{Ns} - \mu N)}, \qquad \Omega = -k_B T \ln \mathcal{Z}, \qquad \langle N \rangle = k_B T \, \partial_\mu \ln \mathcal{Z}$$

Section summary Grand canonical methods handle particle exchange cleanly.

5 Formulation of Quantum Statistics

5.1 Core ideas

Quantum statistics accounts for indistinguishable particles. Bosons occupy symmetric states and can pile up; fermions occupy antisymmetric states and obey Pauli exclusion. Occupation-number language replaces classical labeling of particles.

For review, be able to derive Bose-Einstein and Fermi-Dirac distributions, use density of states, and identify classical limits. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

5.2 Mathematical spine

$$\bar{n}_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} \mp 1}, \qquad (-)\ \text{bosons}, \quad (+)\ \text{fermions}$$

Section summary Indistinguishability changes the counting of many-particle states.

6 The Theory of Simple Gases

6.1 Core ideas

Simple gases show how partition functions become equations of state. The ideal gas follows from translational states; corrections come from interactions, internal modes, and quantum degeneracy. Equipartition works only for quadratic classical modes.

For review, be able to derive ideal gas law, thermal wavelength, Sackur-Tetrode entropy, and limits of equipartition. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

6.2 Mathematical spine

$$PV = Nk_BT, \qquad \lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}, \qquad Z_N = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N$$

Section summary Ideal gases are the baseline for statistical mechanics.

7 Ideal Bose Systems

7.1 Core ideas

Ideal bosons can macroscopically occupy the ground state, producing Bose-Einstein condensation. Photons and phonons are bosonic gases with variable particle number and zero chemical potential in equilibrium.

For review, be able to compute critical temperature qualitatively, distinguish condensate and thermal cloud, and use Planck distribution. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

7.2 Mathematical spine

$$N_0/N = 1 - (T/T_c)^{3/2}, \qquad u(\omega)d\omega = \frac{\hbar\omega\, g(\omega)d\omega}{e^{\beta\hbar\omega} - 1}$$

Section summary Bosons reveal collective occupation of single quantum states.

8 Ideal Fermi Systems

8.1 Core ideas

Fermions fill states up to the Fermi energy at low temperature. Degeneracy pressure, heat capacity linear in T, and Fermi surfaces explain electrons in metals, white dwarfs, and many quantum fluids.

For review, be able to compute Fermi energy, use density of states near the Fermi surface, and explain Pauli pressure. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

8.2 Mathematical spine

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}, \qquad f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$$

Section summary Fermi systems are controlled by states near the Fermi surface.

9 Cluster Expansion and Pseudopotential Methods

9.1 Core ideas

Interactions correct ideal-gas behavior. Virial and cluster expansions organize dilute-gas corrections by density. Effective pseudopotentials replace complicated short-range interactions with low-energy scattering parameters.

For review, be able to interpret virial coefficients, know when dilute expansions work, and connect scattering length to effective interactions. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

9.2 Mathematical spine

$$\frac{P}{k_B T} = n + B_2(T)n^2 + B_3(T)n^3 + \cdots , \qquad g = \frac{4\pi\hbar^2 a_s}{m}$$

Section summary Interaction effects can be organized systematically at low density.

10 Phase Transitions and Critical Phenomena

10.1 Core ideas

Phase transitions occur when free energies become nonanalytic in the thermodynamic limit. First-order transitions have latent heat; continuous transitions have diverging correlation length and universal critical exponents.

For review, be able to use order parameters, Landau free energy, susceptibility, correlation length, and scaling ideas. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

10.2 Mathematical spine

$$F[m] = F_0 + am^2 + bm^4 - hm, \qquad \xi \sim |T - T_c|^{-\nu}, \qquad \chi \sim |T - T_c|^{-\gamma}$$

Section summary Critical behavior is governed by symmetry, dimension, and fluctuations.

11 Fluctuations

11.1 Core ideas

Fluctuations are not noise to ignore; they determine response and reveal microscopic physics. Variances of energy, particle number, and order parameters connect to heat capacity, compressibility, and susceptibility.

For review, be able to derive fluctuation-response relations, estimate relative fluctuations, and explain why fluctuations grow near criticality. Keep the physical question visible: identify the degrees of freedom, the conserved quantities, the approximation being made, and the observable that would be measured.

11.2 Mathematical spine

$$\langle (\Delta E)^2 \rangle = k_B T^2 C_V, \qquad \langle (\Delta N)^2 \rangle = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{T,V}$$

Section summary Fluctuations quantify stability and response.