

Statistical Mechanics

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*<https://github.com/M-a-s-o/notes>

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Lecture 1

Exam. Oral exam on every part of the course in detail with proofs. Extra topics are not evaluated. The exam can be done whenever with enough notice.

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References. Some references are

- Mehran Kardar, also Tong (which are based on it): statistical physics, statistical field theory, kinetic theory. Most of the material is covered in the first set of notes.
- Kerson Huang;
- Le Bellac, “Quantum and Statistical Field Theory”, for the renormalization group.

Program. The course is divided into four parts:

- The first part is statistical mechanics of equilibrium: one discusses the problem of equilibrium in statistical mechanics. One studies the statistical ensembles: micro-canonical, canonical and gran-canonical. One discusses ideal gases, interacting gases and quantum gases (Fermi–Dirac, Bose–Einstein distributions and Bose–Einstein condensation).
- In the second part of the course, one studies critical phenomena: liquid-gas transitions and the study of spin-systems (like Ising). One studies critical exponents and universality. One studies Landau theory and Landau–Ginzburg theory. One way to deal with the quantum field theory formalism is to study statistical systems.
- The third part concerns the renormalization group: block spin transformations, relevant and irrelevant couplings. Extra (not covered): quantum field theory approach with beta functions and the Wilson–Fisher fixed point.
- The fourth part is kinetic theory of gases, study the problem of the approach to equilibrium, Boltzmann equation. Extra: hydrodynamics.

Part I

Statistical mechanics of equilibrium

Statistical mechanics deals with systems with a very large number of particles $N \sim 10^{23}$. From analytical mechanics, one would study the phase space of this enormous system. The state of the system is called microstate, it is a point in $D = 6N$ dimensional phase space Γ . The coordinates of the point are

$$(\mathbf{p}, \mathbf{q}) \in \mathbb{R}^{6N}$$

The equations of motion for the system are

$$\dot{\mathbf{q}} = \partial_{\mathbf{p}} H, \quad \dot{\mathbf{p}} = -\partial_{\mathbf{q}} H$$

Solving the equations is virtually impossible and also it is not even interesting. For a macroscopic system, only a few quantities are interesting: the temperature, the pressure, etc. One would like to characterize the system with a few quantities, one does not need to know the motion of every particle in phase space. Typically, a macroscopic state (or macrostate) is defined by fixing few macroscopic quantities: energy, pressure, volume, temperature, etc. Even if a system is macroscopically at equilibrium — the macrostate is fixed —, the point (i.e. the microstate) in the phase space Γ can move. One moves away from the analytical mechanical approach of studying a system and one focuses on the macroscopic behaviour. This is possible with the theory of statistical ensembles introduced by Gibbs.

1 Gibbs ensembles

See Kardar, Statistical Physics of Particles, §§3.1, 3.2, Tong, Kinetic Theory, §2.1. There are many-to-one correspondences between microstates and macrostates. Each point in the phase space Γ corresponds to a microstate. There are many \mathcal{N} points which are compatible with a given macrostate. Since there is a many-to-one correspondence, then as $N \rightarrow \infty$ also $\mathcal{N} \rightarrow \infty$. The collection of compatible microstates is called “ensemble”. This collection is a distribution of points in the phase space Γ . One may define the probability distribution $\rho(\mathbf{p}, \mathbf{q}, t)$ as function of the position in the phase space and time. The relative (infinitesimal) number of compatible microstates is then

$$\rho(\mathbf{p}, \mathbf{q}, t) d^{3N}p d^{3N}q = \rho(\mathbf{p}, \mathbf{q}, t) d\Gamma = \frac{d\mathcal{N}}{\mathcal{N}}$$

Integrating the distribution over the entire phase space, one must find unity

$$\int_{\Gamma} \rho(\mathbf{p}, \mathbf{q}, t) d\Gamma = 1$$

If one knows the solutions to the equations of motion, knowing the distribution at some initial time t_i , one may extract the distribution at some later final time t_f . [r] One assumes that the Hamiltonian of the system is time-independent. This implies that the trajectories in the phase space are time-reversal invariant, they do not cross. Therefore, the total number of points in the phase space, hence the probability, is conserved: it satisfies a continuity equation. The probability distribution is essentially an incompressible fluid.

Consider a spherical region γ in the phase space and a direction \mathbf{n} . Integrating the probability distribution in such region gives

$$I = \partial_t \int_{\gamma} \rho(\mathbf{p}, \mathbf{q}, t) d\Gamma$$

Since the Hamiltonian is time-independent, what leaves the volume is what passes through its boundary, so

$$I = - \int_{\partial\gamma} \rho \mathbf{v} \cdot \mathbf{n} dS, \quad \mathbf{v} = (\dot{\mathbf{p}}, \dot{\mathbf{q}})$$

This is the continuity equation. By applying Stokes’s theorem, one finds

$$\partial_t \int_{\gamma} \rho(\mathbf{p}, \mathbf{q}, t) d\Gamma = - \int_{\gamma} \nabla \cdot (\rho \mathbf{v}) d\Gamma$$

This argument must be true for every place in the phase space: it must hold locally. It must hold for every γ , therefore

$$\partial_t \rho(\mathbf{p}, \mathbf{q}, t) + \nabla \cdot (\rho \mathbf{v}) = 0$$

The divergence can be rewritten as

$$\begin{aligned} \nabla \cdot (\rho \mathbf{v}) &= \sum_{i=1}^N \partial_{\mathbf{p}_i} (\rho \dot{\mathbf{p}}_i) + \sum_{i=1}^N \partial_{\mathbf{q}_i} (\rho \dot{\mathbf{q}}_i) = \sum_{i=1}^N (\dot{\mathbf{p}}_i \partial_{\mathbf{p}_i} \rho + \dot{\mathbf{q}}_i \partial_{\mathbf{q}_i} \rho) + \sum_{i=1}^N \rho (\partial_{\mathbf{p}_i} \dot{\mathbf{p}}_i + \partial_{\mathbf{q}_i} \dot{\mathbf{q}}_i) \\ &= \sum_{i=1}^N (\dot{\mathbf{p}}_i \partial_{\mathbf{p}_i} \rho + \dot{\mathbf{q}}_i \partial_{\mathbf{q}_i} \rho) + 0 = \sum_{i=1}^N (-\partial_{\mathbf{q}_i} H \partial_{\mathbf{p}_i} \rho + \partial_{\mathbf{p}_i} H \partial_{\mathbf{q}_i} \rho) = \{\rho, H\} \end{aligned}$$

At the first line, in the last parenthesis, one applies the equations of motion

$$\partial_{\mathbf{q}_i} \dot{\mathbf{q}}_i = \partial_{\mathbf{q}_i \mathbf{p}_i}^2 H, \quad \partial_{\mathbf{p}_i} \dot{\mathbf{p}}_i = -\partial_{\mathbf{q}_i \mathbf{p}_i}^2 H$$

One finds the Poisson bracket of the probability distribution with the Hamiltonian. [r] Therefore

$$d_t \rho(\mathbf{p}, \mathbf{q}, t) = \partial_t \rho(\mathbf{p}, \mathbf{q}, t) + \{\rho, H\} = 0$$

This is the Liouville theorem. The probability distribution in a statistical ensemble behaves as an incompressible fluid.

From the probability distribution one may compute the averages of the ensemble, so that one may identify them with the macroscopic quantities like energy, pressure, etc. The expectation values

$$\langle O \rangle = \int_{\Gamma} \rho(\mathbf{p}, \mathbf{q}, t) O(\mathbf{p}, \mathbf{q}) d\Gamma$$

are identified with the thermodynamic quantities. Skipping the question of whether a system can be in equilibrium, one defines the equilibrium as the condition

$$d_t \langle O \rangle = 0$$

In general, the total time derivative of the expectation value of $O(\mathbf{p}, \mathbf{q})$ is

$$\begin{aligned} d_t \langle O \rangle &= \int [\partial_t \rho(\mathbf{p}, \mathbf{q}, t)] O(\mathbf{p}, \mathbf{q}) d\Gamma \\ &= - \int d\Gamma O(\mathbf{p}, \mathbf{q}) \sum_{\alpha=1}^{3N} (\partial_{q_\alpha} \rho \partial_{p_\alpha} H - \partial_{p_\alpha} \rho \partial_{q_\alpha} H) \end{aligned}$$

At the first line, the time dependence comes only from the explicit dependence on time of ρ , since the dependence from \mathbf{p} and \mathbf{q} is eliminated due to the fact that the two variables are integrated. At the second line, one has used the continuity equation. Consider the first addendum in the parenthesis

$$\int d\Gamma O(\mathbf{p}, \mathbf{q}) \partial_{p_\alpha} \rho \partial_{q_\alpha} H = - \int d\Gamma \rho(\mathbf{p}, \mathbf{q}, t) \partial_{p_\alpha} O \partial_{q_\alpha} H - \int d\Gamma \rho(\mathbf{p}, \mathbf{q}, t) O \partial_{q_\alpha p_\alpha}^2 H$$

where one supposes that ρ vanishes at the boundary. The last term cancels a similar contribution from the second addendum. Therefore

$$d_t \langle O \rangle = \sum_{\alpha=1}^{3N} \int d\Gamma \rho(\mathbf{p}, \mathbf{q}, t) (\partial_{q_\alpha} O \partial_{p_\alpha} H - \partial_{p_\alpha} O \partial_{q_\alpha} H) = \langle \{O, H\} \rangle$$

The last parenthesis is again a Poisson bracket.

At equilibrium, the total time derivative is zero, therefore the partial derivative of the probability density ρ must be identically zero

$$d_t \langle O \rangle = 0 \iff \partial_t \rho(\mathbf{p}, \mathbf{q}, t) = 0$$

Therefore, at equilibrium, the probability density has no explicit time dependence, but is only a function of \mathbf{p} and \mathbf{q} . The existence of an equilibrium distribution is the basic assumption of statistical mechanics. This condition also is not enough to prove that a system eventually evolves to equilibrium.

1.1 Statistical ensemble in quantum mechanics

See Kardar, SPoP, §6.5. In quantum mechanics, the state of a system is ray in a Hilbert space. If the system is large, the wave function has many variables and so is statistical (in a classical sense): there is still the same type of problems. Again, there are many microstates (which are rays in the Hilbert space) which are compatible with a given macrostate. This macrostate is fixed by few macroscopic variables: energy, pressure, etc. In this case one must also develop a statistical approach. There are microstates $|\psi_i\rangle$ each with a statistical (ensemble) probability p_i that is normalized

$$\sum_i p_i = 1$$

This is a discrete version of the classical case. One may compute ensemble averages as

$$\langle A \rangle = \sum_{i \in \text{CMS}} p_i \langle \psi_i | A | \psi_i \rangle$$

where CMS stands for compatible microstates. One is taking two averages: the quantum expectation value, a fundamental unknown, and the statistical expectation value, which is a practical unknown. The state $|\psi_i\rangle$ is a microstate, also called pure state, even if it is a superposition of other states. Instead, a collection of pure states $|\psi_i\rangle$ with (statistical) probability p_i is a mixed state.

Density matrix. The density matrix is an operator defined as

$$\hat{\rho} \equiv \sum_i p_i |\psi_i\rangle\langle\psi_i|$$

It is useful for the computation of a trace

$$\begin{aligned} \text{Tr}(\rho A) &= \sum_n \langle n | \hat{\rho} A | n \rangle = \sum_n \sum_i p_i \langle n | \psi_i \rangle \langle \psi_i | A | n \rangle = \sum_i \sum_n p_i \langle \psi_i | A | n \rangle \langle n | \psi_i \rangle \\ &= \sum_i p_i \langle \psi_i | A | \psi_i \rangle = \langle A \rangle \end{aligned}$$

where $|n\rangle$ is a basis. In quantum statistical mechanics, traces can be replaced with averages.

Since the state $|\psi_i\rangle$ evolves with the Hamiltonian $e^{-iHt} |\psi_i\rangle$, then the density matrix evolves due to the evolution of the pure states

$$\hat{\rho}(0) = \sum_i p_i |\psi_i\rangle\langle\psi_i| \rightarrow \sum_i p_i e^{-iHt} |\psi_i\rangle\langle\psi_i| e^{iHt} = e^{-iHt} \hat{\rho}(0) e^{iHt} = \hat{\rho}(t)$$

The partial derivative with respect to time is

$$\partial_t \hat{\rho}(t) = -iH \hat{\rho}(t) + \hat{\rho}(t) iH = i[\hat{\rho}, H]$$

Therefore, the density matrix satisfies

$$\partial_t \hat{\rho}(t) + \frac{1}{i\hbar} [\hat{\rho}(t), H] = 0$$

This is the von Neumann equation which is the quantum mechanical version of the Liouville theorem that can be obtained from the naive replacement of the Poisson bracket with the $(i\hbar)^{-1}$ commutator.

Semi-classical limit. Comparing classical and quantum statistical mechanics, there is a parallel between a quantum microstate $|\psi_i\rangle$ and a classical microstate $(\mathbf{p}, \mathbf{q}) \in \Gamma$. One would like to understand how to go from quantum to classical: the semi-classical limit.

Consider N particles in a box of volume $V = L^3$. A particle in this box is described by a wave function

$$\psi(x) = \frac{1}{\sqrt{V}} e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{x}}$$

with a quantized momentum¹

$$\mathbf{p} = \frac{2\pi\hbar}{L}(n_1, n_2, n_3)$$

The number of states with position in $\mathbf{q} + [0, d\mathbf{q}]$ and momentum in $\mathbf{p} + [0, d\mathbf{p}]$ is

$$d^3n = \frac{d^3q d^3p}{(2\pi\hbar)^3}$$

One should also add a $(N!)^{-1}$ to account for identical particles. [r] One may observe that the sum \sum_i gives a very precise measure in the semi-classical limit

$$\int \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N} N!}$$

The reduced Planck's constant is present only for dimensional reason, because in the semi-classical limit it cancels out. On the other hand, the factorial is important and does not cancel. This is related to the Gibbs paradox. When doing statistical analysis, the factorial does not appear, but this brings problems and one has to manually add it. The only explanation for its necessity comes from the semi-classical limit.

1.2 Review of probability theory

See Kardar, SPoP, §2. Given a function f taking values f_i at the states i of the system, with probability p_i , one defines

- the mean value

$$\langle f \rangle = \sum_i f_i p_i$$

- the variance

$$(\Delta f)^2 = \langle f - \langle f \rangle \rangle^2 = \langle f^2 \rangle - \langle f \rangle^2 = \sum_i f_i^2 p_i - \left[\sum_i f_i p_i \right]^2$$

- the probability of taking some value F is

$$P(f = F) = \sum_i p_i \delta(f_i - F) = \langle \delta(f_i - F) \rangle$$

- the entropy of a distribution is

$$S = - \sum_i p_i \ln p_i = - \langle \ln p_i \rangle$$

One may see the meaning of entropy. Consider a distribution with $p_1 = 1$ and $p_i = 0$ for $i \neq 1$. This distribution has zero entropy, $S = 0$: there is zero uncertainty. Viceversa, if all outcomes are equally probable, $p_i = N^{-1}$, then the entropy is

$$S = - \sum_i \frac{1}{N} \ln \frac{1}{N} = \ln N$$

Proposition. The entropy takes the maximum value for the uniform distribution.

Proof. One may utilize a constrained extremization using Lagrange multipliers

$$\begin{aligned} 0 &\equiv \partial_{p_j} \left[- \sum_i p_i \ln p_i + \lambda \left(\sum_i p_i - 1 \right) \right] = - \sum_i \delta_{ij} \ln p_i - \sum_i p_i \frac{1}{p_i} \delta_{ij} + \lambda \sum_i \delta_{ij} \\ &= - \ln p_j - 1 + \lambda \implies p_j = e^{\lambda-1} \end{aligned}$$

¹The boundary conditions are chosen to be periodic.

Using the constraint

$$1 = \sum_{j=1}^N p_j = N e^{\lambda-1}$$

one finds

$$p_j = \frac{1}{N}$$

Therefore, the uniform distribution maximizes the entropy. \square

Recap. There is a distribution ρ of compatible microstates with a given macrostate. The equilibrium condition is

$$d_t \langle O \rangle = 0 \iff \partial_t \rho_{\text{eq}} = 0 = \{\rho_{\text{eq}}, H\}$$

This condition does not specify the distribution. One assumes that the equilibrium exists (as one may see at the end of the course). Given a macrostate, the equilibrium distribution is such that

- it maximizes the entropy,
- it does not introduce any bias,
- it treats all the compatible microstates as equiprobable.

The three propositions are equivalent. [r]

In order to find the equilibrium distribution, one first fixes the macrostate (by fixing the energy, temperature or chemical potential), then requires that the distribution treats all microstates as equiprobable (in practice one maximizes the entropy).

Lecture 2

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Previous lecture. The idea of the statistical approach is to define the Gibbs ensemble as the collection of microstates (a microstate is a point in the phase space $\Gamma = \mathbb{R}^{6N}$ compatible with a given macrostate which is a state fixed by defining a few microscopic quantities like energy, temperature and pressure). There are many particles in the system and so many compatible microstates. The distribution of microstates integrated gives the fraction of compatible microstates

$$\rho(\mathbf{p}, \mathbf{q}, t) d\Gamma = \frac{d\mathcal{N}}{\mathcal{N}}$$

The distribution is normalized. The distribution behaves as an incompressible fluid

$$d_t \rho = 0 = \partial_t \rho + \{\rho, H\}$$

From the distribution one may compute the ensemble averages

$$\langle O(\mathbf{p}, \mathbf{q}) \rangle = \int \rho(\mathbf{p}, \mathbf{q}, t) O(\mathbf{p}, \mathbf{q}) d\Gamma$$

Equilibrium is defined by requiring

$$d_t \langle O(\mathbf{p}, \mathbf{q}) \rangle = 0 \iff \partial_t \rho_{\text{eq}} = 0 = \{\rho_{\text{eq}}, H\}$$

The value of the macroscopic quantities do not change in time.

One assumes that the distribution at equilibrium ρ_{eq} exists and that it has the properties:

- it maximizes the entropy,
- it does not introduce any bias,
- it treats all the compatible microstates as equiprobable.

This condition is enough to obtain the equilibrium distribution once the macrostate is fixed.

Macrostates. The macrostates can be fixed by fixing the energy, the temperature and the chemical potential μ , to obtain respectively the microcanonical, the canonical and the gran-canonical ensembles. Each has a different distribution at equilibrium. These different distributions give different averages of the same observable. However, this is a problem: there must be only one average since it is associated to a macroscopic quantity. This problem is resolved by noting that, in the thermodynamic limit $N, V \rightarrow \infty$, the three averages tend to the same value. Therefore, macroscopic quantities like the energy have a non-zero possibility of taking a value different from the average but the variance of the samples must behave asymptotically as

$$\frac{\Delta E}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \rightarrow 0, \quad N \rightarrow \infty$$

This is not proven but can be seen through a parallel with the central limit theorem: in the thermodynamic limit, the three averages tend to the same value and the possibility that the system is not at the average is extremely suppressed. To perform computations, one may use whatever ensemble is easier because one is interested in the thermodynamic limit anyway.

Central limit theorem. The mechanism of the three averages tending to the same value is similar to the central limit theorem. Consider a system with N random variables $\mathbf{x} = (x_1, \dots, x_N)$ with joint probability

$$p(\mathbf{x}) = \prod_{i=1}^N p(x_i)$$

Let

$$X \equiv \sum_{i=1}^N x_i$$

The probability that the system obtains the value X is

$$p_N(X) = \int dx_1 \cdots dx_N \prod_{i=1}^N p(x_i) \delta(x - \sum_i x_i)$$

Taking the Fourier transform gives

$$\begin{aligned} p_N(k) &= \int dX e^{-ikX} p_N(X) = \int dX \int dx_1 \cdots dx_N \prod_{i=1}^N p(x_i) \delta(x - \sum_i x_i) e^{-ikX} \\ &= \int dx_1 \cdots dx_N \prod_{i=1}^N p(x_i) e^{-ik(x_1 + \cdots + x_N)} = [p(k)]^N \end{aligned}$$

with

$$p(k) = \int dx_i e^{-ikx_i} p(x_i)$$

One may expand this expression to have

$$p(k) = \int dx p(x) \left[1 - ikx - \frac{1}{2}k^2x^2 + i\frac{k^3}{3!}x^3 + \cdots \right] = 1 - ik\langle x \rangle - \frac{1}{2}k^2\langle x^2 \rangle + i\frac{k^3}{3!}\langle x^3 \rangle + \cdots$$

Taking the logarithm, expanding it in a power series and resumming the terms, one may reorganize them to obtain the cumulants (see Lab of Computational Physics)

$$\ln p(k) = -ik\langle x \rangle_c - \frac{k^2}{2}\langle x^2 \rangle_c + \cdots$$

where

$$\langle x \rangle_c = \langle x \rangle, \quad \langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2 = \sigma^2, \quad \cdots$$

One may rewrite

$$\begin{aligned}
 p_N(X) &= \int \frac{dk}{2\pi} e^{ikX} [p_N(k)]^N = \int \frac{dk}{2\pi} e^{ikX} e^{N \ln p_N(k)} \\
 &= \int \frac{dk}{2\pi} e^{ikX} e^{-ikN\langle x \rangle} e^{-\frac{1}{2}Nk^2\sigma^2} \exp\left[\frac{i}{6}Nk^3\langle x^3 \rangle_c + \dots\right] \\
 &= \int \frac{dk}{2\pi} e^{ikX} e^{-ikN\langle x \rangle} e^{-\frac{1}{2}Nk^2\sigma^2} \left[1 + \frac{i}{6}Nk^3\langle x^3 \rangle_c + \dots\right] \\
 &= \int \frac{dy}{2\pi\sqrt{N}} \exp\left[i\frac{y}{\sqrt{N}}(X - N\langle x \rangle)\right] e^{-\frac{1}{2}y^2\sigma^2} \left[1 + \frac{i}{6}N\frac{y^3}{N^{\frac{3}{2}}}\langle x^3 \rangle_c\right] \\
 &\sim \int \frac{dy}{2\pi\sqrt{N}} \exp\left[i\frac{y}{\sqrt{N}}(X - N\langle x \rangle)\right] e^{-\frac{1}{2}y^2\sigma^2} = \frac{1}{\sqrt{2\pi\sigma^2N}} \exp\left[-\frac{(X - N\langle x \rangle)^2}{2\sigma^2N}\right]
 \end{aligned}$$

At the second line one has inserted the found expression for $p(k)$. At the second line, the exponential contains subleading terms. At the fourth line one may change $k = \frac{y}{\sqrt{N}}$. At the fifth line, one is in the limit $N \rightarrow \infty$.

The integral is a Gaussian integral. Even if the probability of measuring $p(x_i)$ is generic with mean $\langle x \rangle$ and standard deviation σ , the probability of measuring $p_N(X)$ for $N \rightarrow \infty$ becomes a Gaussian with mean $N\langle x \rangle$ and standard deviation $\sqrt{N}\sigma$. Therefore, in the thermodynamic limit, the relative error scale as

$$\frac{\sigma\sqrt{N}}{N\langle x \rangle} \sim \frac{1}{\sqrt{N}} \rightarrow 0, \quad N \rightarrow \infty$$

Regardless of the ensemble used, the result in the thermodynamic limit is the same. The central limit theorem holds with very general assumptions.

1.3 Micro-canonical ensemble

See Kardar, SPoP, §4.2. The macrostate is characterized by a fixed energy

$$H(p, q) = E = \text{const.}$$

One collects all the microstates compatible with the macrostate. Though, one should not introduce any bias. The equilibrium distribution is

$$\rho_{\text{eq}}(p, q) = \frac{1}{\Omega(E)} \delta(H(p, q) - E)$$

where the number of microstates with fixed energy E is

$$\Omega(E) = \int d\Gamma \delta(H(p, q) - E)$$

There are some technical issue which can be avoided. It is more convenient to find the state within an infinitesimal range.

Remark. The number of microstates with a given energy $\Omega(E)$ is typically of the order e^N where N is the total number of particles.

This observation implies that the entropy is

$$\begin{aligned}
 S &= -k \langle \ln \rho \rangle = -k \int d\Gamma \rho \ln \rho = -k \int d\Gamma \frac{\delta(H - E)}{\Omega(E)} \ln \frac{1}{\Omega(E)} \\
 &= -k \frac{1}{\Omega(E)} \ln \frac{1}{\Omega(E)} \int d\Gamma \delta(H - E) = -k \ln \frac{1}{\Omega(E)} = k \ln \Omega(E)
 \end{aligned}$$

where $k \approx 1.3 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant. The entropy is the logarithm of the total number of microstates. Since $\Omega(E) \sim e^N$ then the entropy goes like

$$S \sim kN$$

From this one sees that the entropy is an extensive quantity and the normalization by the Boltzmann constant is natural

$$S \sim kN \sim O(N^0)$$

Remark. Recall $\Omega(E) \sim e^N$. Consider two isolated systems with energies E_1 and E_2 . Considering them both, the total number of accessible microstates is

$$\Omega(E_T) = \Omega(E_1)\Omega(E_2)$$

Therefore, the entropy is

$$S_T = k \ln \Omega(E_T) = k \ln [\Omega(E_1)\Omega(E_2)] = k \ln \Omega(E_1) + k \ln \Omega(E_2) = S_1 + S_2$$

This means that entropy is additive.

Remark. [r] The property of being extensive and additive only holds when including the $N!$ from the semi-classical limit.

Remark. The microcanonical equilibrium distribution ρ_{eq} is compatible with the equilibrium condition of Liouville's

$$\partial_t \rho_{\text{eq}} = 0 = \{\rho_{\text{eq}}, H\}$$

because the distribution just depends on the energy.

Second law of thermodynamics. The microcanonical ensemble means working with combinatorics. Consider two separate systems with energies E_1 and E_2 . The total energy of them both is just the sum. Let the two systems come into thermal contact. Let the interaction be weak, i.e. the interaction Hamiltonian is small with respect to the free Hamiltonian. The energy of the first system is E_i while the one of the second is $E_T - E_i$. The total system is still isolated. The entropy of the total system before the interaction is just the sum of the entropies. After the thermal contact, the total number of accessible microstates is

$$\Omega_{\text{final}}(E_T) = \sum_i \Omega_1(E_i)\Omega_2(E_T - E_i)$$

The number of accessible states is much larger due to the presence of the sum. The final entropy is

$$S_{\text{final}}(E_T) = k \ln \Omega_{\text{final}}(E_T) \geq S_{\text{initial}} = S_1(E_1) + S_2(E_2)$$

This is the second law of thermodynamics: entropy grows since there more accessible compatible microstates.

Zeroth law of thermodynamics. The zeroth law is the law of equilibrium. Recall that $\Omega(E) \sim e^N$ and that the entropy is extensive $S(E) \sim N$. Therefore, the number of microstates is

$$\Omega(E) = \sum_i \Omega_1(E_i)\Omega_2(E_T - E_i) = \sum_i \exp \left[\frac{1}{k} [S_1(E_i) + S_2(E_T - E_i)] \right]$$

Since the exponent is big, then the value of the sum is dominated by the saddle point (or stationary point) of the energy E_i . Any variation away from such value produces very suppressed contributions. The stationary point can be found as

$$0 = \partial_{E_i} [S_1(E_i) + S_2(E_T - E_i)]_{E_i=E^*} = [\partial_E S_1 - \partial_E S_2]_{E=E^*}$$

Since

$$\partial_E S = \frac{1}{T}$$

then one finds

$$\boxed{T_1 = T_2}$$

when the two systems settle at $E = E^*$. The thermal equilibrium coincides with the situation that the energy extremizes the number of total accessible microstates. The two systems can exchange energy, heat and may reach the equilibrium configuration with energies E^* and $E_T - E^*$ corresponding to the situation the equilibrium temperature $T_1 = T_2 = T_{\text{eq}}$.

