Part II — Statistical Physics
Theorems

Based on lectures by H. S. Reall

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These notes are not endorsed by the lecturers, and I have modified them (often significantly) after lectures. They are nowhere near accurate representations of what was actually lectured, and in particular, all errors are almost surely mine.

Part IB Quantum Mechanics and "Multiparticle Systems" from Part II Principles of Quantum Mechanics are essential

Fundamentals of statistical mechanics
Microcanonical ensemble. Entropy, temperature and pressure. Laws of thermodynamics. Example of paramagnetism. Boltzmann distribution and canonical ensemble. Partition function. Free energy. Specific heats. Chemical Potential. Grand Canonical Ensemble. [5]

Classical gases
Density of states and the classical limit. Ideal gas. Maxwell distribution. Equipartition of energy. Diatomic gas. Interacting gases. Virial expansion. Van der Waal's equation of state. Basic kinetic theory. [3]

Quantum gases
Density of states. Planck distribution and black body radiation. Debye model of phonons in solids. Bose–Einstein distribution. Ideal Bose gas and Bose–Einstein condensation. Fermi-Dirac distribution. Ideal Fermi gas. Pauli paramagnetism. [8]

Thermodynamics
Thermodynamic temperature scale. Heat and work. Carnot cycle. Applications of laws of thermodynamics. Thermodynamic potentials. Maxwell relations. [4]

Phase transitions
Liquid-gas transitions. Critical point and critical exponents. Ising model. Mean field theory. First and second order phase transitions. Symmetries and order parameters. [4]

Contents

0 Introduction

1 Fundamentals of statistical mechanics

1.1 Microcanonical ensemble

Law (Second law of thermodynamics)**.** The entropy of an isolated system increases (or remains the same) in any physical process. In equilibrium, the entropy attains its maximum value.

Proposition. Two interacting systems in equilibrium have the same temperature.

Proposition. Suppose two systems with initial energies $E_{(1)}, E_{(2)}$ and temperatures T_1, T_2 are put into contact. If $T_1 > T_2$, then energy will flow form the first system to the second.

1.2 Pressure, volume and the first law of thermodynamics

Proposition. Consider as before two interacting systems where the total volume $V = V_1 + V_2$ is fixed by the individual volumes can vary. Then the entropy of the combined system is maximized when $T_1 = T_2$ and $p_1 = p_2$.

Proposition (First law of thermodynamics)**.**

$$\mathrm{d}E = T\;\mathrm{d}S - p\;\mathrm{d}V.$$

1.3 The canonical ensemble

Proposition. For two non-interacting systems, we have $Z(\beta) = Z_1(\beta)Z_2(\beta)$.

1.4 Helmholtz free energy

Proposition.

$$F = -kT\log Z.$$

Alternatively,

$$Z = e^{-\beta F}.$$

1.5 The chemical potential and the grand canonical ensemble

Proposition.

$$\langle E\rangle - \mu\langle N\rangle = -\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{\mu,V}.$$

Proposition.

$$\langle N\rangle = \sum_n p(n)N_n = \frac{1}{\beta}\left(\frac{\partial \log \mathcal{Z}}{\partial \mu}\right)_{T,V}.$$

Proposition.

$$\Delta N^2 = \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta^2}\left(\frac{\partial^2 \log Z}{\partial \mu^2}\right)_{T,V} = \frac{1}{\beta}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} \sim N.$$

So we have

$$\frac{\Delta N}{\langle N\rangle} \sim \frac{1}{\sqrt{N}}.$$

Proposition.

$$S = k\frac{\partial}{\partial T}(T \log \mathcal{Z})_{\mu,N}.$$

Proposition.

$$\mathrm{d}\Phi = -S\ \mathrm{d}T - p\ \mathrm{d}V - N\ \mathrm{d}\mu.$$

1.6 Extensive and intensive properties

2 Classical gases

2.1 The classical partition function

2.2 Monoatomic ideal gas

Proposition. For a monoatomic gas, we have

$$Z_1(V,T) = V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} = \frac{V}{\lambda^3},$$

Proposition (Ideal gas law)**.**

$$pV = NkT.$$

Law (Equipartition of energy)**.** Each degree of freedom of an ideal gas contributes $\frac{1}{2}kT$ to the average energy.

2.3 Maxwell distribution

2.4 Diatomic gases

2.5 Interacting gases

3 Quantum gases

3.1 Density of states

3.2 Black-body radiation

3.3 Phonons and the Debye model

3.4 Quantum ideal gas

3.5 Bosons

3.6 Bose–Einstein condensation

3.7 Fermions

3.8 Pauli paramagnetism

4 Classical thermodynamics

4.1 Zeroth and first law

Law (Zeroth law of thermodynamics)**.** If systems A and B are individually in equilibrium with C, then A and B are in equilibrium.

Law (First law of thermodynamics)**.** The amount of work required to change an isolated system from one state to another is independent of how the work is done, and depends only on the initial and final states.

4.2 The second law

Law (Kelvin's second law)**.** There exists no process whose sole effect is to extract heat from a heat reservoir and convert it into work.

Law (Clausius's second law)**.** There is no process whose sole effect is to transfer heat from a colder body to a hotter body.

Proposition. Clausius's second law implies Kelvin's second law.

Proposition. Kelvin's second law implies Clausius's second law.

4.3 Carnot cycles

Theorem. Of all engines operating between heat reservoirs, reversible engines are the most efficient. In particular, all reversible engines have the same efficiency, and is just a function of the temperatures of the two reservoirs.

4.4 Entropy

4.5 Thermodynamic potentials

Proposition.

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V\\
\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V\\
-\left(\frac{\partial S}{\partial p}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_p\\
\left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p.
\end{aligned}$$

4.6 Third law of thermodynamics

Law (Third law of thermodynamics)**.** As $T \to 0$, we have

$$\lim_{T\to 0} S = S_0,$$

which is independent of other parameters (e.g. V, B etc). In particular, the limit is finite.

5 Phase transitions

5.1 Liquid-gas transition

5.2 Critical point and critical exponents

5.3 The Ising model

5.4 Landau theory