

Part II — Statistical Physics

Theorems with proof

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]

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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.

Proof. Recall that the equilibrium energy E_* is found by maximizing

$$S_1(E_i) + S_2(E_{\text{total}} - E_i)$$

over all possible E_i . Thus, at an equilibrium, the derivative of this expression has to vanish, and the derivative is exactly

$$\left. \frac{dS_1}{dE} \right|_{E_{(1)}=E_*} - \left. \frac{dS_2}{dE} \right|_{E_{(2)}=E_{\text{total}}-E_*} = 0$$

So we need

$$\frac{1}{T_1} = \frac{1}{T_2}.$$

In other words, we need

$$T_1 = T_2. \quad \square$$

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 from the first system to the second.

Proof. Since we are not in equilibrium, there must be some energy transfer from one system to the other. Suppose after time δt , the energy changes by

$$\begin{aligned} E_{(1)} &\mapsto E_{(1)} + \delta E \\ E_{(2)} &\mapsto E_{(2)} - \delta E, \end{aligned}$$

keeping the total energy constant. Then the change in entropy is given by

$$\delta S = \frac{dS_1}{dE} \delta E_{(1)} + \frac{dS_2}{dE} \delta E_{(2)} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E.$$

By assumption, we know

$$\frac{1}{T_1} - \frac{1}{T_2} < 0,$$

but by the second law of thermodynamics, we know δS must increase. So we must have $\delta E < 0$, i.e. energy flows from the first system to the second. \square

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 $p_1 = p_2$.

Proof. We have previously seen that we need $T_1 = T_2$. We also want

$$\left(\frac{dS}{dV}\right)_E = 0.$$

So we need

$$\left(\frac{dS_1}{dV}\right)_E = \left(\frac{dS_2}{dV}\right)_E.$$

Since the temperatures are equal, we know that we also need $p_1 = p_2$. □

Proposition (First law of thermodynamics).

$$dE = T dS - p dV.$$

1.3 The canonical ensemble

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

Proof. Since the systems are not interacting, we have

$$Z = \sum_{n,m} e^{-\beta(E_n^{(1)} + E_m^{(2)})} = \left(\sum_n e^{-\beta E_n^{(1)}}\right) \left(\sum_m e^{-\beta E_m^{(2)}}\right) = Z_1 Z_2. \quad \square$$

1.4 Helmholtz free energy

Proposition.

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

Alternatively,

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

Proof. We use the fact that

$$\frac{d}{d\beta} = kT^2 \frac{d}{dT}.$$

Then we can start from

$$\begin{aligned} F &= E - TS \\ &= -\left(\frac{\partial \log Z}{\partial \beta}\right) - TS \\ &= kT^2 \left(\frac{\partial \log Z}{\partial T}\right)_V - kT \frac{\partial}{\partial T} (T \log Z)_V \\ &= -kT \log Z, \end{aligned}$$

and we are done. Good. □

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.

$$d\Phi = -S dT - p dV - N d\mu.$$

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

Proof. We consider the big vector

$$\mathbf{X} = \begin{pmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \\ \vdots \\ \mathbf{x}_N \end{pmatrix},$$

where each \mathbf{x}_i is the position of the i th atom. Then the Lagrangian is

$$L = \frac{1}{2} \dot{\mathbf{X}}^2 - V(\mathbf{X}),$$

where V is the interaction potential that keeps the solid a solid.

We suppose V is minimized at some particular $\mathbf{X} = \mathbf{X}_0$. We let

$$\delta\mathbf{X} = \mathbf{X} - \mathbf{X}_0.$$

Then we can write

$$L = \frac{1}{2} m \delta\dot{\mathbf{X}}^2 - V_0 - \frac{1}{2} \delta\mathbf{X}^T \mathbf{V} \delta\mathbf{X} + \dots,$$

where \mathbf{V} is the Hessian of V at \mathbf{X}_0 , which is a symmetric positive definite matrix since we are at a minimum. The equation of motion is then, to first order,

$$m \delta\ddot{\mathbf{X}} = -\mathbf{V} \delta\mathbf{X}.$$

We assume that $\mathbf{X} = \text{Re}(e^{i\omega t} \mathbf{Q})$ for some \mathbf{Q} and ω , and then this reduces to

$$\mathbf{V} \mathbf{Q} = m\omega^2 \mathbf{Q}.$$

This is an eigenvalue equation for \mathbf{V} . Since \mathbf{V} is a $3n \times 3n$ symmetric matrix, it has $3N$ independent eigenvectors, and so we are done, and these are the $3N$ normal modes.

If we wanted to, we can diagonalize \mathbf{V} , and then the system becomes $3N$ independent harmonic oscillators. \square

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.

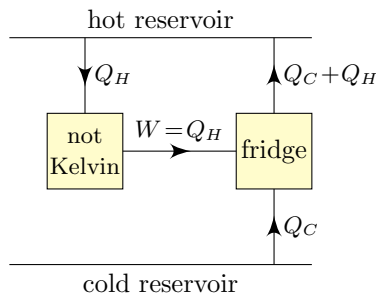
4.2 The second law

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.

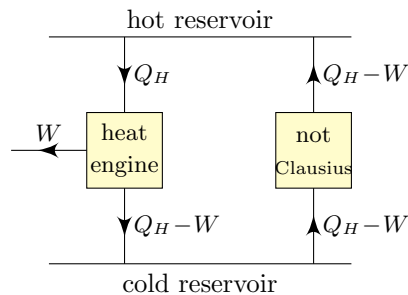
Proof. Suppose there were some process that violated Kelvin's second law. Let's use it to run a fridge:



and this violates Clausius's law. □

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

Proof. If we have a not Clausius machine, then we can do

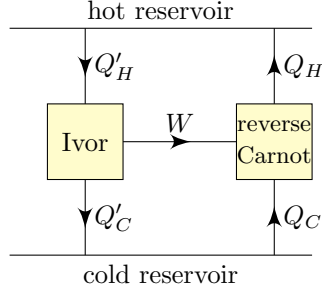


Then this has a net effect of taking heat W from the hot reservoir and done work W . This violates Kelvin's law. □

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.

Proof. Consider any other engine, Ivor. We use this to drive Carnot (an arbitrary reversible engine) backwards:



Now we have heat $Q'_H - Q_H$ extracted from the hot reservoir, and $Q'_C - Q_C$ deposited in the cold, and we have

$$Q'_H - Q_H = Q'_C - Q_C.$$

Then Clausius' law says we must have $Q'_H - Q_H \geq 0$. Then the efficiency of Ivor is

$$\eta_{\text{Ivor}} = \frac{Q'_H - Q'_C}{Q'_H} = \frac{Q_H - Q_C}{Q'_H} \leq \frac{Q_H - Q_C}{Q_H} = \eta_{\text{Carnot}}.$$

Now if Ivor is also reversible, then we can swap the argument around, and deduce that $\eta_{\text{Carnot}} \leq \eta_{\text{Ivor}}$. Combining the two inequalities, they must be equal. \square

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 $T \rightarrow 0$, we have

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

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