Remark. The energy E^* is the dominant value. One would like to find this quantity in a statistical framework. One may study the probability that the system 1 has energy E_1

$$\begin{aligned} p_1(E_1) &= \int \rho_T(E_T) \delta(H_1 - E_1) d\Gamma_1 d\Gamma_2 = \int \frac{\delta(H_T - E_T)}{\Omega(E_T)} \delta(H_1 - E_1) d\Gamma_1 d\Gamma_2 \\ &= \frac{1}{\Omega(E_T)} \int \delta(H_2 - (E_T - E_1)) d\Gamma_2 \int \delta(H_1 - E_1) d\Gamma_1 \\ &= \frac{1}{\Omega(E_T)} \Omega_2(E_T - E_1) \Omega_1(E_1) = \frac{1}{\Omega(E_T)} \exp \left[\frac{1}{k} [S_2(E_T - E_1) + S_1(E_1)] \right] \end{aligned}$$

at the second line, one has noticed that

$$\int \delta(H_T - E_T) \delta(H_1 - E_1) d\Gamma_1 d\Gamma_2 = \int \delta(H_2 - (E_T - E_1)) \delta(H_1 - E_1) d\Gamma_1 d\Gamma_2$$

As noted before, the exponential is dominated by the entropy at the energy E^* . One may expand

$$E_1 = E^* + \Delta E$$

Therefore

$$\begin{aligned} p_1(E_1) &= \frac{1}{\Omega(E_T)} \exp \left[\frac{1}{k} [S_2(E_T - E^*) + S_1(E^*)] \right] e^{\frac{1}{k} \Delta E \cdot 0} \\ &\quad \times \exp \left[\frac{1}{2k} [S_2''(E_T - E^*) + S_1''(E^*)] (\Delta E)^2 \right] \times \text{sub-leading} \end{aligned}$$

The linear term in ΔE is zero since E^* is an extremum. Since

$$S''(E) = \partial_E^2 S(E) = \partial_E \frac{1}{T} = -\frac{1}{T^2} \partial_E T = -\frac{1}{T^2} \frac{1}{C}$$

with C being the heat capacity, then the probability that the system 1 has energy E_1

$$p_1(E_1) \approx \exp \left[-\frac{1}{2kT^2} \left(\frac{1}{C_1} + \frac{1}{C_2} \right) (\Delta E)^2 \right]$$

is a Gaussian with mean value $\langle E_1 \rangle = E^*$ and standard deviation

$$\sigma = T \sqrt{k \frac{C_1 C_2}{C_1 + C_2}} \sim \sqrt{N}$$

recalling that the heat capacity is positive and extensive, $C \sim N$. As expected the relative error is

$$\frac{\sigma}{\langle E_1 \rangle} = \frac{\sigma}{E^*} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \rightarrow 0, \quad N \rightarrow \infty$$

Generalization. Consider two separated systems. Each is characterized by a fixed energy E_i and volume V_i . When the two systems come into contact, they can exchange heat and work. Both energy and volume may redistribute. The equilibrium situation is given by the first system with values (E_i, V_i) and the second with $(E_T - E_i, V_T - V_i)$. The number of accessible microstates is

$$\Omega_{\text{final}}(E_T, V_T) = \sum_i \Omega_1(E_i, V_i) \Omega_2(E_T - E_i, V_T - V_i) = \sum_i \exp \left[\frac{1}{k} [S_1(E_i, V_i) + S_2(E_T - E_i, V_T - V_i)] \right]$$

The procedure is the same as before, but with one interaction more. Since the entropy scales like $S \sim N$, one looks for the saddle point to obtain two equations

$$\left. \partial_E S_1(E, V) \right|_{E^*} = \left. \partial_E S_2(E, V) \right|_{E^*} \implies T_1 = T_2$$

and

$$\left. \partial_V S_1(E, V) \right|_{V^*} = \left. \partial_V S_2(E, V) \right|_{V^*} \implies P_1 = P_2$$

where the pressure is

$$P = T \partial_V S$$

There is both thermal equilibrium and mechanical equilibrium.

This procedure can be generalized. For every extensive quantity X there is a conjugate intensive quantity

$$J = -T \partial_X S$$

The entropy is a function of the extensive quantities

$$S = S(E, V, N, M, \dots)$$

For example, for the volume V is the pressure $-P$, for the number of particles N is the chemical potential μ , for the magnetization M is the magnetic field B .

For the case in which $S(E, V, N)$, one repeats the procedure above and one finds three equilibrium conditions

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2$$

Thermal, mechanical and chemical equilibrium are associated to the dominant values E^* , V^* and N^* .

Lecture 3

Previous lecture. The saddle point extremization in the limit of large N corresponds to the equilibrium conditions.

Since $\Omega_{\text{final}} \geq \Omega_{\text{initial}}$ then one finds that entropy is always increasing in thermodynamical processes

$$S = k \ln \Omega \implies \Delta S \geq 0$$

Example (Two-state system). Consider N non-interacting particles taking spin $|+\rangle$ or $|-\rangle$ with energies

$$E_+ = \varepsilon \quad E_- = 0$$

Let N_+ be the number of spin up particles and similarly for N_- and spin down particles. The total energy is

$$E_{\text{tot}} = N_+ \varepsilon + N_- \cdot 0 = N_+ \varepsilon$$

The system is isolated and one may use the micro-canonical ensemble. The number of states of the total system which have energy E_{tot} is

$$\Omega(E_{\text{tot}}) = \binom{N}{N_+} = \frac{N!}{(N_+)!(N - N_+)!}$$

The entropy is therefore

$$S(E_{\text{tot}}) = k \ln \frac{N!}{(N_+)!(N - N_+)!}$$

Notice that the entropy is zero $S = 0$ for $N = N_+$ or $N = N_-$: there is no ambiguity. Also, it is maximum when the configurations are maximally random

$$N_+ = N_- = \frac{1}{2}N$$

1.3.1 Ideal gas

See Kardar, SPoP, §4.4. Consider a system of N non-interacting point-like particles. The Hamiltonian is

$$H(\mathbf{p}, \mathbf{q}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}$$

Assume that the system is isolated

$$H(\mathbf{p}, \mathbf{q}) = E = \text{const.}$$

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but allow $E - \Delta E \leq H \leq E + \Delta E$: this hypothesis allows a simpler derivation and it is also physically sound. The number of micro-states is given by

$$\Omega(E) = \int d\Gamma \delta(H - E), \quad d\Gamma = \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N} N!}$$

Firstly, notice that the Hamiltonian depends only on the momenta, so

$$\int d^{3N}q = V^N$$

secondly, the Dirac delta implies that it holds

$$\sum_{i=1}^N \mathbf{p}_i^2 = 2mE = \text{const.}$$

however, since $E - \Delta E \leq H \leq E + \Delta E$, the integration over the momenta is an integration over a $3N$ -dimensional spherical shell of radius

$$R = \sqrt{2mE}$$

with thickness²

$$\Delta R = \sqrt{\frac{2m}{E}} \Delta E$$

The surface area of a d -dimensional ball is

$$A = S_d R^{d-1}$$

where S_d is the coefficient obtained from integrating over the angles. For example, the surface of a 3-ball, i.e. a three dimensional figure, is a 2-sphere and the area is $A = S_3 R^2 = 4\pi R^2$. The coefficient can be obtained in the following way

$$\begin{aligned} \pi^{\frac{d}{2}} &= \left[\int_{\mathbb{R}} e^{-x^2} dx \right]^d = \int d^d x e^{-(x_1^2 + \dots + x_d^2)} = S_d \int_0^\infty r^{d-1} e^{-r^2} dr, \quad r^2 = y \\ &= \frac{1}{2} S_d \int_0^\infty y^{\frac{d}{2}-1} e^{-y} dy = \frac{1}{2} S_d \Gamma(d/2) \end{aligned}$$

where $\Gamma(z)$ is the Euler Gamma function. Therefore

$$S_d = \frac{2\pi^{\frac{d}{2}}}{\Gamma(d/2)}$$

The number of micro-states is

$$\Omega(E, V, N) = \frac{V^N}{(2\pi\hbar)^{3N} N!} S_d R^{d-1} = \frac{V^N}{(2\pi\hbar)^{3N} N!} \frac{2\pi^{\frac{3N}{2}}}{\Gamma(3N/2)} (2mE)^{\frac{3N-1}{2}} \Delta R$$

One is interested in studying the entropy

$$S = k \ln \Omega(E, V, N)$$

in the limit $N \rightarrow \infty$. One may assume that $3N/2$ is an even integer and may drop the -1 factors in the exponent and in the Gamma function expressed as factorial. One may use the approximations

$$\ln \Delta R \sim \ln \sqrt{E} \sim \ln \sqrt{N}$$

the second relation is motivated by the fact that the energy is extensive and so it scales with the number of particles. This contribution is sub-leading. One may also utilize Stirling's formula

$$\ln N! \sim N \ln N - N$$

²Kardar uses an interval of length $2\Delta E$, so to compute the thickness with infinitesimals, one should multiply the right-hand side by two.

Thus, one obtains the Sackur–Tetrode equation

$$\begin{aligned} S = k \ln \Omega &\sim k \left[N \ln V + \frac{3N}{2} \ln \frac{2mE\pi}{4\pi^2\hbar^2} - \frac{3N}{2} \ln \frac{3N}{2} + \frac{3N}{2} - N \ln N + N \right] \\ &= kN \ln \left[\frac{V}{N} e \left(\frac{2mE}{2\pi\hbar^2 3N} \right)^{\frac{3}{2}} \right] = kN \ln \left[\frac{V}{N} e \left(\frac{meE}{3\pi\hbar^2 N} \right)^{\frac{3}{2}} \right] \end{aligned}$$

Now from the entropy, one may derive the thermodynamics. The energy is

$$\frac{1}{T} = \partial_E S = \partial_E [kN \ln E^{\frac{3}{2}} + \dots] = kN \frac{3}{2} \frac{1}{E} \implies \boxed{E = \frac{3}{2} NkT}$$

This result is expected from the equipartition theorem. Notice also that Planck's constant does not appear. The ideal gas law is

$$p = T \partial_V S = T \partial_V [kN \ln V + \dots] = T \frac{kN}{V} \implies \boxed{pV = NkT}$$

Gibbs's paradox. The factor of $N!$ is related to Gibbs's paradox. The entropy can be written as

$$S = kN \ln \left[\frac{V}{N} \sigma(T) \right]$$

where

$$\sigma(T) \equiv e \left(\frac{meE}{\pi\hbar^2 3N} \right)^{\frac{3}{2}} = e \left(\frac{e}{\pi\hbar^2} \frac{mkT}{2} \right)^{\frac{3}{2}}$$

at the second equality one insert the expression from the energy and one sees that σ is just a function of the temperature. The entropy is a homogeneous function of degree 1, it is well-behaved under a rescaling of extensive quantities

$$S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$$

However, if the factor $N!$ is not present in the phase space measure $d\Gamma$, then one has

$$\tilde{S} = kN \ln[V\sigma(T)]$$

The expression of the energy and the ideal gas law can still be both obtained, but the entropy is no longer a homogeneous function

$$\tilde{S}(\lambda E, \lambda V, \lambda N) = \lambda \tilde{S}(E, V, N) + \lambda kN \ln \lambda$$

Consider two ideal gases (N_1, V_1) and (N_2, V_2) , adjacent to each other, but separated. If their temperature is equal $T_1 = T_2 = T$, then by letting the two gases mix, one finds a variation of the entropy $\Delta \tilde{S}$. Before the mixing, the system has entropy

$$\tilde{S}_i = kN_1 \ln[V_1 \sigma(T)] + kN_2 \ln[V_2 \sigma(T)] = kN_1 \ln V_1 + kN_2 \ln V_2 + k(N_1 + N_2) \ln \sigma(T)$$

After the mixing, one finds

$$\tilde{S}_f = kN_1 \ln[(V_1 + V_2) \sigma(T)] + kN_2 \ln[(V_1 + V_2) \sigma(T)]$$

The variation in the entropy is

$$\Delta \tilde{S} = \tilde{S}_f - \tilde{S}_i = kN_1 \ln \frac{V_1 + V_2}{V_1} + kN_2 \ln \frac{V_1 + V_2}{V_2} > 0$$

The variation is positive since there are more accessible states. When mixing two identical gases

$$\frac{N_1}{V_1} = \frac{N_2}{V_2}, \quad T_1 = T_2$$

the variation should be zero $\Delta\tilde{S} = 0$, because it is just the same gas in two different compartments. However, the formula above states that the variation must be strictly positive in this case. This is Gibbs's paradox.

The correct result is obtained when considering the factor $N!$ in the entropy

$$\begin{aligned}\Delta S = S_f - S_i &= k(N_1 + N_2) \ln \frac{V_1 + V_2}{N_1 + N_2} \sigma(T) - kN_1 \ln \frac{V_1}{N_1} \sigma(T) - kN_2 \ln \frac{V_2}{N_2} \sigma(T) \\ &= k(N_1 + N_2) \ln \frac{V_1 + V_2}{N_1 + N_2} + k(N_1 + N_2) \ln \sigma(T) \\ &\quad - kN_1 \ln \frac{V_1}{N_1} - kN_2 \ln \frac{V_2}{N_2} - k(N_1 + N_2) \ln \sigma(T) \\ &= k(N_1 + N_2) \ln \frac{V_1 + V_2}{N_1 + N_2} - k(N_1 + N_2) \ln \frac{V_1}{N_1} \\ &= k(N_1 + N_2) \left[\ln \frac{V_1 + V_2}{N_1 + N_2} - \ln \frac{V_1}{N_1} \right] = 0\end{aligned}$$

In fact, let

$$x \equiv \frac{V_1}{N_1} = \frac{V_2}{N_2}$$

then

$$V_1 = xN_1, \quad V_2 = xN_2 \implies V_1 + V_2 = x(N_1 + N_2)$$

from which

$$\frac{V_1 + V_2}{N_1 + N_2} = x = \frac{V_1}{N_1}$$

From this one observes that quantum mechanics carries non-trivial information even in the semi-classical limit.

1.4 Canonical ensemble

See Tong, Statistical Physics, §1.3. In the canonical ensemble, the macro-state has a fixed temperature, while the energy (not the average energy) can vary. The situation of the canonical ensemble is that of a system S immersed in a big reservoir R . The total Hamiltonian is

$$H = H_R + H_S + H_{\text{int}}, \quad H_{\text{int}} \ll H_S \ll H_R$$

The system and the reservoir are isolated from the environment, therefore the total energy is constant and the combined system can be described with the micro-canonical approach

$$E_T = E_R + E_S = \text{const.}$$

The total number of micro-states must consider all the possible ways in which the energy can be distributed between the system and the reservoir

$$\Omega(E_T) = \sum_i \Omega_R(E_T - E_i) = \sum_i \exp \left[\frac{1}{k} S_R(E_T - E_i) \right]$$

where S_R is the entropy of the reservoir. The sum is over the micro-states of the system S with energy E_i , not over the possible energies: many micro-states may have the same energy. The probability that the system S is in the state i is

$$P_S(i) = \frac{\Omega_R(E_T - E_i)}{\Omega(E_T)}$$

The numerator may be rewritten as

$$\begin{aligned}\Omega_R(E_T - E_i) &= \exp \left[\frac{S_R(E_T - E_i)}{k} \right] \approx \exp \left[\frac{S_R(E_T)}{k} - \frac{E_i}{k} \partial_{E_i} S_R(E_T) \right] \\ &= \exp \left[\frac{S_R(E_T)}{k} \right] \exp \left[-\frac{E_i}{k} \frac{1}{T} \right]\end{aligned}$$

where one Taylor expands knowing that the reservoir implies

$$E_i \ll E_T, \quad T = T_R = T_S$$

The denominator is just the sum of the numerator over the states, therefore one finds

$$\Omega(E_T) = \sum_i \exp\left[\frac{S_R(E_T)}{k}\right] \exp\left[-\frac{E_i}{kT}\right]$$

One obtains the Boltzmann distribution

$$P_S(i) \approx \frac{e^{-\frac{E_i}{kT}}}{\sum_i e^{-\frac{E_i}{kT}}}$$

Its denominator is the Boltzmann partition function

$$Z = \sum_i e^{-\beta E_i}, \quad \beta = \frac{1}{kT}$$

where the sum is over the compatible micro-states.

Helmholtz free energy. See Tong, SP, §1.3.4. The free energy can be defined from the partition function

$$F = -kT \ln Z$$

From the free energy one may find all the thermodynamic quantities of interest. The average energy is

$$\langle E \rangle = \sum_i P(i) E_i = \frac{1}{Z} \sum_i E_i e^{-\beta E_i} = -\partial_\beta \ln Z$$

The entropy is

$$S = -k \sum_i P(i) \ln P(i) = -\frac{k}{Z} \sum_i e^{-\beta E_i} \ln \frac{e^{-\beta E_i}}{Z} = \frac{1}{T} \langle E \rangle + k \ln Z = \frac{E}{T} - \frac{F}{T}$$

The symbol of average is typically dropped, but always understood since the average is always identified with the macroscopic quantity. The free energy can be rewritten as

$$F = E - TS$$

The free energy $F(T, V, N)$ is a thermodynamic potential used to work with T , V and N . Computing its variation gives

$$dF = dE - dT S - T dS = (T dS - p dV + \mu dN) - S dT - T dS = -p dV + \mu dN - S dT$$

where one recalls that

$$dE = T dS - p dV + \mu dN$$

obtained by rearranging the variation of the entropy. Thus, the pressure, the entropy and the chemical potential are

$$p = -\partial_V F, \quad S = -\partial_T F, \quad \mu = \partial_N F$$

In the canonical ensemble, the partition function gives the macroscopic quantities of interest.

There are also other thermodynamic potentials

- The enthalpy to work with S , p and V

$$H = E + pV$$

- The Gibbs free energy to work with T , p and N

$$G = E - TS + pV = H - TS$$

All the thermodynamic potentials are related by Legendre transforms. Notice that the fourth potential is the internal energy E . To easily remember the differentials of the thermodynamic potentials, one may utilize the Born square³.

³See https://en.wikipedia.org/wiki/Thermodynamic_square.

Lecture 4

Previous lecture. In the canonical ensemble, the macro-state as fixed T , V and N . The partition function is a sum over the states and not over the energy levels

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$$Z(T, V, N) = \sum_i e^{-\beta E_i}$$

The density distribution is

$$\rho(i) = \frac{1}{Z} e^{-\beta E_i}$$

From the partition function one may define the free energy and from it obtain the macroscopic physical observables.

Comments on the Boltzmann distribution. The Boltzmann distribution is compatible with the Liouville theorem

$$\partial_t \rho_S(i) = 0, \quad \{\rho_S(i), H\} = 0$$

since the distribution is function of the energies E_i only. One has to check that it maximizes the entropy with the constraints

$$\sum_i P(i) = 1, \quad \sum_i P(i) E_i = \langle E \rangle$$

In fact

$$\begin{aligned} 0 &= \partial_{P(j)} \left[- \sum_i P(i) \ln P(i) + \lambda_1 \left(\sum_i P(i) - 1 \right) + \lambda_2 \left(\sum_i P(i) E_i - \langle E \rangle \right) \right] \\ &= - \ln P(j) - 1 + \lambda_1 + \lambda_2 E_j \end{aligned}$$

from which

$$P_j = c e^{d E_j}$$

From the constraints, one may find the constants

$$c = \frac{1}{Z}, \quad d = -\beta$$

to obtain the Boltzmann distribution.

1.4.1 Ideal gas

See Kardar, SPoP, §4.7, Tong, SP, §2.2. Instead of repeating the procedure of the micro-canonical ensemble, one may compute the partition function. Consider N non-interacting particles. The Hamiltonian of the system is given by

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}$$

The state i is a part in the phase space $\Gamma = \mathbb{R}^{6N}$. The probability distribution is

$$P_S(\mathbf{p}, \mathbf{q}) = \frac{1}{Z} \exp \left[-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \right]$$

One may compute the partition function

$$\begin{aligned} Z &= \sum_i e^{-\beta E_i} = \int d\Gamma \exp \left[-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \right] = \int \left[\prod_{i=1}^N \frac{d^3 q_i d^3 p_i}{(2\pi\hbar)^{3N} N!} \right] \exp \left[-\beta \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \right] \\ &= \frac{V^N}{(2\pi\hbar)^{3N} N!} \left[\frac{2\pi m}{\beta} \right]^{\frac{3N}{2}} \equiv \frac{1}{N!} \left[\frac{V}{\lambda^3} \right]^N = \frac{1}{N!} (Z_1)^N \end{aligned}$$

Recall that one is summing the compatible micro-states (which are points in the phase space such that $H = E_i$). At the first line the sum is over the states i . At the second line, Z_1 is the single-particle partition function. One also defines the de Broglie thermal wavelength

$$\lambda \equiv \frac{2\pi\hbar}{\sqrt{2\pi mkT}} = \frac{h}{\sqrt{2\pi mkT}}$$

which schematically embodies the Heisenberg uncertainty principle

$$E \sim kT, \quad p \sim \sqrt{2mE} \implies \lambda \sim \frac{\hbar}{p}$$

From the partition function one may derive the thermodynamic quantities.

Helmholtz free energy. The free energy is

$$\begin{aligned} F &= -kT \ln Z = -kTN \ln \frac{V}{\lambda^3} + kT \ln N! \sim -kTN [\ln V - \ln N + 1 - 3 \ln \lambda], \quad N \rightarrow \infty \\ &= -kTN \left[\ln V - \ln N + 1 + \frac{3}{2} \ln \frac{2\pi mkT}{h^2} \right] \end{aligned}$$

Entropy and energy. The entropy is

$$S = -\partial_T F = -\frac{F}{T} + \frac{3}{2} Nk$$

from which the energy is

$$E = F + TS = \frac{3}{2} NkT$$

This agrees again with the equipartition theorem.

Pressure. The pressure is

$$p = -\partial_V F = \frac{NkT}{V} \implies pV = NkT$$

Chemical potential. The chemical potential is

$$\mu = \partial_N F = \frac{F}{N} + kT = kT \ln \frac{N\lambda^3}{V}$$

From the chemical potential, one may define the fugacity

$$z \equiv e^{\frac{\mu}{kT}} = \frac{N\lambda^3}{V}$$

Notice that V/N is the classical volume per particle and λ^3 is the quantum volume per particle. If

$$\frac{V}{N} \gg \lambda^3$$

then the system can be treated classically and the temperature is high, so there is no wave function overlap or thermal boson effects. If

$$\frac{V}{N} \sim \lambda^3$$

then the quantum statistics effects are important and the temperature is low. The classical (or ideal) case is the high temperature case. In such situation

$$\frac{N}{V} \lambda^3 \ll 1 \implies \mu < 0$$

1.4.2 Fluctuations

See Tong, SP, §1.3.2. The average energy is

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-\beta E_i} = -\partial_\beta \ln Z$$

One may compute the variance. Consider the second derivative

$$\begin{aligned} \partial_\beta^2 \ln Z &= \partial_\beta \left[-\frac{1}{Z} \sum_i E_i e^{-\beta E_i} \right] = -\frac{1}{Z^2} \left[\sum_i E_i e^{-\beta E_i} \right]^2 + \frac{1}{Z} \sum_i E_i^2 e^{-\beta E_i} \\ &= -\langle E \rangle^2 + \langle E^2 \rangle = (\Delta E)^2 \end{aligned}$$

from which

$$(\Delta E)^2 = -\partial_\beta \langle E \rangle$$

Recalling that the heat capacity is

$$C = \partial_T \langle E \rangle$$

then one finds

$$(\Delta E)^2 = -\partial_\beta \langle E \rangle = -\partial_\beta T \partial_T \langle E \rangle = kT^2 C$$

therefore

$$(\Delta E)^2 \sim C, \quad \langle E \rangle \sim N \implies C \sim N$$

The relative fluctuations scale as

$$\frac{\Delta E}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \rightarrow 0, \quad N \rightarrow \infty$$

They are suppressed in the thermodynamic limit and $\langle E \rangle$ is the most probable value of the energy E . To see this, one may consider the probability that the system has energy E_i

$$P(E_i) = \frac{1}{Z} \Omega(E_i) e^{-\beta E_i}$$

where the partition function is

$$Z = \sum_i e^{-\beta E_i} = \sum_{E_i} \Omega(E_i) e^{-\beta E_i} \approx \Omega(E^*) e^{-\beta E^*}, \quad N \rightarrow \infty$$

where the first sum is over the states, while the second is over the energy levels. The approximation holds because, in the thermodynamic limit, the sum is dominated by the maximum value E^* (see Tong, SP, §1.3.3). Therefore, the most probable value of the energy is

$$\begin{aligned} \langle E \rangle &= -\partial_\beta \ln Z \approx -\partial_\beta \ln [\Omega(E^*) e^{-\beta E^*}] = -\partial_\beta \ln \Omega(E^*) - \partial_\beta (-\beta E^*) \\ &= -\partial_\beta E^* \partial_{E^*} \ln \Omega(E^*) + E^* + \beta \partial_\beta E^* = E^* + 0 \end{aligned}$$

where one uses

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k \frac{\partial \ln \Omega(E)}{\partial E} \implies \frac{\partial \ln \Omega(E^*)}{\partial E^*} = \beta$$

Example (Two-state system). See Kardar, SPoP, §4.7, Tong, SP, §1.3.2. Consider N non-interacting particles taking spin $|\pm\rangle$ with energies

$$E_+ = \varepsilon, \quad E_- = 0$$

The partition function is $Z = (Z_1)^N$ because each particle is independent from the rest. The single-particle canonical partition function is

$$Z_1 = \sum_{i=\pm} e^{-\beta E_i} = e^{-\beta \varepsilon} + e^{-\beta \cdot 0} = 1 + e^{-\beta \varepsilon} = 2e^{-\frac{\beta}{2}\varepsilon} \frac{e^{\frac{\beta}{2}\varepsilon} + e^{-\frac{\beta}{2}\varepsilon}}{2} = 2e^{-\frac{\beta}{2}\varepsilon} \cosh \frac{\beta \varepsilon}{2}$$

Thus the partition function of the system is

$$Z = (1 + e^{-\beta \varepsilon})^N = 2^N e^{-\frac{\beta}{2} N \varepsilon} \left[\cosh \frac{\beta \varepsilon}{2} \right]^N$$

from which the energy is

$$\langle E \rangle = -\partial_\beta \ln Z = \frac{N \varepsilon}{1 + e^{-\beta \varepsilon}} = \frac{N \varepsilon}{2} \left[1 - \tanh \frac{\beta \varepsilon}{2} \right]$$

1.5 Gran-canonical ensemble

See Kardar, SPoP, §4.9, Tong, SP, §1.4.2. In the gran-canonical ensemble, the macro-state has fixed temperature and chemical potential, while the energy and number of particles can vary. The situation is similar to the canonical ensemble: the system is immersed in a reservoir with which it exchanges energy and particles. The total Hamiltonian is

$$H_T = H_R + H_S + H_{\text{int}}$$

The reservoir implies

$$E_R \gg E_S, \quad N_R \gg N_S$$

The whole system is isolated from the environment so the total quantities are conserved

$$E_T = E_R + E_S = \text{const.}, \quad N_T = N_R + N_S = \text{const.}$$

The probability distribution of a state is

$$P_S(i) = \frac{\Omega_R(E_T - E_i, N_T - N_i)}{\Omega(E_T, N_T)}$$

The total number of micro-states of the reservoir is

$$\begin{aligned} \Omega_R(E_T - E_i, N_T - N_i) &= \exp \left[\frac{1}{k} S_R(E_T - E_i, N_T - N_i) \right] \\ &\approx \exp \left[\frac{1}{k} S_R(E_T, N_T) \right] \exp \left[-\frac{1}{k} (E_i \partial_{E_i} S_R + N_i \partial_{N_i} S_R) \right] \end{aligned}$$

Since

$$T = T_S = T_R = [\partial_E S_R]^{-1}, \quad \mu = \mu_S = \mu_R = -T \partial_N S_R$$

one finds the gran-canonical distribution

$$P_S(i) = \frac{e^{-\beta E_i + \beta \mu N_i}}{\sum_i e^{-\beta E_i + \beta \mu N_i}}$$

and the gran-canonical partition function

$$\mathcal{Z}(T, V, \mu) = \sum_i e^{-\beta E_i + \beta \mu N_i}$$

where the sum is over the micro-states compatible with fixed T , V and μ . One may relate this partition function to the one of the canonical ensemble

$$\mathcal{Z}(T, V, \mu) = \sum_{N_i=0}^{\infty} e^{\beta \mu N_i} \sum_{\substack{i \text{ w/} \\ \text{fixed } N_i}} e^{-\beta E_i} = \sum_{N_i=0}^{\infty} e^{\beta \mu N_i} Z(T, V, N_i) = \sum_{N=0}^{\infty} z^N Z(T, V, N)$$

where one finds the fugacity $z \equiv e^{\beta \mu}$ and $Z(T, V, N)$ is the canonical partition function.

One may define the gran-canonical potential

$$\Phi = -kT \ln \mathcal{Z}$$

One may extract the information about the system from the partition function and the gran-canonical potential. The derivative with respect to β gives

$$-\partial_\beta \ln \mathcal{Z}(T, V, \mu) = \langle E \rangle - \mu \langle N \rangle$$

Number of particles. The number of particles is

$$\langle N \rangle = \frac{1}{\beta} \partial_\mu \ln \mathcal{Z}$$

Entropy. The entropy is

$$S = -k \sum_i P(i) \ln P(i) = -\frac{k}{\mathcal{Z}} \sum_i e^{-\beta(E_i - \mu N_i)} \ln \frac{1}{\mathcal{Z}} e^{-\beta(E_i - \mu N_i)} = k \ln \mathcal{Z} + \frac{1}{T} (\langle E \rangle - \mu \langle N \rangle)$$

Gran-canonical potential. Inserting the above $k \ln \mathcal{Z}$ inside the potential, one finds (where the average is understood)

$$\Phi(T, V, \mu) = -kT \ln \mathcal{Z} = -TS + E - \mu N = F(T, V, N) - \mu N$$

This is a Legendre transform between μ and N .

Recalling that

$$dF = -S dT - p dV + \mu dN$$

one obtains

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

from which one reads

$$\boxed{p = -\partial_V \Phi, \quad S = -\partial_T \Phi, \quad N = -\partial_\mu \Phi}$$

Notice that the potential depends on one extensive variable, the volume. The potential is extensive too

$$\Phi(T, \lambda V, \mu) = \lambda \Phi(T, V, \mu)$$

Therefore the potential is linear in the volume

$$\Phi(T, V, \mu) = V f(T, \mu) = -pV$$

since

$$p = -\partial_V \Phi$$

This argument is not valid for the Helmholtz free energy $F(T, V, N)$ because it depends on two extensive variables, the volume and the number of particles. For the Gibbs free energy one has

$$G(T, p, N) = \mu N$$

since only the number of particles is extensive.

