Part II — Statistical Physics

Theorems with proof

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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**


**Classical gases**


**Quantum gases**


**Thermodynamics**


**Phase transitions**

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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 $E_\star$ 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

$$\left. \frac{dS_1}{dE} \right|_{E_1=E_\star} - \left. \frac{dS_2}{dE} \right|_{E_2=E_{\text{total}}-E_\star} = 0$$

So we need

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

In other words, we need

$$T_1 = T_2.$$

**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 $\delta t$, the energy changes by

$$E_{(1)} \rightarrow E_{(1)} + \delta E$$

$$E_{(2)} \rightarrow E_{(2)} - \delta E,$$

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 $\delta S$ 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

\[
Z = \sum_{n,m} e^{-\beta(E^{(1)}_n + E^{(2)}_m)} = \left( \sum_n e^{-\beta E^{(1)}_n} \right) \left( \sum_n e^{-\beta E^{(2)}_n} \right) = Z_1Z_2.
\]

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

\[
F = E - TS
\]

\[
= - \left( \frac{\partial \log Z}{\partial \beta} \right) - TS
\]

\[
= kT^2 \frac{\partial \log Z}{\partial T} \bigg|_V - kT \frac{\partial}{\partial T} (T \log Z)_V
\]

\[
= -kT \log Z,
\]

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.

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

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

\[ X = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{pmatrix}, \]

where each \( x_i \) is the position of the \( i \)th atom. Then the Lagrangian is

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

where \( V \) is the interaction potential that keeps the solid a solid.

We suppose \( V \) is minimized at some particular \( X = X_0 \). We let

\[ \delta X = X - X_0. \]

Then we can write

\[ L = \frac{1}{2} m \dot{\delta X}^2 - V_0 - \frac{1}{2} \delta X^T \nabla^2 V \delta X + \cdots, \]

where \( \nabla^2 V \) is the Hessian of \( V \) at \( X_0 \), which is a symmetric positive definite matrix since we are at a minimum. The equation of motion is then, to first order,

\[ m \ddot{\delta X} = -\nabla V \delta X. \]

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

\[ VQ = m\omega^2 Q. \]

This is an eigenvalue equation for \( V \). Since \( V \) 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 \( V \), and then the system becomes \( 3N \) independent harmonic oscillators.

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:

\[
\begin{align*}
\text{hot reservoir} & \quad Q_H \\
\text{not Kelvin} & \quad W = Q_H \\
\text{fridge} & \quad Q_C \\
\text{cold reservoir} & \quad Q_C + Q_H \\
\end{align*}
\]

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

\[
\begin{align*}
\text{hot reservoir} & \quad Q_H \\
\text{heat engine} & \quad Q_H - W \\
\text{not Clausius} & \quad Q_H - W \\
\text{cold reservoir} & \quad W \\
\end{align*}
\]

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 Igor is

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

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

4.4 Entropy

4.5 Thermodynamic potentials

**Proposition.**

$$\frac{\partial T}{\partial V}_S = -\left( \frac{\partial p}{\partial S} \right)_V$$

$$\frac{\partial S}{\partial V}_T = \left( \frac{\partial p}{\partial T} \right)_V$$

$$-\frac{\partial S}{\partial p}_T = \left( \frac{\partial V}{\partial T} \right)_p$$

$$\frac{\partial T}{\partial p}_S = \left( \frac{\partial V}{\partial S} \right)_p.$$  

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