1.5.1 Fluctuations

Consider the average number of particles

$$\langle N \rangle = \frac{1}{\beta} \partial_\mu \ln \mathcal{Z}$$

Its variance is

$$(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta} \partial_\mu \langle N \rangle = \frac{1}{\beta^2} \partial_\mu^2 \ln \mathcal{Z} \sim N$$

Therefore, the relative fluctuations behave as

$$\frac{\Delta N}{\langle N \rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \rightarrow 0, \quad N \rightarrow \infty$$

Comments on the distribution. One notices that the distribution of states satisfies

$$\partial_t \rho(i) = 0, \quad \{\rho(i), H\} = 0$$

One may check that the gran-canonical distribution maximizes the entropy with the constraints

$$\langle E \rangle = \sum_i E_i P(i), \quad \langle N \rangle = \sum_i N_i P(i), \quad \sum_i P(i) = 1$$

In fact

$$\begin{aligned} 0 &= \partial_{P(i)} \left[- \sum_j P(j) \ln P(j) + \lambda_1 \left(\sum_j P(j) - 1 \right) \right. \\ &\quad \left. + \lambda_2 \left(\sum_j E_j P(j) - E \right) + \lambda_3 \left(\sum_j N_j P(j) - N \right) \right] \\ &= -1 - \ln P(i) + \lambda_1 + \lambda_2 E_i + \lambda_3 N_i \end{aligned}$$

from this one obtains

$$P(i) = ce^{\lambda_2 E_i + \lambda_3 N_i}$$

1.5.2 Ideal gas

The partition function is

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} z^N Z(T, V, N) = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\frac{zV}{\lambda^3} \right]^N = \exp \left[\frac{zV}{\lambda^3} \right]$$

while the gran-canonical potential is

$$\Phi = -kT \ln \mathcal{Z} = -kT \frac{zV}{\lambda^3}$$

Thus, the average pressure is

$$p = -\frac{\Phi}{V} = \frac{kT}{\lambda^3} z$$

The average number of particles is

$$N = \frac{1}{\beta} \partial_{\mu} \ln \mathcal{Z} = \frac{1}{\beta} \frac{V}{\lambda^3} \partial_{\mu} z = \frac{V}{\lambda^3} z, \quad z = e^{\beta \mu}$$

The value of the fugacity can be extracted from the equation of the average number of particles (i.e. the equation above). Inserting its expression into the equation for the average pressure, one finds the ideal gas law

$$p = \frac{kT}{\lambda^3} z = \frac{kT}{V} N \implies pV = NkT$$

For the ideal gas, the system is classical when the temperature is high

$$z = e^{\beta \mu} = \frac{N}{V} \lambda^3 \ll 1 \implies \mu < 0$$

2 Interacting particles

See Kardar, SPoP, §4.4?, sources? [r]. One would like to describe N classical particles interacting with one another with potential $U(\mathbf{q}_1, \dots, \mathbf{q}_N)$ at fixed temperature. The focus is just on weak interactions, but the problem can be equally formulated for stronger interactions. One may use the canonical ensemble. The partition function is

$$Z = \int \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N} N!} \exp \left[-\beta \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{q}_1, \dots, \mathbf{q}_N) \right) \right] = \int \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N} N!} e^{-\beta H}$$

Lecture 5

The distribution of micro-states is

$$\rho(\mathbf{p}, \mathbf{q}) = \frac{1}{Z} e^{-\beta H}$$

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One may calculate the probability density of finding a particle with momentum \mathbf{p}

$$\rho(\mathbf{p}) = \int d\Gamma \rho(\mathbf{p}_i, \mathbf{q}_i) \delta(\mathbf{p}_i - \mathbf{p}) = \mathcal{N} e^{-\beta \frac{\mathbf{p}^2}{2m}}$$

The integration in the position is complicated due to the presence of the potential U . To compute the constant \mathcal{N} , one may utilize the normalization condition

$$\int d^3p \rho(\mathbf{p}) = 1$$

from which one finds

$$1 \equiv \mathcal{N} \int d^3p e^{-\beta \frac{\mathbf{p}^2}{2m}} = \mathcal{N} (2\pi m k T)^{\frac{3}{2}} \implies \mathcal{N} = \frac{1}{(2\pi m k T)^{\frac{3}{2}}}$$

Therefore, one obtains the Maxwell–Boltzmann distribution of the momentum

$$\boxed{\rho(\mathbf{p}) = \frac{1}{(2\pi m k T)^{\frac{3}{2}}} e^{-\beta \frac{\mathbf{p}^2}{2m}}}$$

which is valid for any interaction $U(\mathbf{q}_1, \dots, \mathbf{q}_N)$. From this one computes the average kinetic energy of a particle

$$\langle E_{\text{kin}} \rangle = \frac{1}{2m} \langle \mathbf{p}^2 \rangle = \int d^3p \frac{\mathbf{p}^2}{2m} \rho(\mathbf{p}) = \frac{1}{2m} \frac{4\pi}{(2\pi m k T)^{\frac{3}{2}}} \int dp p^4 e^{-\frac{p^2}{2mkT}} = \frac{3}{2} kT$$

This is expected from the equipartition theorem: there are three degrees of freedom with quadratic terms in the Hamiltonian.

2.1 Classical ideal polyatomic gas

See Tong, SP, §§2.4, 3.4, sources? [r]. Consider a gas of N non-interacting molecules with an internal structure. Assume that there is no long-range interaction between such molecules and the system is classical, so no wave function overlap effects

$$\frac{V}{N} \gg \lambda^3$$

This means that the density of the gas is low enough to have no quantum effects.

The Hamiltonian of the system is the sum of the single-molecule Hamiltonians

$$H = \sum_i H_i$$

and as such the canonical partition function is factorized

$$Z = \frac{1}{N!} (Z_1)^N$$

where Z_1 is the single-molecule partition function. Assume that each molecule contains L particles, one finds

$$\begin{aligned} Z_1 &= \int \frac{d^{3L}p d^{3L}q}{(2\pi\hbar)^{3L}} \exp \left[-\beta \left(\sum_{j=1}^L \frac{\mathbf{p}_j^2}{2m} + U(\mathbf{q}_1, \dots, \mathbf{q}_L) \right) \right] \\ &= Z_{\text{int}}(T) \int \frac{d^3p_{\text{CM}} d^3q_{\text{CM}}}{(2\pi\hbar)^3} \exp \left[-\beta \frac{\mathbf{p}_{\text{CM}}^2}{2M} \right] = \frac{V}{\lambda^3} Z_{\text{int}}(T) \end{aligned}$$

where M is the mass of the molecule and as such λ depends on it. The partition function is factorized into a contribution from the center of mass and a contribution from the interaction. Therefore, the partition function is

$$Z(T, V, N) = \frac{1}{N!} (Z_1)^N = \frac{1}{N!} \left[\frac{V}{\lambda^3} \right]^N Z_{\text{int}}^N(T)$$

while the gran-canonical partition function is

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} z^N Z(T, V, N) = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\frac{zV}{\lambda^3} Z_{\text{int}}(T) \right]^N = \exp \left[\frac{zV}{\lambda^3} Z_{\text{int}}(T) \right]$$

The gran-canonical potential is

$$-pV = \Phi = -kT \ln \mathcal{Z} = -kT \frac{zV}{\lambda^3} Z_{\text{int}}(T)$$

The average number of particles is

$$N = \frac{1}{\beta} \partial_{\mu} \ln \mathcal{Z} = \frac{zV}{\lambda^3} Z_{\text{int}}(T)$$

Recognizing this expression inside the potential, one finds the ideal gas law

$$\Phi = -pV = -kT \frac{zV}{\lambda^3} Z_{\text{int}}(T) = -kTN \implies pV = kNT$$

The law is not sensitive to the internal structure of the molecules. The partition function of the interaction does not appear, but it is clear that the average energy depends on such partition function.

Consider a simple molecule: two atoms interacting through a quadratic potential (e.g. a spring). The Hamiltonian contains three terms

$$H = H_{\text{CM}} + H_{\text{rot}} + H_{\text{vib}} \implies Z_1 = Z_{\text{CM}} Z_{\text{rot}} Z_{\text{vib}}$$

Center-of-mass contribution. The contribution from the center of mass is

$$H_{\text{CM}} = \frac{p_{\text{CM}}^2}{2M}$$

which, by the equipartition theorem, gives the contribution

$$E_{\text{CM}} = \frac{3}{2} kT$$

Rotational contribution. The rotational contributions comes from two degrees of freedom. The rotational Lagrangian is

$$L_{\text{rot}} = \frac{1}{2} I (\dot{\theta}^2 + \sin^2 \theta \dot{\varphi}^2)$$

where I is the moment of inertia. The conjugate momenta are

$$p_{\theta} = \partial_{\dot{\theta}} L_{\text{rot}} = I\dot{\theta}, \quad p_{\varphi} = \partial_{\dot{\varphi}} L_{\text{rot}} = I \sin^2 \theta \dot{\varphi}$$

The Hamiltonian is then

$$H_{\text{rot}} = \dot{\theta} p_{\theta} + \dot{\varphi} p_{\varphi} - L_{\text{rot}} = \frac{p_{\theta}^2}{2I} + \frac{p_{\varphi}^2}{2I \sin^2 \theta} = \frac{1}{2I} \mathbf{L}^2$$

where \mathbf{L} is the angular momentum. The rotational partition function is then

$$\begin{aligned} Z_{\text{rot}} &= \frac{1}{(2\pi\hbar)^2} \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \int dp_{\theta} \int dp_{\varphi} e^{-\beta H_{\text{rot}}} \\ &= \frac{1}{(2\pi\hbar)^2} \sqrt{\frac{2\pi I}{\beta}} \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \sqrt{\frac{2\pi I \sin^2 \theta}{\beta}} \\ &= \frac{2I}{\hbar^2} kT = \frac{2I}{\hbar^2} \frac{1}{\beta} \end{aligned}$$

Therefore, the rotational energy is

$$E_{\text{rot}} = -\partial_{\beta} \ln Z_{\text{rot}} = -\partial_{\beta} \ln \left[\frac{2I}{\hbar^2} \frac{1}{\beta} \right] = kT = 2 \cdot \frac{1}{2} kT$$

The first 2 correctly represents the number of degrees of freedom.

Vibrational contribution. The vibrational Hamiltonian is

$$H_{\text{vib}} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 s^2$$

From the equipartition theorem one finds

$$E_{\text{vib}} = 2 \cdot \frac{1}{2}kT$$

Total contribution. The total contribution to the energy is

$$E_{\text{tot}} = N[E_{\text{CM}} + E_{\text{rot}} + E_{\text{vib}}] = N \left[\frac{3}{2}kT + kT + kT \right] = \frac{7}{2}NkT$$

Therefore, the heat capacity is

$$C = \partial_T E = \frac{7}{2}kN$$

Quantum effects. In reality, the heat capacity changes with the temperature: it is an increasing step function. In order of increasing temperature, the contributions come from translation, rotation and vibration and so the energy and heat capacity change accordingly. See Tong, SP, fig. 11.

The rotational quantum Hamiltonian is

$$\hat{H}_{\text{rot}} = \frac{\hbar^2}{2I} \hat{\mathbf{L}}^2$$

The single-particle partition function is

$$Z_1^{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) \exp \left[-\beta \frac{\hbar^2}{2I} l(l+1) \right]$$

where the parenthesis are the degeneracy of the level l . At high temperatures $\beta \ll 1$, the sum can be approximated by an integral

$$Z_1^{\text{rot}} \approx \int_0^{\infty} dx (2x+1) \exp \left[-\beta \frac{\hbar^2}{2I} x(x+1) \right] = \frac{2I}{\beta \hbar^2}$$

Therefore the rotational energy is

$$E_{\text{rot}} = -\partial_{\beta} \ln Z_1^{\text{rot}} \approx \frac{1}{\beta} = kT$$

This agrees with what one has found above: the classical result found with the equipartition theorem. For low temperatures $\beta \gg 1$, all states effectively decouple and only $l=0$ contributes

$$Z_{\text{rot}} \approx 1 \implies E_{\text{rot}} \approx 0$$

The rotational modes are frozen and only the translational modes contribute to the heat capacity.

Similarly, the Hamiltonian of the vibrations is the simple quantum harmonic oscillator and the single-particle partition function is

$$Z_1^{\text{vib}} = \sum_{n=0}^{\infty} \exp \left[-\beta \hbar \omega \left(n + \frac{1}{2} \right) \right] = e^{-\frac{1}{2}\beta \hbar \omega} \frac{1}{1 - e^{-\beta \hbar \omega}}$$

At high temperatures, one may approximate

$$e^{-\beta \hbar \omega} \approx 1 - \beta \hbar \omega$$

so that the partition function and the energy are

$$Z_1^{\text{vib}} \approx \frac{1}{\beta \hbar \omega} \implies E_{\text{vib}} \approx kT$$

At low temperatures, one finds

$$e^{-\beta\hbar\omega} \approx 0 \implies Z_1^{\text{vib}} \approx e^{-\frac{1}{2}\beta\hbar\omega} \implies E_{\text{vib}} \approx \frac{1}{2}\hbar\omega$$

Therefore, at low temperatures, the non-translational contributions are

$$E_{\text{rot}} + E_{\text{vib}} \approx \frac{1}{2}\hbar\omega$$

and give no contributions to the heat capacity

$$C = \frac{\partial E}{\partial T}$$

2.2 Weakly interacting classical gas

See Kardar, SPoP, §§5.2, 5.3, Tong, SP, §2.5. Consider N point particles with a long-range interaction. Assume no quantum overlap effects

$$\frac{V}{N} \gg \lambda^3$$

and let l be the range of the interaction

$$\frac{V}{N} \gtrsim l^3$$

This assumption implies low density and one may only consider a two-body interaction, while three-body and higher interactions are unlikely and suppressed.

The Hamiltonian of the system is

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} U(|\mathbf{q}_i - \mathbf{q}_j|)$$

The gas consists of neutral particles, but they can get an instantaneous dipole \mathbf{p}_1 that induces an electric field

$$E \sim \frac{p_1}{r^3}$$

and as such a dipole, so one may have dipole-dipole interactions with potential

$$\frac{p_1 p_2}{r^3} \sim \frac{1}{r^6}$$

This is called van der Waals interaction.

At short distances, one assumes a repulsive force to account for the Pauli exclusion principle. One very common potential that is often used to model the force between atoms is the Lennard-Jones potential

$$U(r) \sim \left[\frac{r_0}{r} \right]^{12} - \left[\frac{r_0}{r} \right]^6$$

which can be simplified to

$$U(r) = \begin{cases} \infty, & r \leq r_0 \\ -U_0 \left[\frac{r_0}{r} \right]^6, & r > r_0 \end{cases}$$

Due to the form of the interaction, one expects that the equation of state of the gas is a modification of the ideal gas equation of state

$$\frac{p}{kT} = \frac{N}{V} + B_2(T) \left[\frac{N}{V} \right]^2 + B_3(T) \left[\frac{N}{V} \right]^3 + \dots$$

The correction to the ideal gas law is expressed in terms of a density expansion N/V , called virial expansion. One would like to find the coefficients from the ensemble.

First coefficient. The canonical partition function is

$$\begin{aligned} Z &= \frac{1}{N!} \int \prod_{i=1}^N \frac{d\mathbf{p}_i d\mathbf{q}_i}{(2\pi\hbar)^3} \exp \left[-\beta \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} U(q_{ij}) \right) \right] \\ &= \frac{1}{N!} \frac{1}{\lambda^{3N}} \int \prod_{i=1}^N d\mathbf{q}_i \exp \left[-\beta \sum_{i<j} U(q_{ij}) \right] \end{aligned}$$

where $q_{ij} \equiv |\mathbf{q}_i - \mathbf{q}_j|$. Since the density is low, meaning the system is classical and the temperature is high, one may first attempt to expand

$$\exp \left[-\beta \sum_{i<j} U(q_{ij}) \right] \sim 1 - \beta \sum_{i<j} U(q_{ij}) + \beta^2 \dots$$

This does not work at short distances

$$U(r) \rightarrow \infty, \quad r < r_0$$

A second attempt defines the Mayer function

$$f(q) \equiv e^{-\beta U(q)} - 1$$

Its limits are

$$\lim_{q \rightarrow r_0} f(q) = -1, \quad \lim_{q \rightarrow \infty} f(q) = 0, \quad |f(q)| \in [0, 1]$$

This function can be used as an expansion parameter. One may rewrite the interaction as⁴

$$\exp \left[\sum_{i<j} U(q_{ij}) \right] = \prod_{i<j} e^{-\beta U(q_{ij})} = \prod_{i<j} [1 + f(q_{ij})] = 1 + \sum_{i<j} f(q_{ij}) + \sum_{i<j} \sum_{l<m} f(q_{ij}) f(q_{lm}) + \dots$$

Therefore, the partition function is

$$Z = \frac{1}{N!} \frac{1}{\lambda^{3N}} \int \prod_{i=1}^N d\mathbf{q}_i \left[1 + \sum_{i<j} f_{ij} + \sum_{i<j} \sum_{l<m} f_{ij} f_{lm} + \dots \right], \quad f_{ij} \equiv f(q_{ij})$$

The first addendum is just an integral in the position

$$\int \prod_{i=1}^N d\mathbf{q}_i = V^N$$

Let $i = 1$ and $j = 2$, then the second addendum gives

$$\begin{aligned} \int \left[\prod_{i=1}^N d\mathbf{q}_i \right] f_{ij} &= \left[\int d\mathbf{q}_1 d\mathbf{q}_2 f_{12} \right] \left[\int d\mathbf{q}_3 \dots d\mathbf{q}_N \right] = \left[\int d\mathbf{k} f_{12}(k) \right] \left[\int d\mathbf{r} \right] V^{N-2} \\ &= \left[\int d\mathbf{k} f_{12}(k) \right] V^{N-1}, \quad \mathbf{k} = \mathbf{q}_1 - \mathbf{q}_2, \quad \mathbf{r} = \mathbf{q}_1 + \mathbf{q}_2 \end{aligned}$$

Every term in the sum gives the same contribution, therefore

$$\sum_{i<j} \int \left[\prod_{i=1}^N d\mathbf{q}_i \right] f(q_{ij}) = \frac{1}{2} N(N-1) V^{N-1} \int d\mathbf{k} f(k) \sim \frac{N^2}{2V} V^N \int d\mathbf{k} f(k)$$

where the approximation holds in the thermodynamic limit. Thus, the partition function is

$$Z \sim \frac{V^N}{\lambda^{3N} N!} \left[1 + \frac{N^2}{2V} \int d\mathbf{k} f(k) + \dots \right]$$

⁴Notice that there are some missing conditions on the indices. For example, for the double sum, it should always hold $i < l$. See also https://en.wikipedia.org/wiki/Cluster_expansion.

Recalling that for $x \ll 1$, one may apply the binomial series

$$(1+x)^N \sim (1+Nx)$$

one may expand the partition function in N/V

$$Z \sim \frac{V^N}{\lambda^{3N} N!} \left[1 + \frac{N}{2V} \int d\mathbf{k} f(k) \right]^N$$

The free energy is then

$$\begin{aligned} F &= -kT \ln Z \sim -kT \ln \frac{V^N}{\lambda^{3N} N!} - kTN \ln \left[1 + \frac{N}{2V} \int d\mathbf{k} f(k) \right] \\ &\sim -kT \ln \frac{V^N}{\lambda^{3N} N!} - kTN \frac{N}{2V} \int d\mathbf{k} f(k) = \text{ideal gas} + \text{corrections} \end{aligned}$$

at the second line one has applied

$$\ln(1+x) \sim x$$

The pressure is

$$p = -\partial_V F = kT \frac{N}{V} \left[1 - \frac{N}{2V} \int d\mathbf{k} f(k) \right] + \dots$$

from this one finds the first coefficient

$$B_2(T) = -\frac{1}{2} \int d\mathbf{k} f(k)$$

The first coefficient depends on the first term in the expansion. There still is no information about the particular interaction.

One is interested in the next coefficients. The naive idea is to expand in more terms and collect them accordingly. A more clever way is the cluster expansion: it is a systematic analysis of the perturbative expansion without assuming any detail of the interaction. The form of the interaction is needed only at the end when one is interested in the numerical values.

Lecture 6

2.2.1 Cluster expansion

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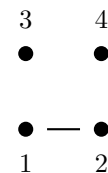
Recall the partition function

$$Z = \frac{1}{N!} \frac{1}{\lambda^{3N}} \int \prod_{i=1}^N d\mathbf{q}_i \left[1 + \sum_{i<j} f_{ij} + \sum_{i<j} \sum_{l<m} f_{ij} f_{lm} + \dots \right]$$

One may check by explicitly writing the products from which the sums above follow, that it holds:

- the indices can be all distinct, i.e. $f_{ij} f_{lm} f_{kn}$;
- repeated indices are allowed, i.e. $f_{ij} f_{lm} f_{mk}$;
- the same pair cannot appear more than once, i.e. no $f_{ij} f_{lm} f_{ij}$;
- on the same f , the indices cannot have the same value, i.e. no $f_{ii} f_{lm} f_{kj}$.

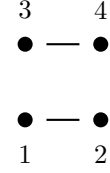
One can graphically represent the integrals in the partition function. The number N of integration variables $d\mathbf{q}_i$ corresponds to the number N of points and each f_{ij} is a link connecting the two points i and j . An example for $N = 4$ is the following

$$\int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 d\mathbf{q}_4 f(q_{12}) = \int d\mathbf{q}_3 d\mathbf{q}_4 \int d\mathbf{q}_1 d\mathbf{q}_2 f(q_{12}) =$$


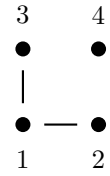
The bottom dots are a 2-cluster, while the upper dots each are 1-clusters. Let m_l be the number of l -clusters, then

$$m_1 = 2, \quad m_2 = 1, \quad m_3 = m_4 = 0 \implies \sum_l l m_l = N = 4$$

Another example is

$$\int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 d\mathbf{q}_4 f_{12} f_{34} = \left[\int d\mathbf{q}_1 d\mathbf{q}_2 f_{12} \right] \left[\int d\mathbf{q}_3 d\mathbf{q}_4 f_{34} \right] =$$


where one has $m_2 = 2$. Finally

$$\int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 d\mathbf{q}_4 f_{12} f_{13} = \left[\int d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 f_{12} f_{13} \right] \left[\int d\mathbf{q}_4 \right] =$$


with $m_1 = 1$ and $m_3 = 1$.

Definition. An l -cluster is a connected part of the graph with l connected points.

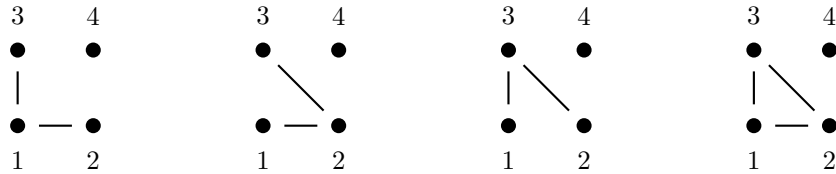
A graph with N points can be decomposed into l -clusters with the condition

$$N = \sum_{l=1}^N m_l l$$

with m_l the number of l -clusters. The graphs above are some partitions of four points. For example, for $N = 4$ one finds

- $m_1 = 4, m_2 = m_3 = m_4 = 0$ so $4 \cdot 1 = 4$;
- $m_1 = 2, m_2 = 1, m_3 = m_4 = 0$, so $2 \cdot 1 + 1 \cdot 2 = 4$;
- $m_2 = 2, m_1 = m_3 = m_4 = 0$, so $2 \cdot 2 = 4$;
- $m_1 = m_3 = 1, m_2 = m_4 = 0$, so $1 \cdot 1 + 1 \cdot 3 = 4$;
- $m_4 = 1, m_1 = m_2 = m_3 = 0$, so $1 \cdot 4 = 4$.

Notice that there are four 3-clusters connecting 1, 2 and 3 with different numbers of links (which correspond to powers of f)



The last graph has three links, f^3 , while the others have two, f^2 . The coefficients of the virial expansion are not organized in powers of the Mayer function f . The importance is on how many points are connected and not on how many links there are. This is reflected in the cluster expansion. The l -clusters can have different numbers of links.

Defining the contribution of the l -clusters to be

$$U_l \equiv \int \left[\prod_{j=1}^N d\mathbf{q}_j \right] (\text{all } l\text{-clusters})$$

the multiplicity of the contribution of an l -cluster U_l is

$$N! \prod_l \frac{1}{(l!)^{m_l} m_l!}$$

The factor $l!$ counts the permutations of points in the l -cluster, while the $m_l!$ factor counts the permutation of l -clusters. An example contribution is U_3 which is the sum of the four diagrams above.

The partition function is then

$$Z(T, V, N) = \frac{1}{\lambda^{3N} N!} \sum_{\{m_l\}} N! \prod_l \frac{(U_l)^{m_l}}{(l!)^{m_l} m_l!} = \frac{1}{\lambda^{3N}} \sum_{\{m_l\}} \prod_l \frac{(U_l)^{m_l}}{(l!)^{m_l} m_l!}$$

where the sum is over all distinct divisions of N points into a set of clusters $\{m_1, m_2, m_3, \dots\}$ such that

$$\sum_{l=1}^N m_l l = N$$

This constraint complicates computations, but can be removed by using the gran-canonical partition function⁵

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \sum_{N=0}^{\infty} z^N Z(T, V, N) = \sum_{N=0}^{\infty} \frac{z^N}{\lambda^{3N}} \sum_{\substack{\{m_l\} \\ \text{constraint}}} \prod_l \frac{(U_l)^{m_l}}{(l!)^{m_l} m_l!} \\ &= \sum_{N=0}^{\infty} \sum_{\substack{\{m_l\} \\ \text{constraint}}} \left[\frac{z}{\lambda^3} \right]^{\sum_l m_l l} \prod_l \frac{(U_l)^{m_l}}{(l!)^{m_l} m_l!} = \sum_{N=0}^{\infty} \sum_{\substack{\{m_l\} \\ \text{constraint}}} \prod_l \left[\frac{z}{\lambda^3} \right]^{m_l l} \frac{(U_l)^{m_l}}{(l!)^{m_l} m_l!} \\ &= \sum_{\{m_l\}} \prod_l \left[\frac{z}{\lambda^3} \right]^{m_l l} \frac{1}{m_l!} \left[\frac{U_l}{l!} \right]^{m_l} = \prod_l \sum_{m_l=0}^{\infty} \frac{1}{m_l!} \left[\left(\frac{z}{\lambda^3} \right)^l \frac{U_l}{l!} \right]^{m_l} \\ &= \prod_{l=1}^{\infty} \exp \left[\left(\frac{z}{\lambda^3} \right)^l \frac{U_l}{l!} \right] = \exp \left[\frac{V}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l \right] \end{aligned}$$

At the third line one removes the constraint. At the last line, one defines

$$b_l \equiv \frac{\lambda^3 U_l}{V l! \lambda^{3l}}$$

The sum over all diagrams has been rewritten as the exponential of the sum over all connected diagrams, meaning all clusters.

Observables and coefficients. The average pressure can be found from

$$pV = -\Phi = kT \ln \mathcal{Z}(T, V, \mu) = kT \frac{V}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l$$

while the average number of particles is

$$N = \frac{1}{\beta} \partial_{\mu} \ln \mathcal{Z}(T, V, \mu) = \frac{V}{\lambda^3} \sum_{l=1}^{\infty} l b_l z^l$$

One may find the fugacity z in terms of the average number of particles N at some order from the equation above. Inserting this result into the equation for average pressure, one may find the pressure in terms of the density N/V at a given order. At the second order in z one finds

$$\lambda^3 \frac{N}{V} = z + 2b_2 z^2 + o(z^2) \implies z \approx \lambda^3 \frac{N}{V} - 2b_2 \left[\lambda^3 \frac{N}{V} \right]^2 + \dots$$

⁵This is done because it is an equivalent description to the canonical ensemble in the thermodynamic limit, $N, V \rightarrow \infty$.

where one isolates z and substitutes the result into z^2 (this is equivalent to solving the quadratic equation, expanding the square root and truncating at the desired order). Substituting this expression into the pressure gives

$$\frac{p}{kT} \approx \frac{1}{\lambda^3}(z + b_2 z^2) \approx \frac{N}{V} \left[1 - b_2 \lambda^3 \frac{N}{V} \right]$$

where $b_1 = 1$. By comparison with the virial expansion

$$\frac{p}{kT} = \frac{N}{V} + B_2(T) \left[\frac{N}{V} \right]^2 + B_3(T) \left[\frac{N}{V} \right]^3 + \dots$$

one sees

$$B_2(T) = -b_2 \lambda^3$$

Expanding to higher orders, one finds

$$B_3 = \lambda^6(4b_2^2 - 2b_3), \quad \dots$$

Computation of coefficients. Expanding the coefficients gives

$$\begin{aligned} B_2(T) &= -b_2 \lambda^3 = -\frac{U_2}{2V} = -\frac{1}{2V} \int d\mathbf{q}_1 d\mathbf{q}_2 f(q_{12}) = -\frac{1}{2V} \int d\mathbf{q} \int d\mathbf{k} f_{12}(k) \\ &= -\frac{1}{2} \int d\mathbf{k} f_{12}(k) = -\frac{1}{2} \int d\mathbf{k} [e^{-\beta U(k)} - 1] \end{aligned}$$

where one sets

$$q = q_1 + q_2, \quad k = q_1 - q_2$$

Using the potential

$$U(r) = \begin{cases} \infty, & r \leq r_0 \\ -U_0 \left[\frac{r_0}{r} \right]^6, & r > r_0 \end{cases}$$

one sees

$$\begin{aligned} \int d\mathbf{r} [e^{-\beta U(r)} - 1] &= 4\pi \int_0^\infty r^2 dr [e^{-\beta U(r)} - 1] \\ &= 4\pi \int_0^{r_0} r^2 dr (-1) + 4\pi \int_{r_0}^\infty r^2 dr [e^{-\beta U(r)} - 1] \\ &\sim -\frac{4}{3}\pi r_0^3 - 4\pi \int_{r_0}^\infty r^2 dr \beta U(r) = -\frac{4}{3}\pi r_0^3 + 4\pi \int_{r_0}^\infty r^2 dr \beta U_0 \left[\frac{r_0}{r} \right]^6 \\ &= -\frac{4}{3}\pi r_0^3 + \frac{4}{3}\pi \beta U_0 r_0^3 = \frac{4}{3}\pi r_0^3 \left[\frac{U_0}{kT} - 1 \right] \end{aligned}$$

At the third line, one recalls the high temperature condition $\beta \ll 1$ inside the second integral and expands the exponential noting that the potential is not problematic in the region $r > r_0$. Therefore, the coefficient is

$$B_2(T) = - \left[\frac{a}{kT} - b \right], \quad a = \frac{2\pi}{3} r_0^3 U_0, \quad b = \frac{2\pi}{3} r_0^3$$

the two parameters contain information about the potential, in particular about the hard repulsion. Thus, the virial expansion at the first non-trivial order reads

$$\begin{aligned} \frac{p}{kT} &= \frac{N}{V} - \left[\frac{N}{V} \right]^2 \left[\frac{a}{kT} - b \right] = \frac{N}{V} \left[1 + b \frac{N}{V} \right] - \frac{a}{kT} \left[\frac{N}{V} \right]^2 \\ &= \frac{N}{V} \left[\frac{1}{1 - b \frac{N}{V}} \right] - \frac{a}{kT} \left[\frac{N}{V} \right]^2 + o(N^2/V^2) \approx \frac{N}{V - bN} - \frac{a}{kT} \left[\frac{N}{V} \right]^2 \end{aligned}$$

where at the second line one has used the geometric series

$$1 + x \approx \frac{1}{1 - x}, \quad x \ll 1$$

So, at order $(N/V)^2$, the average pressure is

$$p = \frac{kTN}{V - bN} - a \left[\frac{N}{V} \right]^2$$

The parameter b reduces the volume V due to the volume of each particle (i.e. the repulsion). The parameter a reduces the pressure due to the long-range interaction (i.e. U_0) weighted by $(N/V)^2$ which is approximately the number of interaction pairs. The equation can also be rewritten as the van der Waals equation

$$kT = \left[p + a \left(\frac{N}{V} \right)^2 \right] \left[\frac{V}{N} - b \right]$$

This is the first correction to the ideal gas law which is a qualitative description of the phase transition from gas to liquid [r].

Remark. The cluster expansion is very general. It applies to any interaction with asymptotic behavior

$$U(r) \sim \frac{1}{r^n}, \quad n \geq 4$$

The number 4 is specific to three spatial dimensions and can be read from the convergence of the integrals above.

Lecture 7

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3 Ideal quantum gas

See Tong, SP, §§3.1, 3.5, 3.6. Consider the ideal gas without long-range interactions, but in the case where quantum effects are relevant

$$\frac{V}{N} \approx \lambda^3$$

To use the canonical ensemble, one needs to compute the partition function Z by summing over all compatible micro-states of the system.

Assume the system has energy levels $|k\rangle$ with eigenvalues E_k . To specify a micro-state, one has to give the set of occupation numbers $\{n_k\}$ of each energy level, i.e. the number of particles in each level. For fermions, the possible values of the occupation number are just two $n_k = 0, 1$ due to the Pauli exclusion principle while bosons can appear in any quantity $n_k \in \mathbb{N}_0$. The total number of particles and the total energy is then

$$N = \sum_k n_k, \quad E = \sum_k n_k E_k$$

So the partition function is

$$Z(T, V, N) = \sum_{\substack{\{n_k\} \\ \text{constraint}}} \exp \left[-\beta \sum_k n_k E_k \right]$$

where the sum is over all possible sets $\{n_k\}$ that obey the constraint that their sum is N . To remove the constraint, one utilizes the gran-canonical partition function

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \sum_{N=0}^{\infty} z^N Z(T, V, N) = \sum_{N=0}^{\infty} z^{\sum_k n_k} \sum_{\substack{\{n_k\} \\ \text{constraint}}} e^{-\beta \sum_k n_k E_k} \\ &= \sum_{N=0}^{\infty} \sum_{\substack{\{n_k\} \\ \text{constraint}}} \exp \left[-\beta \sum_k n_k (E_k - \mu) \right], \quad z = e^{\beta \mu} \\ &= \sum_{\{n_k\}} \prod_k e^{-\beta n_k (E_k - \mu)} = \prod_k \sum_{n_k} e^{-\beta (E_k - \mu) n_k} = \prod_k \mathcal{Z}_k \end{aligned}$$

where \mathcal{Z}_k is the single-level gran-canonical partition function. This is similar to what happens in the classical ideal gas where the canonical partition function factorizes into single-particle partition functions

$$Z(T, V, N) = (Z_1)^N$$

The ideal quantum gas partition function does not factorize into single-particle partition functions because the gas inherently has an interaction, but which differs from the classical long-range interaction. The gran-canonical potential is

$$\Phi = -kT \ln \mathcal{Z}(T, V, \mu) = -kT \sum_k \ln \left[\sum_{n_k} e^{\beta(\mu - E_k)n_k} \right]$$

For bosons, the inner summation is

$$\sum_{n_k=0}^{\infty} e^{\beta(\mu - E_k)n_k} = \frac{1}{1 - e^{\beta(\mu - E_k)}}$$

Assuming that the ground state has energy $E_0 = 0$, the radius of convergence of the geometric series requires

$$|e^{\beta(\mu - E_k)}| < 1 \implies \boxed{\mu < 0}$$

This property of the chemical potential is also true classically. For fermions, the sum has two terms

$$\sum_{n_k=0}^1 e^{\beta(\mu - E_k)n_k} = 1 + e^{\beta(\mu - E_k)}$$

Therefore, the gran-canonical potential is

$$\Phi = -kT \left[\pm \sum_k \ln(1 \pm e^{\beta(\mu - E_k)}) \right]$$

where the $+$ sign is for fermions, while the $-$ sign is for bosons.

The average number of particles is then

$$\langle N \rangle = \frac{1}{\beta} \partial_\mu \ln \mathcal{Z}(T, V, \mu) = -\partial_\mu \Phi = \sum_k \frac{e^{\beta(\mu - E_k)}}{1 \pm e^{\beta(\mu - E_k)}} = \sum_k \frac{1}{e^{-\beta(\mu - E_k)} \pm 1} = \sum_k \langle n_k \rangle$$

From this one reads the fermions' Fermi–Dirac distribution

$$\langle n_k \rangle = \frac{1}{e^{-\beta(\mu - E_k)} + 1}$$

and the bosons' Bose–Einstein distribution

$$\langle n_k \rangle = \frac{1}{e^{-\beta(\mu - E_k)} - 1}$$

At high temperatures $\beta \ll 1$, one expects that the two distributions tend to the Boltzmann distribution due to a lower density. However, one cannot simply expand the exponential because the chemical potential has a non-trivial dependence on the temperature T . Since one is interested in the high temperature limit, one may use the result of the ideal gas and suppose that its leading contribution is the same as in a regime not quite in such limit. Recall that in the ideal gas ($T \rightarrow \infty$) in the canonical ensemble, from the fugacity one has found

$$\frac{\mu}{kT} = \ln \frac{\lambda^3 N}{V} \sim -\frac{3}{2} \ln T$$

or equivalently

$$z = e^{\beta\mu} = \lambda^3 \frac{N}{V} \ll 1, \quad T \rightarrow \infty$$

this limit can be equivalently expressed as $z \rightarrow 0$. Therefore, the two distributions behave as

$$[e^{-\beta(\mu-E_k)} \pm 1]^{-1} = \left[\frac{e^{\beta E_k}}{z} \pm 1 \right]^{-1} \sim z e^{-\beta E_k}, \quad z \rightarrow 0$$

where one recognizes the Boltzmann distribution.

In the high temperature limit, the information about the statistics is lost. One would like to study both high temperatures and corrections to infinite temperature. One looks at the virial expansion of the ideal gas. One would like also to study the low temperature regime. Finally, one obtains a master set of equations from which one can study the behaviour of the quantum gas in either low or high temperatures.

3.1 Equations of state

In the following, one approximates sums with integrals since they are easier to evaluate. Consider a gas in a very large cubic box of volume $V = L^3$. The energy eigenstate of a non-interacting particle is

$$\psi = \frac{1}{\sqrt{V}} e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{x}}$$

where the momentum is quantized

$$p_i = \frac{2\pi\hbar}{L} n_i, \quad n_i \in \mathbb{Z}$$

The sum over the energy levels can be approximated as

$$\sum_{\mathbf{n}} \approx \int d^3n = \frac{V}{(2\pi\hbar)^3} \int d^3p = \frac{V}{(2\pi\hbar)^3} 4\pi \int_0^\infty p^2 dp \equiv \int dE g(E)$$

where the density of states $g(E)$ is the number of states with energy in the interval $[E, E + dE]$ which takes the form of

$$g(E) = \frac{V}{2\pi^2\hbar^3} p^2(E) \frac{dp}{dE}$$

The momentum $p(E)$ is given by the dispersion relation. In the non-relativistic case, one has

$$E = \frac{p^2}{2m} \implies p = \sqrt{2mE}, \quad dp = \sqrt{\frac{m}{2E}} dE$$

so the density of states is

$$g(E) = \frac{gV}{2\pi^2\hbar^3} m \sqrt{2mE} \sim \sqrt{E}$$

where g is the g -factor related to the spin magnetic moment and intrinsic angular momentum. In the relativistic case, the dispersion relation is Einstein's

$$E^2 = m^2 c^4 + p^2 c^2 \implies p^2 c^2 = E^2 - m^2 c^4 \implies 2pc^2 dp = 2E dE$$

from which the density is

$$g(E) = \frac{gV}{2\pi^2\hbar^3 c^3} \sqrt{E^2 - m^2 c^4} E$$

In the massless and ultra-relativistic cases, the behaviour of the density is $g(E) \sim E^2$.

Pressure. The average pressure can be computed from the gran-canonical potential

$$\begin{aligned} pV = -\Phi &= \pm kT \sum_k \ln(1 \pm e^{\beta(\mu-E_k)}) \approx \frac{\pm kT gV m \sqrt{2m}}{2\pi^2\hbar^3} \int_0^\infty dE \sqrt{E} \ln(1 \pm z e^{-\beta E}) \\ &= \frac{\pm kT gV m \sqrt{2m}}{2\pi^2\hbar^3} (kT)^{\frac{3}{2}} \int_0^\infty dx \sqrt{x} \ln(1 \pm z e^{-x}), \quad x \equiv \beta E \\ &= \frac{(kT)^{\frac{5}{2}}}{2\pi^2\hbar^3} gV m \sqrt{2m} \frac{2}{3} \int_0^\infty \frac{x^{\frac{3}{2}} z e^{-x}}{1 \pm z e^{-x}} = \frac{4kTV}{3\lambda^3} \frac{g}{\sqrt{\pi}} \int_0^\infty dx \frac{x^{\frac{3}{2}}}{(e^x/z) \pm 1} \\ &= \mp \frac{gkTV}{\lambda^3} \text{Li}_{\frac{5}{2}}(\mp z) \end{aligned}$$

Only at the last line, the $-$ sign is for fermions while the $+$ sign is for bosons. At the first line one approximates the sum with an integral

$$\sum_k \approx \int dE g(E)$$

At the third line one has integrated by parts deriving the logarithm and integrating the square root: the boundary term vanishes. At the last line, one uses an integral representation of the polylogarithm function.

Polylogarithm and Gamma functions. The polylogarithm is defined by the series

$$\text{Li}_s(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^s}$$

convergent in $|z| < 1$, which can be analytically continued through the integrals

$$\text{Li}_s(z) = \frac{1}{\Gamma(s)} \int_0^{\infty} dt \frac{t^{s-1}}{(e^t/z) - 1}, \quad \text{Li}_s(-z) = -\frac{1}{\Gamma(s)} \int_0^{\infty} dt \frac{t^{s-1}}{(e^t/z) + 1}$$

with domains of convergence, in which it is also holomorphic, given respectively by

$$z \in \mathbb{C} \setminus [1, \infty), \quad z \in \mathbb{C} \setminus (-\infty, -1]$$

with both having $\text{Re } s > 0$. For $s = 1$ it reduces to the logarithm

$$\text{Li}_1(z) = \sum_{k=1}^{\infty} \frac{z^k}{k} = -\ln(1 - z)$$

The Euler Gamma function is defined by

$$\Gamma(z) = \int_0^{\infty} dt t^{z-1} e^{-t}, \quad \text{Re } z > 0$$

On the natural numbers it reduces to the factorial

$$k \in \mathbb{N} \implies \Gamma(k+1) = k!$$

A few important values are

$$\Gamma(1/2) = \sqrt{\pi}, \quad \Gamma(3/2) = \frac{1}{2}\sqrt{\pi}, \quad \Gamma(5/2) = \frac{3}{4}\sqrt{\pi}$$

Number of particles. The average number of particles is

$$\begin{aligned} N = \sum_k n_k &\approx \int_0^{\infty} dE g(E) n(E) = \frac{gVm\sqrt{2m}}{2\pi^2\hbar^3} \int_0^{\infty} dE \frac{\sqrt{E}}{(e^{\beta E}/z) \pm 1} \\ &= \frac{gVm\sqrt{2m}}{2\pi^2\hbar^3} (kT)^{\frac{3}{2}} \int_0^{\infty} dx \frac{x^{\frac{1}{2}}}{(e^x/z) \pm 1}, \quad x \equiv \beta E \\ &= \mp \frac{gV}{\lambda^3} \text{Li}_{\frac{3}{2}}(\mp z) \end{aligned}$$

Energy. The average energy is

$$E = \sum_k n_k E_k \approx \int_0^{\infty} dE g(E) n(E) E = \frac{gVm\sqrt{2m}}{2\pi^2\hbar^3} \int_0^{\infty} dE \frac{E^{\frac{3}{2}}}{(e^{\beta E}/z) \pm 1} = \mp \frac{3}{2} \frac{gV}{\lambda^3} kT \text{Li}_{\frac{5}{2}}(\mp z)$$

Summary. For a non-relativistic quantum gas, the observables are

$$\begin{aligned}\frac{p}{kT} &= \mp \frac{g}{\lambda^3} \text{Li}_{\frac{5}{2}}(\mp z) \\ \frac{E}{kT} &= \mp \frac{3}{2} \frac{gV}{\lambda^3} \text{Li}_{\frac{5}{2}}(\mp z) \\ \frac{N}{V} &= \mp \frac{g}{\lambda^3} \text{Li}_{\frac{3}{2}}(\mp z)\end{aligned}$$

where the $-$ sign is for fermions while the $+$ sign is for bosons.

From the first two equations one finds

$$\boxed{pV = \frac{2}{3}E}$$

which is also true for the classical ideal gas. In fact, in the classical case, one has

$$E = \frac{3}{2}NkT, \quad pV = NkT \implies pV = \frac{2}{3}E$$

For an ultra-relativistic quantum gas, one finds instead

$$g(E) \sim E^2 \implies pV = \frac{1}{3}E$$

3.2 High temperatures

For a classical ideal gas, $T \rightarrow \infty$, one has

$$z = \lambda^3 \frac{N}{V} \ll 1$$

So one would like to study the equations of state for small values of the fugacity $|z| < 1$. One may utilize the series definition of the polylogarithm. For example, at second order one sees

$$\begin{aligned}\frac{p}{kT} &= \mp \frac{g}{\lambda^3} \left[\mp z + \frac{z^2}{2^{\frac{5}{2}}} + \dots \right] \\ \frac{N}{V} &= \mp \frac{g}{\lambda^3} \left[\mp z + \frac{z^2}{2^{\frac{3}{2}}} + \dots \right]\end{aligned}$$

From the second equation, one finds

$$z = \frac{\lambda^3 N}{gV} \pm \frac{1}{2^{\frac{3}{2}}} z^2 \approx \frac{\lambda^3 N}{gV} \pm \frac{1}{2^{\frac{3}{2}}} \left[\frac{\lambda^3 N}{gV} \right]^2$$

This is the result of the ideal gas plus a correction. This expression can be inserted into the first equation to have

$$\frac{p}{kT} = \frac{g}{\lambda^3} \left[\frac{\lambda^3 N}{gV} \pm \frac{1}{2^{\frac{3}{2}}} \left(\frac{\lambda^3 N}{gV} \right)^2 \right] \mp \frac{g}{\lambda^3 2^{\frac{5}{2}}} \left(\frac{\lambda^3 N}{gV} \right)^2 = \frac{N}{V} \pm \left[\frac{N}{V} \right]^2 \frac{\lambda^3}{2^{\frac{5}{2}} g} + o(N^2/V^2)$$

again this is the ideal gas plus a correction. From this one reads the first virial coefficient

$$B_2(T) = \pm \frac{\lambda^3}{2^{\frac{5}{2}} g}$$

The correction is proportional to

$$\frac{N}{V} \lambda^3 \ll 1$$

which is small. The fermions have a $+$ sign due to the Pauli exclusion principle: by confining the particles, the pressure rises quicker. On the other hand, bosons have a $-$ sign since they do not exhibit such behaviour. Both types of particles are similar in the classical limit. However, at low temperatures the behaviour is very different.

Lecture 8

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3.3 Low temperatures

For bosons, one has $\mu < 0$ and the low temperature limit corresponds to

$$z = e^{\beta\mu} \rightarrow 1$$

For fermions, one has $z \in \mathbb{R}^+$ and the limit corresponds to $z \rightarrow \infty$.

3.3.1 Degenerate Fermi gas

See Tong, SP, §3.6.2. The average occupation number for the Fermi–Dirac distribution is

$$\langle n_E \rangle = \frac{1}{e^{\beta(E-\mu)} + 1} \rightarrow \begin{cases} 1, & E < \mu \\ 0, & E > \mu \end{cases}$$

In the low temperature limit, all the particles are located below a minimum energy called Fermi energy

$$E_F = \mu(0)$$

This energy can be computed from the average number of particles at zero temperature

$$\begin{aligned} N &= \int_0^\infty dE g(E) n(E) = \int_0^\infty dE \frac{g(E)}{e^{\beta(E-\mu)} + 1} \rightarrow \int_0^{E_F} dE g(E) \\ &= \frac{gV m \sqrt{2m}}{2\pi^2 \hbar^3} \int_0^{E_F} dE \sqrt{E} = \frac{gV m \sqrt{2m}}{3\pi^2 \hbar^3} (E_F)^{\frac{3}{2}} \end{aligned}$$

from which

$$E_F = \frac{\hbar^2}{2m} \left[\frac{6\pi^2 N}{g V} \right]^{\frac{2}{3}} = \frac{\lambda^2}{4\pi} kT \left[\frac{6\pi^2 N}{g V} \right]^{\frac{2}{3}}$$

One may define the Fermi temperature

$$T_F = \frac{E_F}{k}$$

It is the temperature below which the effects due to the fermions' statistics become relevant. For the electrons in a metal it is $T_F \sim 10^4$ K, while in a white dwarf it is $T_F \sim 10^7$ K.

The average energy is

$$\langle E \rangle = \int_0^\infty dE \frac{g(E) E}{e^{\beta(E-\mu)} + 1} \rightarrow K \int_0^{E_F} dE \sqrt{E} E = K \frac{2}{5} E_F^{\frac{5}{2}}$$

where K is a constant, while the average number of particles is

$$\langle N \rangle = K \int_0^{E_F} dE \sqrt{E} = K \frac{2}{3} E_F^{\frac{3}{2}}$$

from which

$$\langle E \rangle = \frac{3}{5} E_F \langle N \rangle$$

For a non-relativistic quantum gas it holds

$$pV = \frac{2}{3} E = \frac{2}{5} E_F N$$

The pressure is non-zero even at zero temperature due to the fermionic statistics.

3.3.2 Low temperature Fermi gas and Sommerfeld expansion

See Tong, SP, §§3.6.3, 3.6.4. One may study what happens when the temperature T is low, but not zero. One expects a correction to the degenerate Fermi gas behaviour. One expects a quantity of active electrons of order $g(E_F)kT$. The distribution of occupation numbers differs from the one at $T = 0$ only for a short range of energies kT around E_F . See Tong, SP, fig. 22.

One therefore expects a quadratic correction to the energy of the degenerate case

$$\langle E \rangle = \frac{3}{5} E_F N + K g(E_F) (kT)^2 \sim T^2$$

where K is a constant. In the zero temperature limit, the fugacity is

$$z = e^{\beta\mu} \sim e^{\beta E_F} \rightarrow \infty$$

One needs to expand the polylogarithm $\text{Li}_s(z)$ for $z \rightarrow \infty$.

Sommerfeld expansion. To this end one utilizes the Sommerfeld expansion. Let

$$f_n(z) \equiv -\text{Li}_n(-z)$$

then

$$\begin{aligned} \Gamma(n)f_n(z) &= \int_0^\infty dx \frac{x^{n-1}}{(e^x/z) + 1} = \int_0^{\ln z} dx \frac{x^{n-1}}{(e^x/z) + 1} + \int_{\ln z}^\infty dx \frac{x^{n-1}}{(e^x/z) + 1} \\ &= \int_0^{\ln z} dx x^{n-1} - \int_0^{\ln z} dx \frac{x^{n-1}}{1 + ze^{-x}} + \int_{\ln z}^\infty dx \frac{x^{n-1}}{(e^x/z) + 1} \\ &= \frac{1}{n} \ln^n z - \int_0^{\ln z} du \frac{(\ln z - u)^{n-1}}{1 + e^u} + \int_0^\infty dv \frac{(\ln z + v)^{n-1}}{1 + e^v} \\ &\approx \frac{1}{n} \ln^n z - \int_0^\infty du \frac{(\ln z - u)^{n-1}}{1 + e^u} + \int_0^\infty dv \frac{(\ln z + v)^{n-1}}{1 + e^v} \\ &= \frac{1}{n} \ln^n z + \int_0^\infty dy \frac{(\ln z + y)^{n-1} - (\ln z - y)^{n-1}}{1 + e^y} \\ &= \frac{1}{n} \ln^n z + \int_0^\infty dy \frac{(\ln z)^{n-1}}{1 + e^y} \left[\left(1 + \frac{y}{\ln z}\right)^{n-1} - \left(1 - \frac{y}{\ln z}\right)^{n-1} \right] \\ &= \frac{1}{n} \ln^n z + \int_0^\infty dy \frac{(\ln z)^{n-1}}{1 + e^y} \left[1 + (n-1)\frac{y}{\ln z} - 1 + (n-1)\frac{y}{\ln z} + o(y/\ln z) \right] \\ &\sim \frac{1}{n} \ln^n z + \int_0^\infty dy 2(n-1) \frac{y}{1 + e^y} (\ln z)^{n-2} \\ &= \frac{1}{n} \ln^n z + 2(n-1)(\ln z)^{n-2} \int_0^\infty dy \frac{y}{1 + e^y} \\ &= \frac{1}{n} \ln^n z + \frac{\pi^2}{6} (n-1)(\ln z)^{n-2} \end{aligned}$$

At the second line, one has rewritten the first integrand as

$$\frac{x^{n-1}}{(e^x/z) + 1} = x^{n-1} \frac{ze^{-x}}{1 + ze^{-x}} = x^{n-1} \left[1 - \frac{1}{1 + ze^{-x}} \right]$$

At the third line, one has substituted in the second integral

$$e^u = ze^{-x}, \quad x = \ln z - u$$

and in the third integral

$$e^v = ez^{-1}, \quad x = \ln z + v$$

At the fourth line, the upper integration limit in the second integral is approximated with infinity since $\ln z \gg 1$. At the seventh line, one uses the binomial series to expand the argument of the bracket since

$$\frac{y}{\ln z} \ll 1$$

Therefore

$$f_n(z) \sim \frac{(\ln z)^n}{n\Gamma(n)} \left[1 + \frac{\pi^2}{6} \frac{n(n-1)}{(\ln z)^2} \right] = \frac{(\ln z)^n}{\Gamma(n+1)} \left[1 + \frac{\pi^2}{6} \frac{n(n-1)}{(\ln z)^2} \right], \quad z \rightarrow \infty$$

Equations of state. One may expand the equations of state for fermions

$$\frac{p}{kT} = \frac{g}{\lambda^3} f_{\frac{5}{2}}(z), \quad \frac{N}{V} = \frac{g}{\lambda^3} f_{\frac{3}{2}}(z), \quad pV = \frac{2}{3}E$$

The density is

$$\frac{N}{V} = \frac{g}{\lambda^3} f_{\frac{3}{2}}(z) \sim \frac{g}{\lambda^3} \frac{(\ln z)^{\frac{3}{2}}}{\frac{3}{4}\sqrt{\pi}} \left[1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2} \right]$$

from which one may extract

$$(\ln z)^{\frac{3}{2}} \sim \frac{3}{4} \frac{\sqrt{\pi}\lambda^3}{g} \frac{N}{V} \left[1 - \frac{\pi^2}{8} \frac{1}{(\ln z)^2} \right] = \left[\frac{E_F}{kT} \right]^{\frac{3}{2}} \left[1 - \frac{\pi^2}{8} \frac{1}{(\ln z)^2} \right]$$

and find

$$\ln z \sim \frac{E_F}{kT} \left[1 - \frac{\pi^2}{8} \frac{1}{(\ln z)^2} \right]^{\frac{2}{3}} \sim \frac{E_F}{kT} \left[1 - \frac{\pi^2}{12} \frac{1}{(\ln z)^2} \right] \sim \frac{E_F}{kT} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 \right]$$

From this, the chemical potential is

$$\mu(T) = \frac{1}{\beta} \ln z = kT \ln z \sim E_F \left[1 - \frac{\pi^2}{12} \frac{1}{(\ln z)^2} \right] \sim E_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 \right]$$

one notices that the deviation from the degenerate Fermi gas is quadratic in the temperature. Recalling

$$pV = \frac{2}{3}E$$

the energy is

$$\begin{aligned} \frac{E}{N} &= \frac{3}{2} kT \frac{f_{\frac{5}{2}}(z)}{f_{\frac{3}{2}}(z)} \sim \frac{3}{2} kT \frac{(\ln z)^{\frac{5}{2}}}{(\ln z)^{\frac{3}{2}}} \frac{\Gamma(5/2)}{\Gamma(7/2)} \frac{1 + \frac{\pi^2}{6} \frac{1}{(\ln z)^2} \frac{15}{4}}{1 + \frac{\pi^2}{6} \frac{1}{(\ln z)^2} \frac{3}{4}} \\ &\sim \frac{3}{2} kT (\ln z)^{\frac{2}{5}} \left[1 + \frac{\pi^2}{6} \frac{1}{(\ln z)^2} \left(\frac{15}{4} - \frac{3}{4} \right) \right] = \frac{3}{5} kT \ln z \left[1 + \frac{\pi^2}{2} \frac{1}{(\ln z)^2} \right] \\ &\sim \frac{3}{5} E_F \left[1 + \frac{\pi^2}{2} \left(\frac{kT}{E_F} \right)^2 \right] \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 \right] \sim \frac{3}{5} E_F \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 \right] \end{aligned}$$

At the second line, one uses the binomial series to expand

$$(1+x)^{-1} \sim 1-x, \quad x \ll 1$$

At the third line, one has inserted the expression for $\ln z$.

From this, the heat capacity is

$$C = d_T E \sim Nk \frac{T}{T_F} \sim T$$

In a material at low temperature, the heat capacity

$$C = \alpha T + \beta T^3$$

gets contributions from the electron gas and the phonons, i.e. the vibrations of the material's lattice.

3.3.3 Bose–Einstein condensate

See Tong, SP, §3.5.3. Remember that for bosons it holds

$$\sum_{n_k} e^{\beta(\mu - E_k)n_k} = \frac{1}{1 - e^{\beta(\mu - E_k)}}$$

from which

$$\mu < 0 \implies z \in (0, 1)$$

At low temperatures T one has $z \rightarrow 1$. The equations of state are

$$\frac{p}{kT} = \frac{g}{\lambda^3} \text{Li}_{\frac{5}{2}}(z), \quad \frac{N}{V} = \frac{g}{\lambda^3} \text{Li}_{\frac{3}{2}}(z), \quad pV = \frac{2}{3}E$$

Notice that the polylogarithm is a monotonous function of z . Moreover, at $z = 1$ it is equal to the Riemann zeta function

$$\text{Li}_n(1) = \zeta(n)$$

For this section, it is useful to know that $\zeta(3/2) \approx 2.612$. Noting that

$$\lambda \sim \frac{1}{\sqrt{T}}$$

from the equation of state of the number of particles, one finds

$$\frac{N}{V} \sim T^{\frac{3}{2}} \text{Li}_{\frac{3}{2}}(z)$$

By keeping the density fixed, as the temperature T lowers, the fugacity z grows and so does the polylogarithm. When the fugacity reaches $z = 1$, the equation no longer makes sense. There is a problem: this is the hint of a new behaviour. Let the critical temperature T_c be the temperature at $z = 1$, then

$$\frac{N}{gV} = \frac{1}{\lambda^3(T_c)} \text{Li}_{\frac{3}{2}}(1) = \left[\frac{mkT_c}{2\pi} \right]^{\frac{3}{2}} \frac{1}{h^3} \text{Li}_{\frac{3}{2}}(1)$$

where one finds the temperature

$$T_c = \frac{2\pi\hbar^2}{mk} \left[\frac{N}{gV \text{Li}_{\frac{3}{2}}(1)} \right]^{\frac{2}{3}}$$

For temperatures lower than T_c , from the equation of state of the density N/V , one finds that the number of particles should decrease, but this cannot happen. The problem lies in the approximation of the sum over the energy states with an integral

$$\sum_k \rightarrow \int dE g(E)$$

The energy density goes like $g(E) \sim \sqrt{E}$: the contribution from the ground state is missing⁶. To solve the problem, one adds by hand such contribution

$$N = \frac{gV}{\lambda^3} \text{Li}_{\frac{3}{2}}(z) + \langle n_0 \rangle, \quad \langle n_0 \rangle = \frac{z}{1 - z}$$

For $T \rightarrow 0$, one has $z \rightarrow 1$ and $\langle n_0 \rangle \rightarrow \infty$. More precisely, the behaviour of the fugacity is

$$z \sim 1 - \frac{1}{N}$$

and so it approaches 1 in the thermodynamic limit $N \rightarrow \infty$. From the equation above, the average occupation number of the ground state is

$$\frac{\lambda^3}{gV} \langle n_0 \rangle = \frac{\lambda^3}{gV} N - \text{Li}_{\frac{3}{2}}(z)$$

⁶Notice that the energy of the ground state is conventionally set to $E_0 = 0$.

It is positive when

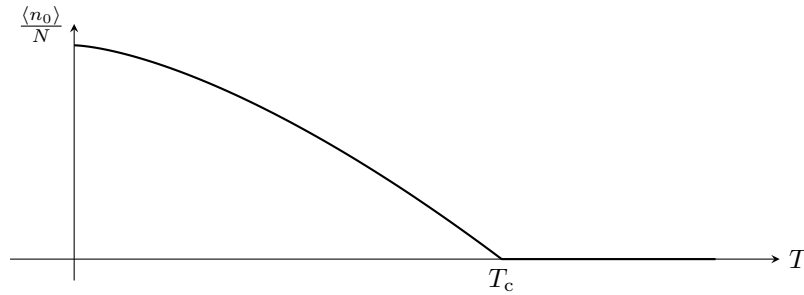
$$\frac{\lambda^3}{gV}N > \text{Li}_{\frac{3}{2}}(1) = \frac{\lambda^3(T_c)}{gV}N \implies \lambda^3 > \lambda^3(T_c) \implies T < T_c$$

For $T < T_c$, the relative occupation number of the ground state is

$$\frac{\langle n_0 \rangle}{N} = 1 - \frac{gV}{\lambda^3 N} \text{Li}_{\frac{3}{2}}(z) \sim 1 - \frac{gV}{\lambda^3 N} \text{Li}_{\frac{3}{2}}(1) = 1 - \frac{\lambda^3(T_c)}{\lambda^3(T)} = 1 - \left[\frac{T}{T_c} \right]^{\frac{3}{2}}, \quad z \rightarrow 1$$

Below the critical temperature T_c , a macroscopic number of particles join in the ground state to form the Bose–Einstein condensate.

The graph of the relative occupation number of the ground state as a function of the temperature has a discontinuity in the derivative at $T = T_c$ which is indicative of a phase transition. The order of a phase transition is related to the order of the discontinuous derivative.



The first observation of a Bose–Einstein condensate was made at a critical temperature of about $T_c \sim 10^{-7}$ K.

Lecture 9

Dependence of the fugacity on the temperature. See Tong, SP, §3.5.4. From the corrected equation of the average number of particles

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$$\frac{N}{gV} \lambda^3 = \text{Li}_{\frac{3}{2}}(z) + \frac{\lambda^3}{gV} \frac{z}{1-z}$$

one may numerically find the fugacity $z(T)$ as a function of the temperature T . It is a smooth solution. One may also find the fugacity $z(T)$ in the thermodynamic limit $N, V \rightarrow \infty$.

One may start with the first objective. From the equation above one may subtract $\text{Li}_{\frac{3}{2}}(1)$ on both sides to have

$$\frac{N}{gV} \lambda^3 - \frac{N}{gV} \lambda_c^3 = \frac{\lambda^3}{gV} \frac{z}{1-z} + \text{Li}_{\frac{3}{2}}(z) - \text{Li}_{\frac{3}{2}}(1)$$

recalling that the definition of T_c is

$$\frac{N}{gV} \lambda_c^3 = \text{Li}_{\frac{3}{2}}(1)$$

Consider the last two addenda in the limit $z \rightarrow 1$. From the series definition, one notices that

$$z \, d_z \text{Li}_n(z) = \text{Li}_{n-1}(z)$$

which can be inserted in the Taylor expansion of the polylogarithm

$$\text{Li}_{\frac{3}{2}}(z) = \text{Li}_{\frac{3}{2}}(1) + (z-1) [d_z \text{Li}_{\frac{3}{2}}(z)]_{z=1} = \text{Li}_{\frac{3}{2}}(1) + (z-1) \left[\frac{1}{z} \text{Li}_{\frac{1}{2}}(z) \right]_{z=1}$$

However, the polylogarithm in the bracket diverges at $z = 1$, so one needs to study this divergence. From the integral representation one has

$$\begin{aligned}\text{Li}_{\frac{1}{2}}(z) &= \frac{1}{\Gamma(1/2)} \int_0^\infty dx \frac{x^{-\frac{1}{2}}}{(e^x/z) - 1} \sim \frac{1}{\Gamma(1/2)} \int_0^\varepsilon dx \frac{x^{-\frac{1}{2}}}{(1+x)z^{-1} - 1}, \quad z \rightarrow 1 \\ &= \frac{z}{\Gamma(1/2)} \int_0^\varepsilon dx \frac{x^{-\frac{1}{2}}}{1+x-z} \sim \frac{2z}{\sqrt{1-z}} \frac{1}{\Gamma(1/2)} \int_0^\varepsilon \frac{du}{1+u^2}, \quad u \equiv \sqrt{\frac{x}{1-z}} \\ &= c \frac{z}{\sqrt{1-z}}\end{aligned}$$

where c is a constant. Therefore

$$\text{Li}_{\frac{3}{2}}(z) = \text{Li}_{\frac{3}{2}}(1) + c \frac{z-1}{z} \frac{z}{\sqrt{1-z}} = \text{Li}_{\frac{3}{2}}(1) - c\sqrt{1-z}$$

Thus the equation of interest is

$$\frac{N}{gV}(\lambda^3 - \lambda_c^3) = \frac{\lambda^3}{gV} \frac{z}{1-z} + \text{Li}_{\frac{3}{2}}(z) - \text{Li}_{\frac{3}{2}}(1) = \frac{\lambda^3}{gV} \frac{z}{1-z} - c\sqrt{1-z}$$

which can be written in an equivalent form

$$\boxed{A(T^{-\frac{3}{2}} - T_c^{-\frac{3}{2}}) = \frac{B}{V} \frac{z}{1-z} - c\sqrt{1-z}}$$

with $A, B, c > 0$ constants [r] but B depends on T through λ ?. Solving numerically this equation, one finds the fugacity as function of the temperature $z = z(T)$ and it is a smooth function, of class C^∞ .

The second objective, $N, V \rightarrow \infty$, has two cases

- Let $T > T_c$. The left-hand side of the above equation is negative, so one can drop the first addendum on the right-hand side for $V \rightarrow \infty$. This gives

$$A(T^{-\frac{3}{2}} - T_c^{-\frac{3}{2}}) = -c\sqrt{1-z} \implies A \frac{3}{2} \frac{T - T_c}{T_c^{\frac{5}{2}}} = c\sqrt{1-z}$$

where one has expanded the parenthesis in a Taylor series and considered the linear order. From this one obtains

$$1 - z \sim \alpha(T - T_c)^2 \implies z \sim 1 - \alpha(T - T_c)^2$$

Its first two derivatives are

$$d_T z = -2\alpha(T - T_c), \quad d_T^2 z = -2\alpha \neq 0$$

- Let $T < T_c$. The left-hand side is positive. The first addendum on the right-hand side cannot be ignored since it diverges for $z \rightarrow 1$. Both derivatives are zero since $z \sim 1$.

Therefore, in the thermodynamic limit, the fugacity z and its first derivative are continuous at the critical temperature $T = T_c$, but the second derivative $d_T^2 z$ is discontinuous. The pressure behaves as

$$p = \frac{kT}{\lambda^3} g \text{Li}_{\frac{5}{2}}(z) \sim \frac{kT}{\lambda^3} g \text{Li}_{\frac{5}{2}}(1) \sim T^{\frac{5}{2}}$$

The pressure does not depend on the density. The energy is

$$E = \frac{3}{2} p V = \frac{3}{2} \frac{kT}{\lambda^3} g V \text{Li}_{\frac{5}{2}}(z)$$

while the heat capacity is

$$C = d_T E = \frac{3}{2} \frac{kgV}{\lambda^3} \text{Li}_{\frac{5}{2}}(z) + \frac{3}{2} \frac{kTgV}{\lambda^3} d_z \text{Li}_{\frac{5}{2}}(z) d_T z$$

recalling that the de Broglie wavelength depends on the temperature. For $T < T_c$, the derivative is $d_T z = 0$ and the heat capacity is

$$C = \frac{15}{4} \frac{kgV}{\lambda^3} \text{Li}_{\frac{5}{2}}(1) \sim c_1 T^{\frac{3}{2}}$$

while for $T > T_c$, the derivative is $d_T z = -2\alpha(T - T_c)$ and the heat capacity is

$$C = \frac{15}{4} \frac{kgV}{\lambda^3} \text{Li}_{\frac{5}{2}}(1) - c_2(T - T_c) \sim c_1 T^{\frac{3}{2}} - c_2(T - T_c)$$

The heat capacity as a function of the temperature T increases to a maximum at T_c where its derivative is discontinuous and then decreases to

$$C = \frac{3}{2} Nk$$

See Tong, SP, fig. 20. The discontinuity in the derivative of the heat capacity is a sign of a phase transition. Notice that the discontinuity appears only in the thermodynamic limit: phase transitions with their associated discontinuities can only arise in strictly infinite systems. There are no phase transitions in finite systems.

Pressure and ground state correction. The ground state does not contribute to the pressure. Recall that the pressure is

$$p = -\frac{kT}{V} \sum_k \ln(1 - ze^{-\beta E_k}) \approx -\frac{kT}{V} \int dE g(E) \ln(1 - ze^{-\beta E_k})$$

One may add the contribution from the ground state

$$-\frac{kT}{V} \ln(1 - z)$$

but in the thermodynamic limit, $N, V \rightarrow \infty$, it is suppressed. In fact, knowing

$$z \sim 1 - \frac{1}{N} \iff \frac{1}{1 - z} \sim N \sim V, \quad z \rightarrow 1$$

one finds

$$-\frac{kT}{V} \ln(1 - z) \sim \frac{kT}{V} \ln V \rightarrow 0, \quad V \rightarrow \infty$$

3.4 Photon gas

See Tong, SP, §3.2. Photons are massless spin-one particles. Their g -factor is $g = 2$ since there are two physical polarizations. There are no self-interactions, so photons constitute an ideal gas. A few initial observations are

- The equilibrium distribution is due to the interaction of the photons with the boundary of the cavity where the gas is contained.
- The total number of photons N is not conserved.
- Photons are massless, so the gas has an ultra-relativistic dispersion relation

$$\frac{gV}{2\pi^2 \hbar^3} p^2 dp = \frac{gV}{2\pi^2 \hbar^3} \frac{E^2}{c^3} dE = g(E) dE = \frac{V}{\pi^2 c^3} \omega^2 d\omega = g(\omega) d\omega$$

where at the second equality one has inserted $E = pc$ and at the third $E = \hbar\omega$.

Since the total number of photons is not conserved, one may calculate again the canonical partition function

$$Z = \sum_{\{n_k\}} \exp \left[-\beta \sum_k n_k E_k \right]$$

where the set $\{n_k\}$ does not have the restriction that the sum of its elements has to be N . From the partition function one may compute the pressure and the energy (or use the results of the boson gas with $\mu = 0$)

$$pV = -kT \sum_k \ln(1 - e^{\beta(\mu - E_k)}), \quad E = \sum_k \frac{E_k}{e^{-\beta(\mu - E_k)} - 1}$$

Average energy. Approximating the sum with an integral

$$\sum_k \approx \int d\omega g(\omega)$$

The average energy is

$$\begin{aligned} \langle E \rangle &= \int_0^\infty d\omega g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \\ &= \frac{V\hbar}{\pi^2 c^3} \frac{1}{(\beta\hbar)^4} \int_0^\infty dx \frac{x^3}{e^x - 1} = (kT)^4 \frac{V\pi^2}{15c^3\hbar^3}, \quad x = \beta\hbar\omega \end{aligned}$$

The integrand in the first line is the Planck distribution, that is the probability that the energy ω is in the interval $[\omega, \omega + d\omega]$

$$P_{\text{Planck}}(\omega) = E(\omega) d\omega = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

Its graph is the typical black-body radiation graph. The peak is given by Wien's displacement law

$$\omega_{\text{peak}} = 2.8 \frac{kT}{\hbar}$$

The numerical constant is the non-trivial solution to

$$3 - x = 3e^{-x} \implies x = W(-3/e^3) + 3 \approx 2.82144$$

where $W(x)$ is the Lambert W function. From the above law, one sees that the peak wavelength is longer for a cooler gas.

Average pressure. The average pressure

$$\begin{aligned} p &= -\frac{kT}{V} \int_0^\infty d\omega g(\omega) \ln(1 - e^{-\beta\hbar\omega}) = \frac{kT}{V} \int_0^\infty d\omega \frac{1}{3} \omega g(\omega) \frac{\beta\hbar e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \\ &= \frac{1}{3V} \int_0^\infty d\omega g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \frac{1}{3V} \langle E \rangle \end{aligned}$$

At the first line, one integrates by parts integrating $g(\omega)$ and differentiating the logarithm. The equation of state is therefore

$$pV = \frac{1}{3} E$$

High temperatures. In the high temperature limit $\beta \rightarrow 0$, the Planck distribution reduces to the Rayleigh–Jeans law for the distribution of classical radiation. The average energy diverges in the ultraviolet

$$\langle E \rangle = \int_0^\infty d\omega g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \sim \int_0^\infty d\omega g(\omega) \frac{\hbar\omega}{\beta\hbar\omega} = \int_0^\infty d\omega g(\omega) kT \sim \int_0^\infty d\omega \omega^2 \rightarrow \infty$$

This is the ultraviolet catastrophe.

Lecture 10

3.5 Phonon gas

See Tong, SP, §3.3. Consider a solid one-dimensional periodic lattice with spacing a . The Hamiltonian is

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} m \omega_0^2 (q_{i+1} - q_i)^2$$

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The equations of motion are

$$m\ddot{q}_i = m\omega_0^2(q_{i+1} - 2q_i + q_{i-1})$$

which can be solved with the discrete Fourier transform. Consider the ansatz

$$q_l = \frac{1}{\sqrt{N}} \sum_k \hat{q}_k e^{i(kla - \omega_k t)}$$

the equations become

$$-\omega_k^2 = \omega_0^2(e^{ika} + 2 - e^{-ika}) \implies \omega_k^2 = 4\omega_0^2 \sin^2 \frac{ka}{2}$$

from which the dispersion relation is

$$\boxed{\omega_k = 2\omega_0 \left| \sin \frac{ka}{2} \right|}$$

At low frequencies, one has

$$\omega_k \approx \omega_0 ka = c_s k$$

where $c_s = \omega_0 a$ is the speed of sound in the lattice.

One may draw a parallel between photons and phonons. The former have speed c , g -factor of $g = 2$ and there is no ultraviolet cutoff for the energy. The latter have speed c_s , g -factor of $g = 3$ in three dimensions and there is a natural cutoff given by a^{-1} which corresponds to the Debye wavelength $\lambda_D \approx a$ (or equivalently the frequency). One may use the results of the photon gas, but operating the above replacements. One may treat a solid as a quantum gas of non-interacting phonons.

Maximum frequency. Consider three dimensions. The way to determine the maximum frequency ω_D was found by Debye. The number of single phonon states is

$$\int_0^{\omega_D} d\omega g(\omega) = \int_0^{\omega_D} d\omega \frac{gV}{2\pi^2 c_s^3} \omega^2 = \frac{gV}{2\pi^2 c_s^3} \frac{\omega_D^3}{3}$$

and it is equal to the number of degrees of freedom $3N$ of the lattice of N points (see Tong for intuition). From this equality one finds

$$3N = \frac{gV}{2\pi^2 c_s^3} \frac{\omega_D^3}{3} \implies \omega_D = \left[\frac{6\pi^2 N}{V} \right]^{\frac{1}{3}} c_s, \quad g = 3$$

From this one defines the Debye temperature

$$T_D = \frac{\hbar \omega_D}{k}$$

For lead it is about 100 K while for diamond it is about 2000 K. The Debye temperature divides the high and low temperature regimes.

Average energy and heat capacity. The average energy is

$$\langle E \rangle = \int_0^{\omega_D} d\omega g(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} = \frac{3V}{2\pi^2 c_s^3} \frac{(kT)^4}{\hbar^3} \int_0^{T_D/T} dx \frac{x^3}{e^x - 1}, \quad x = \beta \hbar \omega$$

In the low temperature regime, $T \ll T_D$, the integral is

$$\int_0^{T_D/T} dx \frac{x^3}{e^x - 1} \approx \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$$

from which the average energy and the heat capacity are

$$E \approx \frac{3V}{2\pi^2} \frac{(kT)^4}{(c_s \hbar)^3} \frac{\pi^4}{15} \sim T^4, \quad C = d_T E \sim T^3$$

In the high temperature regime, $T \gg T_D$, the integral is

$$\int_0^{T_D/T} dx \frac{x^3}{e^x - 1} \approx \int_0^{T_D/T} dx \frac{x^3}{x} = \frac{1}{3} \left[\frac{T_D}{T} \right]^3$$

so that the average energy and the heat capacity are

$$E \approx \frac{3V}{2\pi^2} \frac{(kT)^4}{(c_s \hbar)^3} \frac{1}{3} \left[\frac{T_D}{T} \right]^3 = \frac{V k^3 T_D^3}{2\pi^2 \hbar^3 c_s^3} kT = 3NkT, \quad C = d_T E = 3Nk$$

At low temperatures, the heat capacity of metals has a contribution from the fermionic nature of electrons and from phonons

$$C \sim \alpha T + \beta T^3$$

4 Magnetic properties of electrons

The magnetic properties of electrons are purely quantum:

- the coupling between the spin and an external magnetic field leads to the Pauli paramagnetism;
- the orbital motion of electrons leads to the Landau diamagnetism.

4.1 Pauli paramagnetism

See Tong, SP, §3.6.6. Consider an ideal gas of electrons in a constant and uniform magnetic field $\mathbf{B} = B\hat{z}$. The electrons interact with the magnetic field through the Hamiltonian

$$H_{\text{int}} = -\boldsymbol{\mu} \cdot \mathbf{B} = g_e \frac{|e|\hbar}{2m} \mathbf{B} \cdot \mathbf{S} = \mu_B B \sigma_3 \implies E_{\text{spin}} = \pm \mu_B B$$

where μ_B is the Bohr magneton and $\boldsymbol{\mu}$ is the magnetic moment of the electron

$$\mu_B = \frac{\hbar|e|\hbar}{2m}, \quad \boldsymbol{\mu} = -\frac{1}{\hbar} g_e \mu_B \mathbf{S}, \quad \mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma}, \quad g_e = 2$$

Assume that the interaction is small with respect to the kinetic Hamiltonian and let the energy levels be

$$E' = E + \mu_B B (N_+ - N_-)$$

where E are the energy levels in the absence of the magnetic field and N_{\pm} is the number of electrons with spin \pm . The equation of state of the number of particles is

$$\begin{aligned} \frac{\langle N_+ \rangle}{V} &= \frac{N_+}{V} = \frac{1}{V} \int dE \frac{g(E)}{e^{\beta(E + \mu_B B - \mu)} + 1} = \frac{1}{\lambda^3} f_{\frac{3}{2}}(ze^{-\beta\mu_B B}) \\ \frac{\langle N_- \rangle}{V} &= \frac{N_-}{V} = \frac{1}{V} \int dE \frac{g(E)}{e^{\beta(E - \mu_B B - \mu)} + 1} = \frac{1}{\lambda^3} f_{\frac{3}{2}}(ze^{\beta\mu_B B}) \end{aligned}$$

One is interested in the magnetization

$$\begin{aligned} M &= -\partial_B E' = -\partial_B [E + \mu_B B (N_+ - N_-)] = -\mu_B (N_+ - N_-) \\ &= -\frac{\mu_B V}{\lambda^3} [f_{\frac{3}{2}}(ze^{-\beta\mu_B B}) - f_{\frac{3}{2}}(ze^{\beta\mu_B B})] \end{aligned}$$

The number of particles is

$$N = N_+ + N_- = \frac{V}{\lambda^3} [f_{\frac{3}{2}}(ze^{-\beta\mu_B B}) + f_{\frac{3}{2}}(ze^{\beta\mu_B B})]$$

High temperatures. At high temperatures, one may approximate

$$z \rightarrow 0 \implies f_{\frac{3}{2}}(z) \sim z$$

The magnetization is

$$M \sim -\frac{\mu_B V}{\lambda^3} [ze^{-\beta\mu_B B} - ze^{\beta\mu_B B}] = 2\frac{\mu_B V}{\lambda^3} z \sinh(\beta\mu_B B)$$

The number of particles is

$$N \sim 2\frac{V}{\lambda^3} z \cosh(\beta\mu_B B)$$

from this one finds

$$\frac{2Vz}{\lambda^3} = \frac{N}{\cosh(\beta\mu_B B)}$$

which can be substituted into the magnetization to find

$$M = \mu_B N \tanh(\beta\mu_B B)$$

The magnetic susceptibility is

$$\chi = \partial_B M = \frac{\beta\mu_B^2 N}{\cosh^2(\beta\mu_B B)}$$

In the limit of weak magnetic field $B \rightarrow 0$, the susceptibility has a dependence on the temperature following Pierre Curie's law

$$\chi \rightarrow \frac{\mu_B^2 N}{kT} \sim \frac{1}{T} > 0$$

A lower temperature means fewer temperature fluctuations which imply more susceptibility to magnetization because the electrons are less agitated.

Low temperatures. At low temperatures, one may approximate

$$z \rightarrow \infty \implies f_n(z) \sim \frac{(\ln z)^n}{\Gamma(n+1)}$$

The magnetization is

$$\begin{aligned} M &\sim -\frac{\mu_B V}{\lambda^3} \frac{(\ln z - \beta\mu_B B)^{\frac{3}{2}} - (\ln z + \beta\mu_B B)^{\frac{3}{2}}}{\Gamma(3/2+1)} \\ &= -\frac{\mu_B V}{\lambda^3} \frac{(\ln z)^{\frac{3}{2}}}{\frac{3}{4}\sqrt{\pi}} \left[\left(1 - \frac{\beta\mu_B B}{\ln z}\right)^{\frac{3}{2}} - \left(1 + \frac{\beta\mu_B B}{\ln z}\right)^{\frac{3}{2}} \right] \\ &\sim -\frac{\mu_B V}{\lambda^3} \left(\frac{E_F}{kT}\right)^{\frac{3}{2}} \frac{3}{4\sqrt{\pi}} \left[1 - \frac{3}{2} \frac{\mu_B B}{E_F} - 1 - \frac{3}{2} \frac{\mu_B B}{E_F}\right] = \frac{\mu_B V}{\lambda^3} \left(\frac{E_F}{kT}\right)^{\frac{3}{2}} \frac{9}{4\sqrt{\pi}} \frac{\mu_B B}{E_F} \\ &= \mu_B^2 g(E_F) B \end{aligned}$$

At the third line, one has substituted

$$z \sim e^{\beta\mu(0)} = e^{\beta E_F} \implies \ln z = \frac{E_F}{kT}$$

The magnetic susceptibility is

$$\chi = \partial_B M = \mu_B^2 g(E_F) > 0$$

It is constant because most electrons are embedded deep within the Fermi sphere and cannot align their spin with the magnetic field due to the Pauli exclusion principle.

Conclusion. In both temperature limits, the susceptibility is positive $\chi > 0$ due to the spin coupling with the magnetic field. So spin is responsible for the Pauli paramagnetism.

4.2 Landau diamagnetism

See, Tong, SP, §3.6.7. Charged fermions in a magnetic field are also subject to the Lorentz force. Consider a minimal coupling between the electrons and the magnetic field

$$H = \frac{1}{2m} \left[\mathbf{p} - \frac{q}{c} \mathbf{A} \right]^2$$

with $q < 0$ for electrons and where p is the canonical momentum (not the physical momentum). The orbital effect is purely quantum because classically one would compute the partition function

$$Z = \int \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N} N!} e^{-\beta H}$$

A simple change of variable $\mathbf{p} \rightarrow \mathbf{p} - q/c \mathbf{A}$ shows that the classical partition function does not depend on the magnetic field: this is the Bohr–van Leeuwen theorem.

Landau levels. Consider the magnetic field

$$\mathbf{B} = \nabla \times \mathbf{A} = (0, 0, B), \quad \mathbf{A} = (-By, 0, 0)$$

The interaction Hamiltonian is

$$H = \frac{1}{2m} \left[p_x + \frac{q}{c} By \right]^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

Since the directions x and z do not appear explicitly, their solutions to the Schrödinger equation

$$\hat{H}\psi = E\psi$$

are plane waves, so the respective momenta are conserved. Consider the ansatz

$$\psi(x, y, z) = e^{\frac{i}{\hbar}(p_x x + p_z z)} \varphi(y)$$

Inserting it into the Schrödinger equation, one finds

$$\left[-\frac{\hbar^2}{2m} \partial_y^2 + \frac{1}{2} m \omega_c^2 (y + y_0)^2 \right] \varphi(y) = \left[E - \frac{p_z^2}{2m} \right] \varphi(y)$$

where

$$y_0 = \frac{p_x}{qB}, \quad \omega_c = \frac{|q|B}{m}$$

The frequency is called cyclotron frequency. The left-hand side is the Hamiltonian of a harmonic oscillator in one dimension, so the bracket on the right-hand side is the energy of such harmonic oscillator

$$E_{\text{osc}} = E - \frac{p_z^2}{2m} = \hbar \omega_c \left(n + \frac{1}{2} \right) \implies E = \frac{p_z^2}{2m} + \hbar \omega_c \left(n + \frac{1}{2} \right)$$

These are the Landau levels. Since the energy does not depend on the momentum p_x , they are highly degenerate as shown in the following. Consider the fermion gas to be inside an infinitely long square rectangular cuboid whose square sides have length L : in other words, x and y are, for example, in $[0, L]$, while $z \in \mathbb{R}$ can take any value. The momenta in x are discrete

$$p_x = \frac{2\pi\hbar}{L} n_x$$

Since $|y_0| \leq L$ one finds

$$|y_0| = \frac{|p_x|}{|q|B} = \frac{1}{|q|B} \frac{2\pi\hbar}{L} |n_x| \leq L \implies |n_x| \leq \frac{|q|BL^2}{2\pi\hbar} \equiv \frac{\Phi}{\Phi_0}$$

where the total flux and the flux quantum are

$$\Phi = BL^2, \quad \Phi_0 = \frac{2\pi\hbar}{|q|}$$

There is only a finite set of allowed degenerate modes. Notice that this result does not include the g -factor of electrons. In fact, for a fixed energy level n of the oscillator and a momentum p_z , then the degeneracy is $2\Phi/\Phi_0$.

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Diamagnetism. One would like to compute the gran-canonical partition function. One has to sum the energy levels of the harmonic oscillator and integrate the phase space related to the z component

$$\begin{aligned}\ln \mathcal{Z} &= \sum_{E_k} \text{degen}(E_k) \ln(1 + ze^{-\beta E_k}) \\ &= \int \frac{dp_z dq_z}{2\pi\hbar} \sum_{n=0}^{\infty} 2 \frac{\Phi}{\Phi_0} \ln \left\{ 1 + z \exp \left[-\beta \frac{p_z^2}{2m} - \beta \hbar \omega_c \left(n + \frac{1}{2} \right) \right] \right\} \\ &= L \sum_{n=0}^{\infty} 2 \frac{\Phi}{\Phi_0} \int_{\mathbb{R}} \frac{dp_z}{2\pi\hbar} \ln \left\{ 1 + \exp \left(-\frac{\beta p_z^2}{2m} \right) \exp \left[\beta \mu - \beta \hbar \omega_c \left(n + \frac{1}{2} \right) \right] \right\}\end{aligned}$$

where k labels the energy levels. One may apply the Euler summation formula

$$\sum_{n=0}^{\infty} f(n + 1/2) = \int_0^{\infty} f(x) dx + \frac{1}{24} f'(0) + \dots$$

to

$$f(x) = 2L \frac{\Phi}{\Phi_0} \int_{\mathbb{R}} \frac{dp_z}{2\pi\hbar} \ln[1 + e^{-\beta \frac{p_z^2}{2m} + \beta x}]$$

Therefore

$$\begin{aligned}\ln \mathcal{Z} &= \sum_{n=0}^{\infty} f(\mu - \hbar \omega_c(n + 1/2)) \\ &= \int_0^{\infty} f(\mu - \hbar \omega_c x) dx + \frac{2L}{24} (-\hbar \omega_c \beta) \frac{\Phi}{\Phi_0} \int_{\mathbb{R}} \frac{dp_z}{2\pi\hbar} \frac{e^{-\beta(\frac{p_z^2}{2m} - \mu)}}{1 + e^{-\beta(\frac{p_z^2}{2m} - \mu)}}\end{aligned}$$

The first addendum is independent of the magnetic field B . The integrand of the second addendum is the average occupation number along the z direction, $\langle n_z \rangle$, the Fermi–Dirac distribution. At zero temperature $T = 0$, the momentum is at maximum the Fermi momentum $|\mathbf{p}_z| \leq p_F$ and the occupation number is $\langle n_z \rangle = 1$. Therefore, one obtains

$$\int_{\mathbb{R}} \frac{dp_z}{2\pi\hbar} \frac{e^{-\beta(\frac{p_z^2}{2m} - \mu)}}{1 + e^{-\beta(\frac{p_z^2}{2m} - \mu)}} = \int_{-p_F}^{p_F} \frac{dp_z}{2\pi\hbar} = \frac{p_F}{\pi\hbar}$$

Thus the logarithm of the partition function is

$$\ln \mathcal{Z} = (B\text{-indep.}) - \frac{1}{24} \frac{q^2 V \beta}{\pi^2 \hbar} \frac{p_F}{m} B^2 = (B\text{-indep.}) - \frac{1}{6} \mu_B^2 g(E_F) B^2 \beta$$

The magnetization is

$$M = -\partial_B E = \frac{1}{\beta} \partial_B \ln \mathcal{Z} = -\frac{1}{3} \mu_B^2 g(E_F) B, \quad E - TS - \mu N = \Phi = -kT \ln \mathcal{Z}$$

while the magnetic susceptibility is

$$\chi = \partial_B M = -\frac{1}{3} \mu_B^2 g(E_F) < 0$$

The susceptibility is negative: this is diamagnetism.

Total effect. At low temperatures, the total effect given by spin and the Lorentz force is

$$\chi = \mu_B^2 g(E_F) - \frac{1}{3} \mu_B^2 g(E_F) = \frac{2}{3} \mu_B^2 g(E_F) > 0$$

The overall effect is paramagnetic.

Part II

Critical phenomena

See Tong, SP, §5. A first example of phase transition is the one of Bose–Einstein condensates: at the critical temperature T_c , the derivative of the relative occupation number of the ground state with respect to the temperature is not continuous.

Phase transitions are equivalent to discontinuities in the derivatives which can only happen in the thermodynamic limit $N, V \rightarrow \infty$.

Definition (Ehrenfest classification). An n -th order phase transition is a discontinuity of the n -th derivative of a thermodynamic free energy (i.e. F or G)⁷.

5 Liquid-gas transitions

Recall that for a weakly interacting classical gas at high temperature and low density, one corrects the ideal gas law utilizing the virial expansion

$$\frac{p}{kT} = \frac{N}{V} + B_2(T) \frac{N^2}{V^2} + \dots$$

If one considers only the first non-trivial correction, the expansion can be expressed as the van der Waals equation

$$kT = \left[p + a \frac{N^2}{V^2} \right] \left[\frac{V}{N} - b \right], \quad a = \frac{2\pi}{3} r_0^3 U_0, \quad b = \frac{2\pi}{3} r_0^3$$

recalling that b describes the repulsion and can be thought of as the volume of the particles, while a is related to the long-range interaction. This equation can be rewritten as

$$p = \frac{kT}{v - b} - \frac{a}{v^2}, \quad v = \frac{V}{N}$$

The plot of the pressure p as a function of v at different temperatures⁸ has a few interesting characteristics (see Tong, fig. 34). There is a critical temperature T_c where the graph has an inflection point. This temperature can be found from

$$d_v p = d_v^2 p = 0 \implies kT_c = \frac{8a}{27b} = \frac{8}{27} U_0$$

At high temperatures, $T > T_c$, the gas behaves as an ideal gas. For low temperatures, $T < T_c$, the following situation occurs (see Tong, fig. 35).

- After the local maximum, the derivative is negative $d_v p < 0$, but small: the system is easy to compress; it holds $v \gg b$ so the system is rarefied. The state is a gas.
- Close to b , before the local minimum, the derivative is negative and large: the system is hard to compress; it holds $v \approx b$ so the system is dense. This state is a liquid.
- Before the local maximum, the derivative is positive. The system has weird properties: by reducing the volume, the pressure decreases too. This state is unstable and unphysical.

From this, one has the intuition that, by lowering the temperature, there is a phase transition between gas and liquid (with some weird properties in between). It is surprising to see such behaviour coming just from the van der Waals equation, i.e. the first correction to the ideal gas.

⁷Tong says “thermodynamic potential”, but also E and H are thermodynamic potentials, yet they are not used for the classification. If they were, then there would be ambiguities: for example, the heat capacity C is a first derivative of the internal energy E and also a second derivative of the free energy F . See also https://en.wikipedia.org/wiki/Phase_transition#Ehrenfest_classification.

⁸A line of constant temperature is called isotherm.

Phase equilibrium. The situation in between is characterized by the two phases in equilibrium. Consider two homogeneous phases (gas and liquid) that coexist separated by a single interface (i.e. the surface of the liquid). At equilibrium, the pressure and temperature of the two are the same

$$p_{\text{gas}} = p_{\text{liquid}}, \quad T_{\text{gas}} = T_{\text{liquid}}$$

These are acceptable since, at the same pressure, the volumes per particle v of the two phases can sit on the same isotherm curve (see figure). The last requirement is chemical equilibrium

$$\mu_{\text{gas}} = \mu_{\text{liquid}}$$

This gives non-trivial conditions, as noticed by Maxwell. Consider the Gibbs free energy

$$G(p, T, N) = E - TS + pV, \quad dG = -S dT + V dp + \mu dN$$

Recalling the argument about intensive and extensive quantities, one finds

$$G = N\mu(p, T)$$

The chemical equilibrium condition can be expressed also as

$$\mu_{\text{gas}} = \mu_{\text{liquid}} \iff \left[\frac{G}{N} \right]_{\text{gas}} = \left[\frac{G}{N} \right]_{\text{liquid}}$$

Varying the Gibbs free energy with respect to the pressure gives

$$V = \partial_p G = N \partial_p \mu \implies \partial_p \mu = \frac{V(p, T)}{N}$$

where one uses both expressions of the Gibbs free energy respectively. Integrating along the isotherm gives the chemical potential of any point on the curve

$$\mu(p, T) = \mu_{\text{liquid}} + \int_{p_{\text{liquid}}}^p dx \partial_x \mu = \mu_{\text{liquid}} + \int_{p_{\text{liquid}}}^p dx \frac{V(x, T)}{N}$$

Integrating up to the point of the gas state in the phase diagram at the same pressure as the liquid state gives the condition of equilibrium

$$\mu_{\text{gas}} = \mu_{\text{liquid}}$$

from which

$$\mu_{\text{gas}}(p_{\text{gas}} = p_{\text{liquid}}, T) = \mu_{\text{liquid}} + \int_{p_{\text{liquid}}}^{p_{\text{gas}}} dx \frac{V(x, T)}{N} \equiv \mu_{\text{liquid}}$$

The integral must vanish: the areas between the graph and the horizontal line at p_{eq} must be equal. This condition is the Maxwell construction. After fixing the temperature, the Maxwell construction gives only one possible value of pressure p and inverse densities v that satisfy chemical equilibrium.

At a fixed temperature $T < T_c$, one can determine the pressure at which the liquid and gas states are in equilibrium. This gives the co-existence curve (see Tong, fig. 37). Before the local minimum, the system is in a liquid state at a temperature T and density v_{liquid}^{-1} . After the local maximum, the system is in a gas state at the same temperature T , but density v_{gas}^{-1} . Inside the co-existence curve, liquid and gas can both exist at the same temperature and pressure, and atoms can freely move between the liquid state and the gas state. This means that while the density of gas and liquid is fixed, the average density of the system is not. It can vary between the gas density and the liquid density simply by changing the amount of liquid. The key point of this argument is that, inside the co-existence curve, the isotherms simply become flat lines, reflecting the fact that the density can take any value.

Clausius–Clapeyron equation. The liquid-gas phase diagram can also be plotted in the (T, p) plane (see fig. 40). The co-existence region is a line separating the two phases. Starting from the gas phase, increasing the pressure at a fixed temperature $T < T_c$ makes the system jump directly to the liquid phase. This appears as a discontinuity in the volume. Such discontinuities are the sign of a phase transition. The volume is

$$V = \partial_p G$$

so the first derivative of the Gibbs free energy has a discontinuity. For $T < T_c$, there is a first order phase transition when one crosses the co-existence line. At the critical temperature T_c , the volume changes with continuity and there is a second-order phase transition.

Along the line of phase transition, the system is at equilibrium

$$p_{\text{gas}} = p_{\text{liquid}}, \quad T_{\text{gas}} = T_{\text{liquid}}, \quad \mu_{\text{gas}} = \mu_{\text{liquid}}$$

Recalling that the Gibbs free energy is

$$G = N\mu(p, T)$$

if the number of particles is constant, then the chemical equilibrium condition becomes

$$G_{\text{gas}} = G_{\text{liquid}}$$

This implies that

$$\begin{aligned} dG_{\text{gas}} &= -S_{\text{gas}} dT + V_{\text{gas}} dp = -S_{\text{liquid}} dT + V_{\text{liquid}} dp = dG_{\text{liquid}} \\ dp(V_{\text{gas}} - V_{\text{liquid}}) &= dT(S_{\text{gas}} - S_{\text{liquid}}) \end{aligned}$$

from which

$$dT p = \frac{S_{\text{gas}} - S_{\text{liquid}}}{V_{\text{gas}} - V_{\text{liquid}}} = \frac{L}{T(V_{\text{gas}} - V_{\text{liquid}})}$$

where the latent heat is

$$L \equiv T(S_{\text{gas}} - S_{\text{liquid}})$$

The second equality is the Clausius–Clapeyron equation. One may find an approximate solution. Assume that the latent heat is constant, that $V_{\text{gas}} \gg V_{\text{liquid}}$ and that the ideal gas law holds $pV = NkT$. Therefore

$$dT p = \frac{S_{\text{gas}} - S_{\text{liquid}}}{V_{\text{gas}} - V_{\text{liquid}}} \approx \frac{L}{TV_{\text{gas}}} \approx \frac{Lp}{NkT^2}$$

whose solution is

$$p(T) = p_0 e^{-\frac{L}{NkT}}$$

Critical point. The critical temperature can be found from

$$d_v p = d_v^2 p = 0$$

However, it can also be found from the three roots of the van der Waals equation

$$pv^3 - (pb + kT)v^2 + av - ab = 0$$

For $T > T_c$, there is a single real root. For $T < T_c$, there are three real roots. At $T = T_c$, the three roots coincide

$$p_c(v - v_c)^3 = 0$$

Comparing the coefficients, one finds

$$-ab = -p_c v_c^3, \quad a = 3p_c v_c^2, \quad -3p_c v_c = -(p_c b + kT_c)$$

from which the values at the critical point are

$$v_c = 3b, \quad p_c = \frac{a}{27b^2}, \quad kT_c = \frac{8a}{27b}$$

One may introduce the reduced variables

$$\bar{v} = \frac{v}{v_c}, \quad \bar{p} = \frac{p}{p_c}, \quad \bar{T} = \frac{T}{T_c}$$

and the van der Waals equation can be rewritten as

$$\bar{p} = \frac{8}{3} \frac{\bar{T}}{\bar{v} - \frac{1}{3}} - \frac{3}{\bar{v}^2}$$

One may notice that this relation is independent of the details of the interaction a and b . Also, since the three critical values are expressed in terms of the two values a and b , one may construct a quantity independent of them called the universal compressibility ratio

$$\frac{p_c v_c}{k T_c} = \frac{3}{8} = 0.375$$

The measured values of this ratio range between 0.28 and 0.3. This ratio seems like a first example of universality (in a qualitative sense), but it does not quite fit the precise definition of universality. Also, notice that the empirical values are not close to the theoretical one because the van der Waals equation is unlikely to be accurate in the liquid regime.

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Critical behaviour. In the proximity of a critical point, one may introduce a set of parameters, called critical exponents, that describe how the system approaches such critical point. An important notion is the one of universality: systems with the same critical exponents belong to the same class of universality.

For the liquid-gas second-order critical point, one defines the following critical exponents

$$v_{\text{gas}} - v_{\text{liquid}} \sim (T_c - T)^\beta, \quad p - p_c \sim (v - v_c)^\delta, \quad \kappa = -\frac{1}{v} \partial_p v \sim (T - T_c)^{-\gamma}$$

where the second equation is taken at $T = T_c$ and κ is the compressibility. The first relation describes how the difference between the inverse densities v of the system's phases goes to zero as the temperature tends to the critical temperature T_c . The second relation characterizes how the system approaches the critical point while varying the pressure, but keeping the temperature fixed at T_c . The third relation studies how the compressibility κ diverges since, at the critical temperature, it holds $d_v p = 0$. For all liquid-gas systems, the measured values are

$$\beta \approx 0.32, \quad \delta \approx 4.8 \quad \gamma \approx 1.2$$

This is the notion of universality: different gases behave the same around their critical point.

One may compute these exponents starting from the same model. Consider the van der Waals interaction, one expects this analysis to be only qualitative. For $T < T_c$, the reduced van der Waals equation has two stable solutions

$$\bar{p}_{\text{liquid}} = \frac{8\bar{T}}{3\bar{v}_{\text{liquid}} - 1} - \frac{3}{\bar{v}_{\text{liquid}}^2} = \frac{8\bar{T}}{3\bar{v}_{\text{gas}} - 1} - \frac{3}{\bar{v}_{\text{gas}}^2} = \bar{p}_{\text{gas}}$$

Solving for the temperature gives

$$\bar{T} = \frac{(3\bar{v}_{\text{liquid}} - 1)(3\bar{v}_{\text{gas}} - 1)(\bar{v}_{\text{gas}} + \bar{v}_{\text{liquid}})}{8\bar{v}_{\text{gas}}^2 \bar{v}_{\text{liquid}}^2}$$

At the critical point $\bar{v}_{\text{gas}} = \bar{v}_{\text{liquid}} \rightarrow 1$, as expected one obtains $\bar{T} \rightarrow 1$. One may study how the system approaches $\bar{T} = 1$ by expanding the right-hand side in $\varepsilon = \bar{v}_{\text{gas}} - \bar{v}_{\text{liquid}}$, or alternatively by writing

$$\bar{v}_{\text{gas}} = 1 + \frac{1}{2}\varepsilon, \quad \bar{v}_{\text{liquid}} = 1 - \frac{1}{2}\varepsilon$$

At leading order, one finds

$$\bar{T} \approx \frac{(2 + 3\varepsilon/2)(2 - 3\varepsilon/2) \cdot 2}{8} \approx 1 - \frac{9}{16}\varepsilon^2 = 1 - \frac{9}{16}(\bar{v}_{\text{gas}} - \bar{v}_{\text{liquid}})^2$$

From this one finds

$$(\bar{v}_{\text{gas}} - \bar{v}_{\text{liquid}})^2 \approx 1 - \bar{T} = \frac{T_c - T}{T_c}$$

Therefore, one may read the critical exponent

$$v_{\text{gas}} - v_{\text{liquid}} \sim (T_c - T)^{\frac{1}{2}} \implies \boxed{\beta = \frac{1}{2}}$$

At the critical temperature $T = T_c$, the first two derivatives of the pressure are zero

$$d_v p = d_v^2 p = 0$$

which, from a Taylor expansion, imply that

$$p - p_c \sim (v - v_c)^3 \implies \boxed{\delta = 3}$$

For the compressibility, one finds

$$\kappa = -\frac{1}{v} d_p v \sim (T - T_c)^{-1} \implies \boxed{\gamma = 1}$$

since $d_v p \sim |T - T_c|$ which is consistent with $d_v p = 0$ at $T = T_c$.

If one takes more terms in the virial expansion, or a more realistic interaction potential (e.g. Lennard–Jones), then one does not obtain theoretical results closer to the measured values of the critical exponents. Even if one improves the description at a microscopic level, it is irrelevant near the critical temperature and more terms do not improve the theoretical values.

Fluctuations. The van der Waals equation describes the qualitative behaviour correctly, but fails on precise quantitative tests. This is because, during its derivation, one has made certain approximations that are valid only at low density. It is not surprising that it fails to get the correct values near the critical point $v = 3b$. There is also a deeper reason why the van der Waals equation fails: fluctuations.

One has assumed fluctuations to be suppressed in the thermodynamic limit

$$\frac{\Delta N}{N} \rightarrow 0, \quad N \rightarrow \infty$$

This is no longer the case. Recall that the average number of particles and the related variance are

$$\langle N \rangle = \frac{1}{\beta} \partial_\mu \ln \mathcal{Z}, \quad (\Delta N)^2 = \frac{1}{\beta^2} \partial_\mu^2 \ln \mathcal{Z}$$

The gran-canonical partition function can be expressed in term of the gran-canonical potential

$$\ln \mathcal{Z} = -\beta \Phi = \beta p V$$

Therefore, the average number of particles and the variance are

$$\langle N \rangle = V \partial_\mu p, \quad (\Delta N)^2 = \frac{1}{\beta} \partial_\mu \langle N \rangle$$

Dividing the two expressions gives

$$\frac{(\Delta N)^2}{N} = \frac{1}{\beta V} \partial_\mu \langle N \rangle \partial_p \mu = \frac{1}{\beta V} \partial_p \langle N \rangle$$

Using the triple product rule of partial derivatives, one may write

$$\partial_p N|_{V,T} = -\partial_V N|_{p,T} \partial_p V|_{N,T}$$

where the subscripts indicate the constant quantities. This relation can be proven as follows. Let $f(x, y, z) = 0$, applying the implicit function theorem gives the functions

$$x = x(y, z), \quad y = y(x, z)$$

Their respective total differential is

$$dx = \partial_y x dy + \partial_z x dz, \quad dy = \partial_x y dx + \partial_z y dz$$

Substituting the second into the first gives

$$dx = \partial_y x (\partial_x y dx + \partial_z y dz) + \partial_z x dz = dx + (\partial_y x \partial_z y + \partial_z x) dz$$

from which

$$\partial_z x = -\partial_y x \partial_z y$$

Therefore, the ratio above is

$$\frac{(\Delta N)^2}{\langle N \rangle} = \frac{1}{\beta V} \partial_p \langle N \rangle = -\frac{1}{\beta V} \partial_V N \partial_p V \sim (T - T_c)^{-\gamma} \rightarrow \infty, \quad T \rightarrow T_c$$

At the second equality one has inserted the expression for $\partial_p N$ and one has noticed that

$$\partial_p v \rightsquigarrow \kappa \sim (T - T_c)^{-\gamma}$$

The fluctuations diverge at the critical point and dominate. This is the reason why the van der Waals equation is mildly successful. The study of critical phenomena deals with correctly accounting for fluctuations.

6 Ising model

See Tong, SP, §5.2. The Ising model is a D -dimensional lattice with N sites, each with a spin taking values up or down $S = \pm 1$. Each site interacts with an external magnetic field B through the Hamiltonian

$$H_B = -B \sum_{i=1}^N S_i$$

and also interacts with the sites directly adjacent

$$H_{\text{int}} = -J \sum_{\langle ij \rangle} S_i S_j$$

where the sum is over the nearest neighbour pairs: fixing i , then j runs over its nearest neighbours. The parameter J determines the behaviour of the magnetism: for $J > 0$ the system is ferromagnetic, i.e. neighbouring spins prefer to be aligned, while for $J < 0$ the spins want to be anti-parallel. The total interaction Hamiltonian is

$$H = -J \sum_{\langle ij \rangle} S_i S_j - B \sum_{i=1}^N S_i$$

The partition function is

$$Z = \sum_{\{S_i\}} e^{-\beta H}$$

where the sum is over all compatible configurations of spins (i.e. the states of the system). Let $J > 0$. Due to the interaction Hamiltonian, the spins want to be all aligned (if the external magnetic field is non-zero $B \neq 0$, then the spins align to it). However, since the temperature is non-zero $T > 0$, the thermal fluctuations randomize the spin orientation. One may study the magnetization is

$$M = \sum_i \langle S_i \rangle = \frac{1}{\beta} \partial_B \ln Z, \quad \langle S_i \rangle = \frac{1}{Z} \sum_{\{S_j\}} S_i e^{-\beta H}$$

Consider the spin-averaged magnetization, an intensive quantity

$$m \equiv \frac{M}{N}$$

It is the order parameter which defines the ordered phase $m \neq 0$ and the disordered phase $m = 0$. When the magnetic field is zero, $B = 0$, there is a second-order phase transition and one may define three critical exponents

$$m \sim (T_c - T)^\beta, \quad m \sim B^{\frac{1}{\delta}}, \quad \chi \sim (T - T_c)^{-\gamma}$$

where the first and last are at $B = 0$, while the second is at $T = T_c$.

6.1 Mean-field theory

The interaction Hamiltonian makes the study of the Ising model complicated: the sum in the partition function cannot, in general, be performed. Mean-field theory is a tool to simplify the interaction in an approximate manner. Consider the interaction between neighbours

$$S_i S_j = [(S_i - m) + m][(S_j - m) + m] = (S_i - m)(S_j - m) + m(S_i - m) + m(S_j - m) + m^2$$

The mean-field approximation means one may assume that the fluctuations of spins away from the average are small⁹

$$\sum_{\langle ij \rangle} (S_i - m)(S_j - m) = 0$$

which allows one to neglect the first term above to obtain

$$\sum_{\langle ij \rangle} S_i S_j = \sum_{\langle ij \rangle} [m(S_i + S_j) - m^2] = \sum_{\langle ij \rangle} [2mS_i - m^2] = 2m \frac{q}{2} \sum_i S_i - m^2 \frac{q}{2} N$$

where $q = 2D$ is the number of nearest neighbours. The factors of $1/2$ are needed to avoid double counting. Therefore, in the mean-field approximation, the Ising interaction Hamiltonian becomes

$$H_{\text{mf}} = \frac{1}{2} J N q m^2 - (J q m + B) \sum_{i=1}^N S_i$$

There is no longer any spin-spin interaction: a given spin feels the average effect of its neighbours' spins through a contribution to the effective magnetic field

$$B_{\text{eff}} \equiv J q m + B$$

This form of the interaction Hamiltonian makes the computation of the partition function easier. The partition is

$$\begin{aligned} Z &= \sum_{\{S_i\}} e^{-\beta H_{\text{mf}}} = e^{-\frac{1}{2} \beta J N q m^2} \sum_{\{S_i\}} e^{\beta B_{\text{eff}} \sum_i S_i} = e^{-\frac{1}{2} \beta J N q m^2} \sum_{\{S_i\}} \prod_{i=1}^N e^{\beta B_{\text{eff}} S_i} \\ &= e^{-\frac{1}{2} \beta J N q m^2} \prod_i \sum_{S_i} e^{\beta B_{\text{eff}} S_i} = e^{-\frac{1}{2} \beta J N q m^2} (e^{\beta B_{\text{eff}}} + e^{-\beta B_{\text{eff}}})^N \\ &= e^{-\frac{1}{2} \beta J N q m^2} 2^N [\cosh(\beta B_{\text{eff}})]^N \end{aligned}$$

Therefore, one obtains a consistency equation for the average magnetization

$$m = \frac{1}{\beta N} \partial_B \ln Z = \tanh[\beta(J q m + B)]$$

This equation can be solved graphically.

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No magnetic field. Let $B = 0$. The average magnetization is

$$m = \tanh(\beta J q m)$$

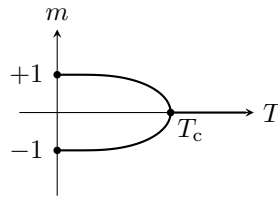
For

$$\beta J q < 1 \iff kT > Jq \iff T > T_c = \frac{Jq}{k}$$

the equation of the magnetization has only a trivial solution $m = 0$. At high temperatures, there is no average magnetization of the system: disorder prevails. For

$$\beta J q > 1 \iff T < T_c$$

there is one trivial solution, which is unstable, and two non-trivial ones $m = \pm m_0$ for which there is a non-zero magnetization. The interaction prevails over the random temperature fluctuations. The phase diagram at $B = 0$ is



In the limit of vanishing temperature $T \rightarrow 0$, the magnetization is $m_0 = 1$: all spins are pointing in the same direction. At the critical temperature $T = T_c$, and above, the magnetization is zero $m = 0$. From the graph one notices that the derivative of the magnetization is discontinuous. This is a second-order phase transition since the magnetization is a first derivative of the free energy which is itself proportional to $\ln Z$.

The interaction Hamiltonian in this case is

$$H = -J \sum_{\langle ij \rangle} S_i S_j$$

It has a \mathbb{Z}_2 symmetry $S_i \rightarrow -S_i$. The system exhibits a microscopic \mathbb{Z}_2 symmetry, but in the ordered phase $T < T_c$, the system chooses a state with magnetization m_0 or $-m_0$ breaking such symmetry. This is spontaneous symmetry breaking.

Non-zero magnetic field. If the magnetic field is non-zero, then the corresponding interaction explicitly breaks the \mathbb{Z}_2 symmetry

$$H = -J \sum_{\langle ij \rangle} S_i S_j - B \sum_{i=1}^N S_i$$

Let $B > 0$, i.e. aligned parallel to the direction of spin. The magnetization is

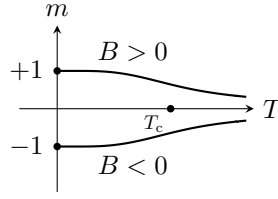
$$m = \tanh[\beta(Jqm + B)]$$

For $T > T_c$ there is only one solution $m > 0$, while for $T < T_c$ there are three solutions: one unstable $m \lesssim 0$, one meta-stable $m < 0$ and one physical $m > 0$. In both regimes, the magnetization is positive $m > 0$. One may study the system at high temperatures. The magnetization is

$$m = \tanh[\beta(Jqm + B)] \sim \beta(Jqm + B) \sim \frac{B}{kT}, \quad T \rightarrow \infty$$

The high temperatures counteract the order given by the magnetic field, yielding a magnetization that approaches zero. At low temperatures $T \rightarrow 0$, the system has a preferred magnetization $m = 1$ and there is no ambiguity in the choice $m = \pm 1$. Similarly for $B < 0$. The \mathbb{Z}_2 symmetry is absent from the beginning. There is no phase transition at T_c when varying the temperature. The phase diagram is the following

⁹This may make more sense for high dimensional lattices, where around each site there are many spins. So the average being small is reasonable.

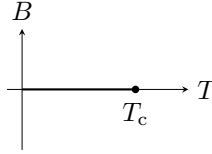


If one fixes the temperature $T < T_c$ and varies the magnetic field going from positive $B > 0$ to negative $B < 0$, the magnetization flips sign accordingly in a discontinuous manner. Since the magnetization is the first derivative of the free energy

$$m \sim \partial_B \ln Z \sim \partial_B F$$

then this is a first-order phase transition.

Conclusion. For spin systems, the mean-field analysis suggests a phase diagram (T, B) very similar to the liquid-gas transition (T, p) . See Tong, fig. 47.



At $T < T_c$, when crossing the equilibrium line, the magnetization jumps: it is a first-order phase transition. In contrast, moving along the temperature axis at $B = 0$ results in a second-order phase transition at the critical temperature $T = T_c$. For $T > T_c$ the system does not undergo any phase transition when varying the temperature or magnetic field: it moves with continuity between its states. This diagram is qualitatively correct for more than one dimension $D > 1$.

6.2 Critical exponents

One may establish a parallel between a liquid-gas system and a spin system. For the former, the inverse density v jumps as one varies the pressure. The critical exponents of interest are

$$v_{\text{gas}} - v_{\text{liquid}} \sim (T_c - T)^\beta, \quad p - p_c \sim (v - v_c)^\delta, \quad \kappa \sim (T - T_c)^{-\gamma}$$

For the latter, the magnetization m jumps as one varies the magnetic field B . The critical exponents are

$$m \sim (T_c - T)^\beta, \quad m \sim B^{\frac{1}{\delta}}, \quad \chi \sim (T - T_c)^{-\gamma}$$

The measured values of these exponents depend on the dimension D . For $D = 3$, the Ising model has the same exponents as the liquid-gas model: the two systems are in the same class of universality.

At this point one may try to utilize the mean-field approximation to compute the critical exponent of the Ising model. Let there be no magnetic field $B = 0$. The magnetization around the critical temperature is

$$\begin{aligned} m &= \tanh(\beta J q m) \sim \beta J q m - \frac{1}{3}(\beta J q m)^3 \\ m \left(1 - \frac{T_c}{T}\right) &\sim -\frac{1}{3}(\beta J q m)^3 \\ m &\sim (T_c - T)^{\frac{1}{2}} \end{aligned}$$

where one recalls

$$T_c = \frac{Jq}{k}$$

The critical exponent β is

$$m \sim (T_c - T)^\beta, \quad \boxed{\beta = \frac{1}{2}}$$

Consider the system at the critical temperature $T = T_c$ with a weak magnetic field. Notice $\beta Jq = 1$. The magnetization is

$$m = \tanh[m + B/(Jq)] \sim m + \frac{B}{Jq} - \frac{1}{3} \left(\frac{B}{Jq} + m \right)^3$$

$$m \sim \left(\frac{3B}{Jq} \right)^{\frac{1}{3}} - \frac{B}{Jq} \sim B^{\frac{1}{3}}$$

The critical exponent δ is

$$m \sim B^{\frac{1}{\delta}}, \quad \boxed{\delta = 3}$$

Consider the magnetic susceptibility

$$\chi = N \partial_B m = N \partial_B \tanh[\beta(Jqm + B)] = \frac{N\beta}{\cosh^2[\beta(Jqm + B)]} \left(1 + \frac{Jq}{N} \chi \right)$$

At zero magnetic field, one finds

$$\chi = \frac{N\beta}{\cosh^2(\beta Jqm)} \left(1 + \frac{Jq}{N} \chi \right)$$

Near the critical temperature $T \rightarrow T_c$, the magnetization is small $m \rightarrow 0$, so one finds

$$\chi \sim N\beta \left(1 + \frac{Jq}{N} \chi \right) \implies \chi(1 - \beta Jq) \sim \beta N \implies \chi \sim (T - T_c)^{-1}$$

The critical exponent γ is

$$\chi \sim (T - T_c)^{-\gamma}, \quad \boxed{\gamma = 1}$$

Utilizing the mean-field approximation, one finds the following critical exponents in any dimension D

$$\beta = \frac{1}{2}, \quad \delta = 3, \quad \gamma = 1$$

The measured values at zero magnetic field are as follows.

- In one dimension $D = 1$, there is an exact solution and there are no phase transitions. This is the lower critical dimension for a system with discrete symmetries. At any temperature T , the magnetization m is zero: disorder always prevails. The mean-field theory fails in one dimension.
- In two dimensions $D = 2$, there is an exact solution by Onsager for $B = 0$

$$\beta = \frac{1}{8}, \quad \delta = 15, \quad \gamma = \frac{7}{4}$$

In this case the mean-field theory is qualitatively correct.

- In three dimensions $D = 3$, there are only numerical results using Monte Carlo methods, the renormalization group, the Ginzburg–Landau perturbative approach and the conformal bootstrap. The exponent are approximately

$$\beta \approx 0.32, \quad \delta \approx 4.8, \quad \gamma \approx 1.2$$

These values are the same as the liquid-gas system. Again, the mean-field theory is qualitatively correct.

- For higher dimension $D \geq 4$, the mean-field theory is exact. Four dimensions $D = 4$ is the upper critical dimension.

6.3 One dimension

See Tong, SP, §5.3. The Ising model in one dimension has an exact solution. Consider a one-dimensional lattice of size N with periodic boundary conditions

$$S_1 = S_{N+1}$$

The interaction Hamiltonian is rewritten as

$$H = -J \sum_{i=1}^N S_i S_{i+1} - B \sum_{i=1}^N S_i = -J \sum_{i=1}^N S_i S_{i+1} - \frac{1}{2} B \sum_{i=1}^N (S_i + S_{i+1})$$

The canonical partition function is

$$Z = \sum_{\{S_i\}} \prod_{i=1}^N \exp \left[\beta J S_i S_{i+1} + \frac{1}{2} \beta B (S_i + S_{i+1}) \right]$$

which can be written in terms of the transfer matrix

$$T_{S_i, S_{i+1}} = \exp \left[\beta J S_i S_{i+1} + \frac{1}{2} \beta B (S_i + S_{i+1}) \right], \quad T = \begin{bmatrix} e^{\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} \end{bmatrix}, \quad S_i = \pm 1$$

to obtain

$$Z = \sum_{\{S_i\}} \langle S_1 | T | S_2 \rangle \langle S_2 | T | S_3 \rangle \cdots \langle S_N | T | S_1 \rangle = \sum_{\{S_i\}} \prod_{i=1}^N \langle S_i | T | S_{i+1} \rangle = \text{Tr } T^N$$

One may diagonalize the transfer matrix. The characteristic polynomial is

$$\begin{aligned} P(\lambda) &= \det \begin{bmatrix} e^{\beta(J+B)} - \lambda & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} - \lambda \end{bmatrix} = (e^{\beta(J+B)} - \lambda)(e^{\beta(J-B)} - \lambda) - e^{-2\beta J} \\ &= \lambda^2 + 2 \sinh(2\beta J) - 2\lambda e^{\beta J} \cosh(\beta B) \end{aligned}$$

from which the eigenvalues are

$$P(\lambda) = 0 \implies \lambda_{\pm} = e^{\beta J} \cosh(\beta B) \pm \sqrt{e^{2\beta J} \cosh^2(\beta B) - 2 \sinh(2\beta J)}$$

Since $\lambda_- < \lambda_+$, the partition function in the thermodynamic limit is

$$Z = \text{Tr } T^N = \lambda_+^N + \lambda_-^N = \lambda_+^N \left[1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N \right] \sim \lambda_+^N, \quad N \rightarrow \infty$$

The magnetization is then

$$\begin{aligned} m &= \frac{1}{N\beta} \partial_B \ln Z = \frac{1}{\beta} \partial_B \ln \lambda_+ = \frac{1}{\beta \lambda_+} \partial_B \lambda_+ \\ &= \frac{1}{\lambda_+} \left[e^{\beta J} \sinh(\beta B) \pm \frac{e^{2\beta J} \cosh(\beta B) \sinh(\beta B)}{\sqrt{e^{2\beta J} \cosh^2(\beta B) - 2 \sinh(2\beta J)}} \right] \end{aligned}$$

The exact solution of the one-dimensional $D = 1$ Ising model in the thermodynamic limit shows that, in the absence of the external magnetic field $B = 0$, the magnetization is zero $m = 0$ for any temperature T . There is no phase transition.

6.4 Two dimensions

The Ising model in two dimensions with no magnetic field has an exact solution. Instead of finding the solution, one studies the model at high and low temperatures. The partition function is

$$Z = \sum_{\{S_i\}} \exp \left[\beta J \sum_{\langle ij \rangle} S_i S_j \right]$$

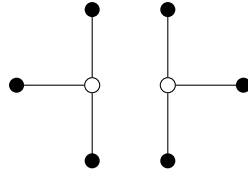
Low temperatures. For low temperatures, one has $\beta J \gg 1$ and the sum of the partition function is dominated by the lower energy states. There are two ground states: the states with all the spins pointing in the same direction, up or down. Each has energy

$$E_0 = -J \sum_{\langle ij \rangle} S_i S_j = -\frac{1}{2} J N q = -2JN, \quad q = 4$$

The first excited states are identical to a ground state, but the spin in only one site is flipped. Each of the four links between such site and its nearest neighbours needs an energy of $2J$ to be flipped. Therefore, the energy of the first excited state is

$$E_1 = E_0 + 8J$$

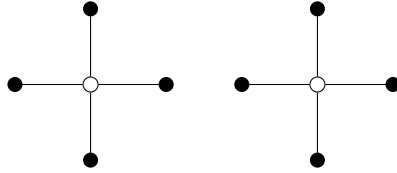
with degeneracy¹⁰ N . Let a link between two anti-parallel spins be called “broken”. The second excited states have two flipped spins in adjacent sites, corresponding to a total of six broken links. Diagrammatically, one may draw only broken links



The energy of the state and its degeneracy are

$$E_2 = E_0 + 12J, \quad 2N$$

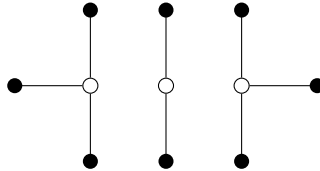
The factor of 2 in the degeneracy comes from the possible orientations. The third excited states have a total of eight broken links



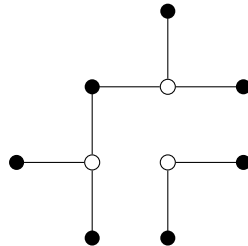
The energy and degeneracy of this graph are

$$E_3 = E_0 + 16J, \quad \frac{1}{2} N(N-5)$$

There are three other graphs with the same energy. With degeneracy $2N$ there is

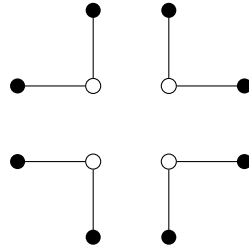


noting that it comes also from the possible orientations. With degeneracy $4N$ there is



¹⁰In the following, the degeneracy is written with respect to one ground state. In fact, when writing the partition function, there is an overall factor of 2 due to both ground states.

noting that there are other three orientations. With degeneracy N there is



Adding all the graphs together gives an expansion of the partition function in power of $e^{-\beta J} \ll 1$

$$\begin{aligned} Z &= 2e^{2\beta NJ} \left[1 + Ne^{-8\beta J} + 2Ne^{-12\beta J} + \left(\frac{1}{2}N(N-5) + 2N + 4N + N \right) e^{-16\beta J} + \dots \right] \\ &= 2e^{2\beta NJ} \left[1 + Ne^{-8\beta J} + 2Ne^{-12\beta J} + \frac{1}{2}N(N+9)e^{-16\beta J} + \dots \right] \end{aligned}$$

The overall factor comes from the ground states. In particular, the overall 2 is the degeneracy.

Lecture 14

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Peierls droplets. As more spins are flipped, the low energy states become droplets, consisting of a region of space in which all the spins are flipped, surrounded by a larger sea in which the spins have their original alignment. The energy cost of such droplet is approximately

$$E \sim 2JL$$

where L is the perimeter of the droplet, which is about the number of broken links. The degeneracy of a droplet scales as

$$e^{\alpha L}, \quad \ln 2 < \alpha < \ln 3$$

The derivation of this behaviour comes from the process of random walk. Consider a random walk in two dimensions with four possible directions. The number of paths of length L is

$$\text{number of paths} = 4^L = e^{L \ln 4}$$

In the present case, however, the paths cannot intersect themselves and have to be closed. One can prove that the coefficient α is constrained as above.

Using the Peierls droplets, the partition function scales as

$$Z \sim \sum_L e^{\alpha L} e^{-2\beta J L}$$

Both the energy and the degeneracy scale with the length L which means that there is an interesting competition between them:

- At low temperatures, $\beta J \gg 1$, the energy term dominates so the spins align and the phase is the ordered phase. The sum in the partition function converges.
- As the temperature rises, one reaches the critical temperature

$$\alpha L = 2\beta J L \implies kT_c = \frac{2J}{\alpha}$$

The partition function no longer converges and there is a phase transition.

- At high temperatures, $\beta J \ll 1$, the degeneracy (i.e. entropy) dominates and the disorder due to thermal fluctuations becomes prevalent.

One may also use the Peierls droplets to see why the Ising model in one dimension does not undergo any phase transition. On a line, the boundary of any droplet always consists of just two points. This means that the energy cost to forming a droplet is always $E = 4J$ with degeneracy N , regardless of the size of the droplet. The partition function is then

$$Z = \sum_L N e^{-4\beta J}$$

In this case the degeneracy N is always dominant. The disordered phase always prevails in one dimension: without magnetic field, the magnetization is zero $m = 0$ at any temperature.

High temperatures. The high temperature limit corresponds to $\beta J \ll 1$. Recall that the partition function is

$$Z = \sum_{\{S_i\}} \exp \left[\beta J \sum_{\langle ij \rangle} S_i S_j \right] = \sum_{\{S_i\}} \prod_{\langle ij \rangle} e^{\beta J S_i S_j}$$

The exponential can be expressed in terms of hyperbolic functions

$$\begin{aligned} e^{\beta J S_i S_j} &= \cosh(\beta J S_i S_j) + \sinh(\beta J S_i S_j) = \cosh(\beta J) + S_i S_j \sinh(\beta J) \\ &= \cosh(\beta J) [1 + S_i S_j \tanh(\beta J)] \end{aligned}$$

where one rewrites them in terms of their Taylor expansion noting that $S_i S_j = \pm 1$. Therefore, the partition function is

$$\begin{aligned} Z &= \sum_{\{S_i\}} \prod_{\langle ij \rangle} \cosh(\beta J) [1 + S_i S_j \tanh(\beta J)] = [\cosh(\beta J)]^{\frac{1}{2}qN} \sum_{\{S_i\}} \prod_{\langle ij \rangle} [1 + S_i S_j \tanh(\beta J)] \\ &= [\cosh(\beta J)]^{\frac{1}{2}qN} \sum_{\{S_i\}} [1 + S_i S_j \tanh(\beta J) + S_i S_j S_l S_m \tanh^2(\beta J) + \dots] \end{aligned}$$

Since $\beta J \ll 1$, one can clearly see a power expansion in the hyperbolic tangent $\tanh(\beta J)$.

The leading term is simple and requires no graphs

$$\sum_{\{S_i\}} 1 = 2^N$$

The first order correction is

$$\sum_{\{S_i\}} S_i S_j = (+1)(+1) + (+1)(-1) + (-1)(+1) + (-1)(-1) = 1 - 1 - 1 + 1 = 0$$

and each power of the hyperbolic tangent can be represented as a line

$$\begin{array}{c} \circ \text{---} \circ \\ i \quad j \end{array} = S_i S_j \tanh(\beta J)$$

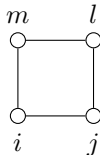
The second order term is

$$\sum_{\{S_i\}} S_i S_j S_l S_m$$

The following diagrams contribute with zero

$$\begin{array}{ccc} \begin{array}{c} \circ \text{---} \circ \\ i \quad j \end{array} & \begin{array}{c} \circ \text{---} \circ \\ l \quad m \end{array} & \begin{array}{c} \circ \text{---} \circ \text{---} \circ \\ i \quad j=l \quad m \end{array} \end{array}$$

The first non-trivial contribution comes from



which corresponds to

$$[\tanh(\beta J)]^4 \sum_{\{S_i\}} S_i S_j S_j S_l S_l S_m S_m S_i = 2^N [\tanh(\beta J)]^4$$

One notices that only even powers contribute: each dot has to be connected with an even number of links. This graph has degeneracy N . The third order term is



and has degeneracy $2N$. For the fourth order term there are four possible graphs, one of which is composed of two disconnected squares and has degeneracy $\frac{1}{2}N(N-5)$. See Tong, p. 164.

Thus, the contributions give the expansion

$$Z[\beta] = 2^N (\cosh \beta J)^{\frac{1}{2}qN} \left[1 + N(\tanh \beta J)^4 + 2N(\tanh \beta J)^6 + \frac{1}{2}N(N+9)(\tanh \beta J)^8 + \dots \right]$$

Kramers–Wannier duality. This expression is very similar to the low temperature expansion $\tilde{\beta} \gg 1$. If one identifies

$$e^{-2\tilde{\beta}J} = \tanh \beta J \iff \sinh 2\tilde{\beta}J = \frac{1}{\sinh 2\beta J}$$

then one can establish a map between the high and low temperature expansions

$$Z[\beta] = \frac{1}{2} (\sinh 2\beta J)^N Z[\tilde{\beta}] = 2^{N-1} (\cosh \beta J \sinh \beta J)^N Z[\tilde{\beta}]$$

This is the Kramers–Wannier duality. The graphs in the two regimes are the dual of each other (see Tong, p. 167).

A phase transition is expected to appear at the self-dual point

$$\beta = \tilde{\beta} \implies \sinh 2\beta J = 1 \implies kT_c = \frac{2J}{\ln(1 + \sqrt{2})} \approx 2.269 J$$

This value coincides with the exact solution of Onsager. Notice how the coefficient of J is consistent with the heuristic Peierls droplet argument

$$kT_c = \frac{2J}{\alpha}, \quad \ln 2 < \alpha < \ln 3$$

Lecture 15

6.5 Landau theory

See Tong, SP, §5.4. The Landau theory is a qualitative approach to the study of phase transitions and critical phenomena. Its main tool are symmetries. The theory has a quantitative extension called Ginzburg–Landau theory.

Notice that, in the mean-field theory, the free energy of the Ising model is

$$F(m) = -\frac{1}{\beta} \ln Z = \frac{1}{2} N J q m^2 - \frac{N}{\beta} \ln [2 \cosh(\beta J q m + \beta B)]$$

It is defined only for systems at equilibrium, meaning values of the magnetization m that solve the consistency equation

$$m = \frac{1}{\beta N} \partial_B \ln Z(m) = \tanh[\beta(J q m + B)]$$

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If one analytically continues $F(m)$ to any value of m , even to states away from equilibrium, then equilibrium corresponds to a minimum of the free energy and so one finds the consistency condition

$$\partial_m F(m) = 0 \iff m = \tanh[\beta(Jqm + B)]$$

Landau proposes that, in order to describe a system approaching a critical point, it is necessary to define an order parameter (e.g. m) which is zero in the disordered phase and different from zero in the ordered phase. Then, one may write the free energy as a power series in the order parameter (respecting always the symmetries of the system). Finally, one studies the equilibrium configurations from which one may draw the phase diagram.

Landau's approach to the Ising model. Consider the Ising model with no magnetic field. The order parameter is the magnetization m and the system exhibits a \mathbb{Z}_2 symmetry, so only even powers of the parameter m are allowed. The Landau ansatz is

$$F(T, m) = F_0(T) + a(T)m^2 + b(T)m^4 + \dots$$

where the coefficient $a(T) \sim T - T_c$ is proportional to the control parameter $T - T_c$ and $b(T) > 0$. One may check that the mean-field approximation is consistent with this ansatz

$$\begin{aligned} F(m) &= \frac{1}{2}NJqm^2 - \frac{N}{\beta} \ln[2 \cosh(\beta Jqm)] \\ &= -\frac{N}{\beta} \ln 2 + \frac{1}{2}NJq(1 - \beta Jq)m^2 + \frac{1}{24}N\beta^3 J^4 q^4 m^4 + \dots \end{aligned}$$

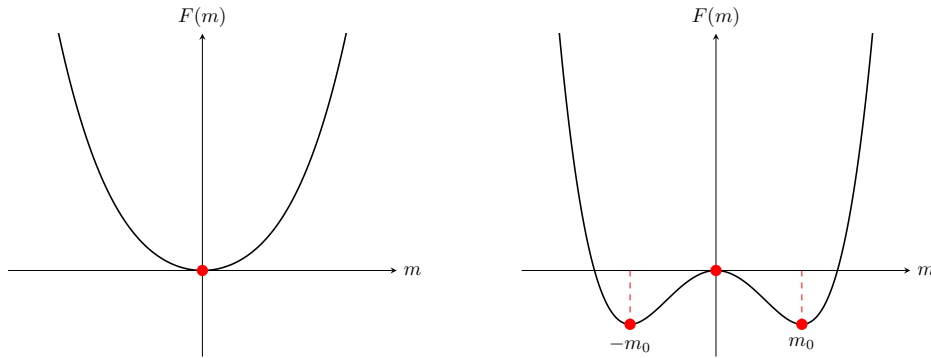
where one recalls

$$1 - \beta Jq = 1 - \frac{T_c}{T}$$

The condition for equilibrium is

$$\partial_m F = 2a(T)m + 4b(T)m^3 = 0$$

The two possible cases are the following. The stationary points are highlighted in red.



The first graph is for $a(T) > 0$, equivalent to $T > T_c$. The equilibrium condition gives

$$\partial_m F = 0 \implies m = 0$$

The second graph corresponds to $a(T) < 0$, that is $T < T_c$. The equilibrium condition implies

$$\partial_m F = 0 \implies m = 0, \pm m_0, \quad m_0 = \sqrt{-\frac{a(T)}{2b(T)}}$$

This means also that

$$m \sim (T_c - T)^{\frac{1}{2}}$$

from which the critical exponent is $\beta = 1/2$ in any dimension: the Landau theory is only qualitative.

The order parameter m is continuous at the phase transition point, so the free energy at quartic order is

$$F(m(T)) = F(T) = \begin{cases} F_0(T), & T > T_c, \quad m = 0 \\ F_0(T) - \frac{a(T)^2}{4b(T)} + \dots, & T < T_c, \quad m = m_0 \end{cases}$$

where one has substituted m with m_0 so the free energy is computed at equilibrium. At the critical temperature, the first coefficient of the expansion is zero

$$a(T) \sim T - T_c = 0 \iff T = T_c$$

Therefore, the free energy $F(T)$ is continuous at the critical point T_c . The entropy is

$$S = -\partial_T F = - \begin{cases} F'_0(T), & T > T_c \\ F'_0(T) - \frac{2a'(T)a(T)}{4b(T)} + (\propto a(T)) + \dots, & T < T_c \end{cases}$$

Since $a(T_c) = 0$, then the entropy is continuous at the critical point T_c , too. The heat capacity is

$$C = \partial_T E = T \partial_T S = -T \begin{cases} F''_0(T), & T > T_c \\ F''_0(T) - [a'(T)]^2(\dots), & T < T_c \end{cases}$$

It is discontinuous at the critical temperature since $a'(T_c) \neq 0$. Therefore, the phase transition is second-order. If one wants to explicitly compute some quantity at equilibrium, one should first substitute the equilibrium value of m and work with $F(m(T))$ rather than with the above ansatz $F(T, m)$.

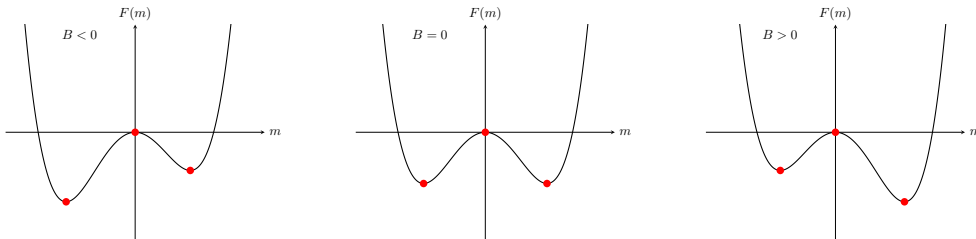
Spontaneous symmetry breaking. Second-order phase transitions correspond to the spontaneous breaking of a (global) symmetry. Without any external magnetic field, the free energy of the Ising model is invariant under the \mathbb{Z}_2 transformation $m \rightarrow -m$. However, below the critical temperature T_c , the system must choose between two ground states $m = +m_0$ or $m = -m_0$. Either choice breaks the \mathbb{Z}_2 symmetry.

First-order phase transition. The Landau approach can also be applied to the case where the magnetic field is present $B \neq 0$. The order parameter is still the magnetization m , but the \mathbb{Z}_2 symmetry is explicitly broken by the presence of the magnetic field.

The ansatz of the free energy includes also odd powers

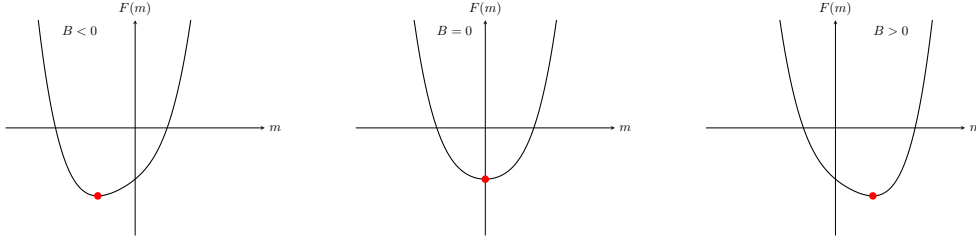
$$F(T, m) = F_0(T) + g(T)m + a(T)m^2 + h(T)m^3 + b(T)m^4 + \dots$$

where the coefficient $a(T) \sim T - T_c$ is proportional to the control parameter, also $g(T) \sim B$ and $h(T) > 0$. The equilibrium analysis follows. Let $T < T_c$, meaning $a < 0$. Then there are three possible cases



In the first graph, the magnetic field is negative. There are three extrema: the left-most is the stable solution with $m < 0$, the center is unstable and the right-most is meta-stable. In the second graph, the magnetic field is absent and there are two stable minima $m = \pm m_0$. In the third graph, the magnetic field is positive and the situation is opposite of the one of the first graph: the right-most minimum is the only one stable and has $m > 0$. If one increases the magnetic field B from negative to positive, keeping the temperature below the critical temperature $T < T_c$, then the magnetization m jumps from negative to positive. There is a discontinuity in a first derivative: this is a first-order phase transition.

Let $T > T_c$, meaning $a > 0$. The three possible cases of the magnetic field are



In this case, when going from negative magnetic field to positive, the magnetization goes continuously from negative to positive: there is no phase transition.

This is consistent with the (B, T) phase diagram from mean-field theory that one has previously seen.

6.6 Ginzburg–Landau theory

See Tong, SP, §5.5, Statistical Field Theory, §§1.3, 2. One would like to include fluctuations, since they become dominant at critical points. So far the magnetization has been constant in all of the lattice. Now one allows the order parameter m (and also the magnetic field) to be a function of the position $m(x)$.

Coarse-graining procedure. The coarse-graining procedure divides the lattice into cells where one defines in each the magnetization

$$m(x) = \frac{1}{N_\alpha} \sum_{i \in \alpha} S_i$$

Each value is associated to the midpoint of the cell α . The magnetization is a discrete variable taking values only at discrete values of the position x given by the midpoint of each cell. By considering small enough cells, one may treat the magnetization $m(x)$ as a function of a continuous variable x , i.e. a field.

Consider the canonical partition function

$$Z = \sum_{\{S_i\}} e^{-\beta H(S_i)} = \int dm(x) \sum_{\{S_i\} | m(x)} e^{-\beta H(S_i)} \equiv \int dm(x) e^{-\beta H[m(x)]}$$

The integral is a functional integral (or path integral): it sums over all field configurations $m(x)$. The sum is done over the spin configurations compatible with a given coarse-grained variable $m(x)$. The integral is complicated and the Hamiltonian $H[m]$ cannot be computed. One makes an ansatz for the form of the Hamiltonian, assuming $B = 0$:

$$H[m] = \int d^D x \left[\frac{1}{2} (\nabla m(x))^2 + \frac{1}{2} r_0 m^2(x) + \frac{1}{4!} v_0 m^4(x) + \dots \right]$$

The first term can be interpreted as a stiffness, a resistance, while the other two coefficients are

$$r_0 \sim T - T_c, \quad v_0 = \text{const.} > 0$$

The partition function is then

$$Z = \int dm(x) e^{-\beta H[m]}$$

Since the Hamiltonian is extensive and behaves as

$$H[m] \sim N \sim V$$

the stationary values of $H[m]$ give the dominant contribution to the partition function Z . Assume that the stationary value of the magnetization is constant¹¹ $m(x) = m_0$. Then, from the Hamiltonian density, one finds

$$0 = \partial_m \mathcal{H} = \partial_m \left[\frac{1}{2} r_0 m_0^2 + \frac{1}{4!} v_0 m_0^4 + \dots \right] = r_0 m_0 + \frac{1}{6} v_0 m_0^3 \implies m_0 = 0, \pm \sqrt{-\frac{6r_0}{v_0}}$$

¹¹The case in which the magnetization that extremizes the Hamiltonian is not constant happens, for example, for solitonic configurations.

which are the same values as the ones obtained previously through the Landau theory (in fact, in such case the magnetization is constant to begin with). Therefore, the dominant value gives

$$Z \sim e^{-\beta H[m_0]}$$

which is similar to result in the Landau theory by swapping $H[m_0]$ with $F(m)$.

Fluctuations. One would like also to include fluctuations around the stationary point. One may expand the magnetization

$$m(x) = m_0 + \delta m(x)$$

into the Hamiltonian density to find

$$\mathcal{H}[m_0 + \delta m(x)] = \mathcal{H}[m_0] + \frac{1}{2}(\nabla \delta m(x))^2 + (\delta m(x))^2 \left[\frac{1}{2}r_0 + \frac{1}{4}v_0 m_0^2 \right] + (\delta m(x))^4 [\dots] + \dots$$

There is no linear term in $\delta m(x)$ since the Hamiltonian is stationary around m_0 . Let

$$\frac{1}{2}a \equiv \frac{1}{2}r_0 + \frac{1}{4}v_0 m_0^2 \sim r_0 \sim T - T_c$$

Truncating at second order gives

$$Z = e^{-\beta H[m_0]} \int d\delta m(x) \exp \left[-\frac{1}{2}\beta \int d^D x (\nabla \delta m(x))^2 + a(\delta m(x))^2 \right]$$

This is a quadratic path integral and as such can be solved analytically.

Lecture 16

Consider the discrete Fourier transform

$$\delta m(x) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{x}} \delta m_{\mathbf{k}}, \quad V = L^D, \quad \mathbf{k} = \frac{2\pi}{L} \mathbf{n}$$

where one notes that, since $\delta m(x) \in \mathbb{R}$ then $\delta m_{\mathbf{k}}^* = \delta m_{-\mathbf{k}}$. The integral in the exponential becomes

$$\begin{aligned} \int d^D x (\nabla \delta m(x))^2 + a(\delta m(x))^2 &= \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} \int d^D x [i\mathbf{k} \cdot i\mathbf{k}' + a] e^{i\mathbf{x} \cdot (\mathbf{k} + \mathbf{k}')} \delta m_{\mathbf{k}} \delta m_{\mathbf{k}'} \\ &= \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} [-\mathbf{k} \cdot \mathbf{k}' + a] \delta m_{\mathbf{k}} \delta m_{\mathbf{k}'} \int d^D x e^{i\mathbf{x} \cdot (\mathbf{k} + \mathbf{k}')} \\ &= \sum_{\mathbf{k}, \mathbf{k}'} [-\mathbf{k} \cdot \mathbf{k}' + a] \delta m_{\mathbf{k}} \delta m_{\mathbf{k}'} \delta(\mathbf{k} + \mathbf{k}') \\ &= \sum_{\mathbf{k}} [k^2 + a] \delta m_{\mathbf{k}} \delta m_{-\mathbf{k}} \\ &= \sum_{\mathbf{k}} [k^2 + a] |\delta m_{\mathbf{k}}|^2 \end{aligned}$$

where¹²

$$\int d^D x e^{i\mathbf{x} \cdot (\mathbf{k} + \mathbf{k}')} = V \delta(\mathbf{k} + \mathbf{k}')$$

The functional integral can be expressed as a functional sum over all the Fourier modes

$$\int d\delta m(x) = \mathcal{N} \prod_{\mathbf{k}} \int d\delta m_{\mathbf{k}} d\delta m_{\mathbf{k}}^*$$

where \mathcal{N} is the normalization. Thus the partition function is

$$Z = \mathcal{N} e^{-\beta H[m_0]} \prod_{\mathbf{k}} \int d\delta m_{\mathbf{k}} d\delta m_{\mathbf{k}}^* e^{-\frac{1}{2}\beta(k^2 + a)|\delta m_{\mathbf{k}}|^2} = \mathcal{N} e^{-\beta H[m_0]} \prod_{\mathbf{k}} \left[\frac{2\pi}{\beta(k^2 + a)} \right]^{\frac{1}{2}}$$

where the sum over momenta has been absorbed into the product.

¹²See <https://math.stackexchange.com/q/3814073/>.

Correlation functions. See also Kardar, Statistical physics of fields, §§3.2, 3.3. The fluctuations are best described by correlation functions

$$\langle \delta m(x) \delta m(0) \rangle = \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} e^{i(\mathbf{k} \cdot \mathbf{x} + \mathbf{k}' \cdot \mathbf{0})} \langle \delta m_{\mathbf{k}} \delta m_{\mathbf{k}'} \rangle$$

In momentum space, the correlation function is

$$\begin{aligned} \langle \delta m_{\mathbf{k}} \delta m_{\mathbf{k}'} \rangle &= \frac{1}{Z} \mathcal{N} e^{-\beta H[m_0]} \\ &\times \prod_{\mathbf{k}''} \int d\delta m_{\mathbf{k}''} d\delta m_{\mathbf{k}''}^* \delta m_{\mathbf{k}} \delta m_{\mathbf{k}'} \exp \left[-\frac{1}{2} \beta (k''^2 + a) |\delta m_{\mathbf{k}''}|^2 \right] \\ &= \frac{\prod_{\mathbf{k}''} \int d\delta m_{\mathbf{k}''} d\delta m_{\mathbf{k}''}^* \delta m_{\mathbf{k}} \delta m_{\mathbf{k}'} e^{-\frac{1}{2} \beta (k''^2 + a) |\delta m_{\mathbf{k}''}|^2}}{\prod_{\mathbf{k}} \int d\delta m_{\mathbf{k}} d\delta m_{\mathbf{k}}^* e^{-\frac{1}{2} \beta (k^2 + a) |\delta m_{\mathbf{k}}|^2}} \\ &= \delta(\mathbf{k} + \mathbf{k}') \frac{\prod_{\mathbf{k}''} \int d\delta m_{\mathbf{k}''} d\delta m_{\mathbf{k}''}^* |\delta m_{\mathbf{k}}|^2 e^{-\frac{1}{2} \beta (k''^2 + a) |\delta m_{\mathbf{k}''}|^2}}{\prod_{\mathbf{k}} \int d\delta m_{\mathbf{k}} d\delta m_{\mathbf{k}}^* e^{-\frac{1}{2} \beta (k^2 + a) |\delta m_{\mathbf{k}}|^2}} \\ &= -\delta(\mathbf{k} + \mathbf{k}') \frac{2}{k^2 + a} \partial_{\beta} \ln \left[\int d\delta m_{\mathbf{k}} \delta m_{\mathbf{k}}^* \exp \left(-\frac{1}{2} \beta (k^2 + a) |\delta m_{\mathbf{k}}|^2 \right) \right] \\ &= -\delta(\mathbf{k} + \mathbf{k}') \frac{1}{k^2 + a} \partial_{\beta} \ln \frac{2\pi}{\beta(k^2 + a)} = \frac{\delta(\mathbf{k} + \mathbf{k}')}{\beta(k^2 + a)} \end{aligned}$$

At the third equality, each $\delta m_{\mathbf{k}}$ is an odd quantity over the domain of integration, therefore the integral is zero (since it is a Gaussian integral with zero mean) unless the momenta \mathbf{k} and \mathbf{k}' are equal (or opposite). At the penultimate equality, notice that every time \mathbf{k}'' is not either \mathbf{k} nor \mathbf{k}' , the numerator and denominator cancel, so there is no reason to keep the product over \mathbf{k}'' .

Going back to position space gives

$$\begin{aligned} \langle \delta m(x) \delta m(0) \rangle &= \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} \langle \delta m_{\mathbf{k}} \delta m_{\mathbf{k}'} \rangle e^{i\mathbf{k} \cdot \mathbf{x}} = \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} \delta(\mathbf{k} + \mathbf{k}') \frac{e^{i\mathbf{k} \cdot \mathbf{x}}}{\beta(k^2 + a)} = \frac{1}{V} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot \mathbf{x}}}{\beta(k^2 + a)} \\ &\rightarrow \frac{1}{\beta} \int \frac{d^D k}{(2\pi)^D} \frac{e^{i\mathbf{k} \cdot \mathbf{x}}}{k^2 + a} \sim \begin{cases} e^{-\frac{x}{\xi}} (x^{\frac{D-1}{2}})^{-1}, & x > \xi \\ (x^{D-2+\eta})^{-1}, & x \lesssim \xi \end{cases} \end{aligned}$$

At the second line, one performs the continuum limit. In the Gaussian approximation, one has

$$\xi = \frac{1}{\sqrt{a}} \sim \frac{1}{\sqrt{T - T_c}}, \quad \eta = 0$$

while in general

$$\xi \sim (T - T_c)^{-\nu}, \quad \eta \neq 0$$

where the parameters ν and η are critical exponents. When two points are far apart, their correlation decays exponentially. When two points are close, their correlation is a power law. The scale ξ is the correlation length which can be interpreted as follows: the number of correlated degrees of freedom is given by ξ^D or, equivalently, ξ is the size of the regions of the system that are correlated. At the critical temperature T_c , the correlation length diverges $\xi \rightarrow \infty$: all the regions of the system are correlated. The whole system has the same collective behaviour.

For distances less than the correlation length $x \lesssim \xi$, the (connected) correlation function behaves as

$$\Gamma(x) \equiv \langle \delta m(x) \delta m(0) \rangle \sim (x^{D-2+\eta})^{-1} = (x^{2\Delta(m)})^{-1}$$

where one finds the scaling dimension to be

$$\Delta(m) = \frac{D - 2 + \eta}{2}$$

The connected correlation function $\Gamma(x)$ has a power law scaling and, under rescaling, is self-similar

$$\Gamma(x/\lambda) = \lambda^{2\Delta(m)} \Gamma(x)$$

from this one sees that $\eta/2$ is the anomalous dimension, since λ carries the dimension of the correlation function. This feature signals that, at the critical temperature, the system has a new (emergent) symmetry called scale-invariance. If one works with dimensionless quantities, the only scale of the system is the correlation length ξ . When the correlation length diverges at the critical temperature (or is zero), the system becomes scale-invariant. In most systems, scale-invariance is further enhanced to conformal invariance. Conformal symmetry is related to the conformal group which is large¹³ and imposes strong constraints on the correlation functions. At the critical point, a system is described by conformal field theories. Conformal invariance is enough to completely fix the functional form of two-point correlation functions up to a multiplicative constant factor.

Gaussian approximation. In the Gaussian approximation one has

$$\eta = 0, \quad \xi = \frac{1}{\sqrt{a}}$$

where one recalls

$$\frac{1}{2}a = \frac{1}{2}r_0 + \frac{1}{4}v_0m_0^2, \quad m_0 = \pm\sqrt{-\frac{6r_0}{v_0}}$$

The critical behaviour of these parameters is

$$r_0 \sim T - T_c, \quad a \sim T - T_c$$

Therefore, in the Gaussian approximation one finds

$$m_0 \sim |T - T_c|^\beta = |T - T_c|^{\frac{1}{2}}, \quad \xi \sim (T - T_c)^{-\nu} = (T - T_c)^{-\frac{1}{2}}$$

from which the critical exponents are

$$\beta = \frac{1}{2}, \quad \nu = \frac{1}{2}$$

The Ginzburg–Landau approach, in the Gaussian approximation, gives the same critical exponents as the mean-field approximation and the Landau theory. To find the correct values of the critical exponents, one needs to include higher order terms which requires statistical field theory. One only needs to include the few relevant interactions in the Hamiltonian and, to decide which are needed, one needs to utilize the renormalization group.

Lecture 17

Upper critical dimension. One may estimate how good the Gaussian approximation is. One may study the behaviour of the fluctuations. In order to trust the calculations, the fluctuations should be smaller than the background around which they are fluctuating:

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$$\text{var}(m) = \langle (m)^2 \rangle - \langle m \rangle^2 \ll 1$$

Since the fluctuations decay after a distance $r > \xi$, then one can gain a measure of their importance by integrating over a ball of radius ξ

$$\begin{aligned} R &= \frac{\int_0^\xi d^D x \langle \delta m(x) \delta m(0) \rangle}{\int_0^\xi d^D x \langle m(x) \rangle^2} \sim \frac{\int_0^\xi d^D x (x^{D-2})^{-1}}{\int_0^\xi d^D x m_0^2} = \frac{\int_0^\xi x^{D-1} dx (x^{D-2})^{-1}}{m_0^2 \int_0^\xi x^{D-1} dx} \\ &\sim \frac{\xi^2}{m_0^2 \xi^D} = \frac{\xi^{2-D}}{m_0^2} \sim \frac{|T - T_c|^{-\frac{2-D}{2}}}{|T - T_c|} = |T - T_c|^{\frac{D-4}{2}} \end{aligned}$$

For higher dimensions¹⁴, $D \geq 4$, fluctuations are negligible around the critical point

$$T \rightarrow T_c \implies R < \infty$$

In the opposite case, $D < 4$, the ratio diverges and fluctuations are dominant. From this, four dimensions $D = 4$ is the upper critical dimensions, where fluctuations are suppressed and the mean-field and Gaussian approximations can be used. For two and three dimensions, one needs to include higher relevant interactions.

¹³It contains the Poincaré group and the special conformal generators.

¹⁴Notice that for $D = 4$ there is a logarithmic divergence.

Lower critical dimension. One dimension $D = 1$ is the lower critical dimension of systems with phase transitions associated to spontaneous symmetry breaking of discrete symmetries (e.g. \mathbb{Z}_2). In one dimension there is no phase transition. The Ising model has an exact solution in which the magnetization is zero at any temperature. From the Peierls droplet model, in one dimension, one sees that it requires always the same energy to create droplets of flipped spins of any size: entropy wins over order. In general, if there is no spontaneous breaking of symmetry, then there is no second-order phase transition, as seen in the Landau theory. However, this correspondence breaks down in one dimension [r]. Notice that a statistical field theory in 1 dimension is related to a quantum field theory in $(0+1)$ dimensions, i.e. quantum mechanics. In quantum mechanics, a theory with a potential symmetric under \mathbb{Z}_2 has a unique ground state (and not two) due to quantum tunnelling. Therefore there is no degeneracy and there is no spontaneous symmetry breaking, so no phase transition. For systems with continuous symmetries, two dimensions is the lower critical dimension (Mermin–Wagner theorem).

7 On the thermodynamic limit

See Tong, SP, §5.4.3. Phase transitions are signaled by discontinuities in the derivatives of a thermodynamic free energy. These discontinuities can only happen in the thermodynamic limit $N, V \rightarrow \infty$.

Consider a system with N particles in a volume V . Assume the particles to be spheres with finite volume. One may put at most $M(V)$ particles in the volume V . The gran-canonical partition function is of the form

$$\mathcal{Z}(z, V) = 1 + zZ_1(V) + z^2Z_2(V) + \cdots + z^{M(V)}Z_{M(V)}(V)$$

where $Z_k(V)$ is the canonical partition function with k particles. The gran-canonical partition function is a polynomial in z of degree $M(V)$. It is an analytic function and all of its derivatives are still analytic: away from the thermodynamic limit, the polynomial cannot constitute a power series and so no discontinuities may appear. Since $Z_k(V) > 0$, then the polynomial has no positive real roots. Consider the pressure and the density

$$\frac{p}{kT} = \frac{1}{V} \ln \mathcal{Z}(z, V), \quad \frac{N}{V} = \frac{1}{v} = \frac{1}{V} z \partial_z \ln \mathcal{Z}(z, V)$$

For a finite volume V , the gran-canonical partition function is a polynomial and the pressure p and inverse density v are analytic functions of the fugacity z . From the second equation, one finds $z = z(v)$ and, substituting it into the first, it gives $p = p(v)$ which is analytic for v real and positive. There are no singularities nor phase transitions at finite volume V or number of particles N .

Lee–Yang theorem. The Lee–Yang theorem states that the limit

$$F_\infty = \lim_{V \rightarrow \infty} \frac{1}{V} \ln \mathcal{Z}(z, V)$$

exists for every $z > 0$ and it is a continuous, non-decreasing function of the fugacity z . The limit does not depend on the shape of the volume (up to some sensible assumptions, such as no fractals). Moreover, let R be a fixed, volume independent, region in the complex z plane which contains part of the real, positive axis $\text{Re } z > 0$. If R contains no zero of the gran-canonical partition function $\mathcal{Z}(z, V)$, then F_∞ is an analytic function of z for all $z \in R$ and the right-hand side converges uniformly to F_∞ . In particular, all derivatives of F_∞ are continuous.

For example, consider a region R containing the whole positive real axis and let the roots of the partition function have all negative real part. The system is in a single phase. The functions

$$\lim_{V \rightarrow \infty} \frac{p(z)}{kT} = F_\infty, \quad \lim_{V \rightarrow \infty} \frac{1}{v(z)} = z \partial_z F_\infty$$

are analytic thanks to uniform convergence. Both the pressure p and the inverse density v are analytic, and so, in the (v, p) plane, the phase curve is analytic and has no discontinuities, so

no phase transitions. As a counter example, if there is a root z_0 on the positive part of the real axis, the region is split in two, R_1 and R_2 . In each, the theorem implies that the above limit is an analytic function, but on the root z_0 there can be discontinuities. The pressure and inverse density are discontinuous or their derivatives are, so in the (v, p) plane the phase curve shows the presence of a region of equilibrium between two phases.

Part III

Renormalization group

See Le Bellac, §3.

8 Spin blocks

The block spin transformation is a renormalization group transformation introduced by Kadanoff to simplify the analysis of the Ising model by reducing the number of degrees of freedom through a grouping of a block of spins. Wilson explored how new and complicated interactions among the blocks arise and how they compensate the loss of degrees of freedom: this is the Wilsonian renormalization group approach.

Block spin transformation in two dimensions. The procedure in two dimensions $D = 2$ is the following. Consider a square lattice of spacing a where there is a spin at each site. The sites can be grouped into blocks where each site is the corner of a square. One then substitutes each block with an average spin, the block spin. In this way one builds a new lattice with spacing $2a$ where at each site sits a block spin. One may rescale the length unit $r \rightarrow r' = r/2$ to maintain a lattice spacing of a . From N spins S_i one goes to $N' = N/4$ block spins S'_α .

The way to assign the block spins is not unique. One may categorize linear and non-linear ways. An example of the latter is a majority rule

$$\begin{aligned} \sum_{i \in \alpha} S_i < 0 &\implies S'_\alpha = -1 \\ \sum_{i \in \alpha} S_i > 0 &\implies S'_\alpha = 1 \end{aligned}$$

If the sums is zero, one may take the top left spin to decide the orientation. An example of the former is the average spin

$$S'_\alpha = \frac{\lambda}{4} \sum_{i=1}^4 S_i, \quad i \in \alpha$$

where λ is a coefficient. From this, one sees that the block spins can take any value, not just ± 1 .

Effective Hamiltonian. Let $kT = 1$ or equivalently consider dimensionless constants inside the Hamiltonian

$$\beta J \rightarrow J, \quad \beta \mu B \rightarrow \mu B$$

The canonical partition function is

$$Z = \sum_{\{S_i\}} e^{-H(S_i)}$$

while the Ising Hamiltonian is

$$H_{\text{Ising}}(S_i) = k_1 \sum_{i=1}^N S_i + k_2 \sum_{\langle ij \rangle} S_i S_j$$

One may use instead a more general Hamiltonian

$$H(S_i) = k_1 \sum_{i=1}^N S_i + k_2 \sum_{nn} S_i S_j + k_3 \sum_{nnn} S_i S_j + k_4 \sum_p S_i S_j S_k S_l + \dots$$

where one sums over nearest neighbours (nn), next-nearest neighbours (nnn), plaquettes p , etc. If one performs the block spin transformation, the block spins S'_α interact through the most general Hamiltonian $H'(S'_\alpha)$ with all possible interactions.

Notice that the block spin transformation is not injective since it is many-to-one. It can be expressed as

$$\sum_{\{S'_\alpha\}} \prod_{\alpha} \delta(S'_\alpha - f(S_i)_{i \in \alpha}) = 1$$

where f is the chosen rule to operate the transformation. It can be inserted into the partition function to have

$$\begin{aligned} Z &= \sum_{\{S_i\}} e^{-H(S_i)} = \sum_{\{S_i\}} \sum_{\{S'_\alpha\}} \prod_{\alpha} \delta(S'_\alpha - f(S_i)) e^{-H(S_i)} \\ &= \sum_{\{S'_\alpha\}} \sum_{\{S_i\}} \prod_{\alpha} \delta(S'_\alpha - f(S_i)) e^{-H(S_i)} \equiv \sum_{\{S'_\alpha\}} e^{-H'(S'_\alpha)} \end{aligned}$$

The Hamiltonian $H'(S'_\alpha)$ is the result of a complicated sum over the spin configurations. As in the Landau theory, one makes an ansatz for this effective Hamiltonian as the most general Hamiltonian respecting the symmetries of the system. Its form is

$$H'(S'_\alpha) = k'_1 \sum_{\alpha=1}^N S'_\alpha + k'_2 \sum_{\langle \alpha \beta \rangle} S'_\alpha S'_\beta + k'_3 \sum_{\langle \alpha \beta \gamma \rangle} S'_\alpha S'_\beta S'_\gamma + \dots$$

The block spin transformation reduces the number of degrees of freedom, but in return it adds many interactions. From the site spin, one goes to the block spin. The coefficients $k = (k_1, \dots, k_n, \dots)$ are mapped into

$$k' = R_{s=2}(k)$$

using the renormalization group transformation, a complicated non-linear transformation.

In general, for a D -dimensional lattice, one may consider blocks with s^D spins, where s is the scale parameter, $s = \sqrt{2}, 2, \sqrt{3}, \dots$. The scale parameter rescales the length unit

$$r \rightarrow r' = \frac{r}{s}$$

which also applies to the correlation length. The rule to construct the block spins is

$$S'_\alpha = \frac{\lambda(s)}{s^D} \sum_{i \in \alpha} S_i$$

One may iterate the block spin transformation

$$R_s \cdots R_s = R_{s^n}$$

The set of transformations has a group-like structure, but the renormalization group is not a group, since there is no inverse. The condition above can be equivalently expressed as the composition of two block spin transformations: a transformation s_1^D followed by s_2^D is equivalent to a single transformation $(s_1 s_2)^D$. This also means that

$$\lambda(s_1) \lambda(s_2) = \lambda(s_1 s_2)$$

which can be satisfied by using

$$\lambda(s) = s^{\Delta(k)}$$

where $\Delta(k)$ is the scaling dimension.

Lecture 18

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Renormalization group equation. One may study the correlation functions

$$\begin{aligned}
 \Gamma(r'_{\alpha\beta}, k') &= \langle S'_\alpha S'_\beta \rangle = \frac{1}{Z} \sum_{\{S'_\gamma\}} S'_\alpha S'_\beta e^{-H'(S'_\gamma)} \\
 &= \frac{1}{Z} \sum_{\{S'_\gamma\}} S'_\alpha S'_\beta \sum_{\{S_i\}} \prod_\gamma \delta\left(S'_\gamma - \frac{\lambda(s)}{s^D} \sum_{i \in \gamma} S_i\right) e^{-H(S_i)} \\
 &= \frac{1}{Z} \sum_{\{S_i\}} \frac{\lambda(s)}{s^D} \left[\sum_{i \in \alpha} S_i \right] \frac{\lambda(s)}{s^D} \left[\sum_{j \in \beta} S_j \right] e^{-H(S_i)} = \frac{\lambda^2(s)}{s^{2D}} \sum_{i \in \alpha} \sum_{j \in \beta} \frac{1}{Z} \sum_{\{S_i\}} S_i S_j e^{-H(S_i)} \\
 &= \frac{\lambda^2(s)}{s^{2D}} \sum_{i \in \alpha} \sum_{j \in \beta} \Gamma(r_{ij}, k) \approx \frac{\lambda^2(s)}{s^{2D}} s^{2D} \Gamma(r_{ij}, k) = \lambda^2(s) \Gamma(r_{ij}, k) = s^{2\Delta} \Gamma(r_{ij}, k)
 \end{aligned}$$

At the last line, one has assumed $\xi \gg sa$ which implies that the correlation function $\Gamma(r_{ij}, k_i)$ varies little as i, j range over the blocks α, β . From this one obtains the renormalization group equation

$$\boxed{\Gamma(r/s, k') = s^{2\Delta} \Gamma(r, k)}, \quad k' = R_s(k)$$

One may study this equation in the proximity of a fixed point

$$k^* = R_s(k^*)$$

from this one sees that, at a fixed point, the correlation functions behave nicely under rescaling: scale invariance is typical of fixed points. One may linearize the renormalization group equation around the fixed point. Under the renormalization group transformation

$$r \rightarrow \frac{r}{s}$$

one rescales also the correlation length ξ . Thus a fixed point (under rescaling) can only exist at $\xi = 0$ or $\xi \rightarrow \infty$. This latter corresponds to a critical point of the system. In general, the fixed points of the renormalization group correspond to critical points of the system. A system at a critical point exhibits scale invariance.

Behaviour near fixed points. One may expand the coefficients around a fixed point

$$k_\alpha = k_\alpha^* + \delta k_\alpha$$

The same is true after a renormalization group transformation. This transformation is linear if the coefficients are close to the fixed point

$$\delta k'_\alpha \approx T_{\alpha\beta} \delta k_\beta$$

In fact

$$(k'_\alpha)^* + \delta k'_\alpha \equiv k'_\alpha \equiv T_{\alpha\beta} (k_\beta^* + \delta k_\beta) = T_{\alpha\beta} k_\beta^* + T_{\alpha\beta} \delta k_\beta$$

Since from the definition of fixed point it holds

$$(k'_\alpha)^* = T_{\alpha\beta} k_\beta^*$$

then one finds the relation above for the variations. Also the linearized renormalization group transformation is

$$T_{\alpha\beta} = \left. \frac{\partial k'_\alpha}{\partial k_\beta} \right|_{k^*}$$

One may diagonalize this matrix. The eigenvalue equation is

$$T_{\alpha\beta} e_\beta^{(i)} = d_i e_\alpha^{(i)}$$

One may decompose the variation as

$$\delta k_\beta = \sum_i t_i e_\beta^{(i)}$$

where t_i are the diagonal and linearized couplings around the fixed point. Recalling the group-like structure

$$T(s_1)T(s_2) = T(s_1 s_2)$$

one finds

$$d_i = s^{\Delta_i}$$

So, under a renormalization group transformation, the linearized and diagonalized couplings t_i behave as

$$t_i \rightarrow t'_i = s^{\Delta_i} t_i, \quad s > 1$$

One may distinguish three cases:

- $\Delta_i > 0$, the coupling is relevant, it becomes greater as the renormalization group transformation is iterated (there are only a few couplings of this type);
- $\Delta_i < 0$, the coupling is irrelevant, it becomes weaker as one iterates (there are infinitely many couplings of this type);
- $\Delta_i = 0$, the coupling is marginal (very rarely there are any coupling of this type).

One may draw the renormalization group flow of the couplings t_i in the space $\{e_\alpha^{(i)}\}$ (where the t_i are the coordinates, i.e. parameter space). One may define the critical surface S_∞ as the locus of points in parameter space that correspond to systems at the critical point (this surface is infinite-dimensional ? [r]). As such, on the surface the correlation length is infinite. The surface contains the fixed point (the origin). By repeatedly applying the renormalization group transformation, the points lying on the surface [r] (i.e. the irrelevant couplings) converge to the fixed point, while any point outside (i.e. the relevant couplings) diverges away from the fixed point.

8.1 Critical exponents of the Ising model

The linearized and diagonalized renormalization group equation is

$$\Gamma(r, t_1, t_2, \dots) = \frac{1}{s^{2\Delta}} \Gamma(r/s, s^{\Delta_1} t_1, s^{\Delta_2} t_2, \dots)$$

For the Ising model, there are two relevant couplings

$$t_1 = \frac{T - T_c}{T_c}, \quad B$$

and there are infinitely many irrelevant couplings. One would like to extract the critical exponents from the renormalization group equation.

On the critical surface. Consider a point on the critical surface by tuning the relevant couplings to zero¹⁵, $t_1 = 0$ and $B = 0$. The correlation length is infinite. The renormalization group equation looks like

$$\Gamma(r; t_1 = 0, \dots, B = 0) = s^{-2\Delta} \Gamma(r/s; t'_1 = 0, \dots, B' = 0)$$

where only the relevant couplings are explicitly written. Taking $s = r/a$, with a the lattice spacing, one finds

$$\Gamma(r; 0, \dots, 0) = \left[\frac{a}{r} \right]^{2\Delta} \Gamma(a; 0, \dots, 0)$$

¹⁵To see this, note that if t_1 say is nonzero, then iteration of the renormalization group transformation moves the representative point away from the fixed point, whence the starting point cannot be on the critical surface. This assumes tacitly that there is no cross-over behaviour. Conversely, if the relevant couplings are all zero, then in the linear approximation the representative point converges to the fixed point, and the starting point must have been on the critical surface.

from which one may extract the dependence on r

$$\Gamma(r) \sim \frac{1}{r^{2\Delta}}$$

Recall that the correlation functions behave as

$$\Gamma(r) \sim \begin{cases} e^{-\frac{r}{\xi}} (r^{\frac{D-1}{2}})^{-1}, & r > \xi \\ (r^{D-2+\eta})^{-1}, & r \lesssim \xi \end{cases}$$

On the critical surface, the second case is the one of interest. Thus, the scaling dimension is

$$\Gamma(r) \sim \frac{1}{r^{D-2+\eta}} \sim \frac{1}{r^{2\Delta}} \implies 2\Delta = D - 2 + \eta$$

Off the critical surface. Consider a point off the critical surface with $B = 0$ and $T > T_c$. Suppose that the renormalization group flow brings the point far enough from the critical surface

$$t'_1 = s^{\Delta_1} t_1 \sim 1 \implies s = t_1^{-\frac{1}{\Delta_1}}$$

From the renormalization group equation, one finds

$$\Gamma(r; t_1, \dots, 0) = s^{-2\Delta} \Gamma(r/s; t'_1, \dots, 0) = s^{-2\Delta} \Gamma(r/t_1^{-\frac{1}{\Delta_1}}; 1, \dots, 0)$$

Since the point is not on the critical surface, the correlation functions behave as

$$\Gamma(r) \sim e^{-\frac{r}{\xi}} (r^{\frac{D-1}{2}})^{-1} = f(r/\xi) (r^{\frac{D-1}{2}})^{-1}$$

From this equation and the first argument of the correlation function on the right-hand side of the equation above, one sees that

$$\xi \sim t_1^{-\frac{1}{\Delta_1}} \sim |T - T_c|^{-\frac{1}{\Delta_1}} \sim |T - T_c|^{-\nu}$$

from which one finds the critical exponent

$$\nu = \frac{1}{\Delta_1}$$

Thus, from $(\eta, \nu) \leftrightarrow (\Delta, \Delta_1)$, one may obtain all other critical exponents through several known expressions

$$\gamma = \beta(\delta - 1), \quad \alpha + 2\beta + \gamma = 2, \quad \dots$$

Magnetization. Consider a uniform magnetic field B . The block spin transformation is

$$S'_\alpha = \frac{s^\Delta}{s^D} \sum_{i \in \alpha} S_i$$

The term appearing in the Hamiltonian is

$$B \sum_i S_i = B s^{D-\Delta} \sum_\alpha S'_\alpha$$

So the transformation for the magnetic field is

$$B \rightarrow B' = s^{D-\Delta} B$$

The renormalization group equation becomes

$$\Gamma(r; t_1, \dots, B) = s^{-2\Delta} \Gamma(r/s; s^{\Delta_1} t_1, \dots, s^{D-\Delta} B)$$

where the dots denote irrelevant couplings. One may proceed more directly by studying the magnetization M . Noting that

$$\Gamma(r) \sim \langle \delta m(r) \delta m(0) \rangle \sim \langle S(r) S(0) \rangle, \quad M = \langle S \rangle$$

one schematically finds

$$M \sim \sqrt{\Gamma}$$

In fact, the magnetization transforms as

$$M(t_1, \dots, B) = s^{-\Delta} M(s^{\Delta_1} t_1, \dots, s^{D-\Delta} B)$$

At the critical temperature $T = T_c$, one has $t_1 = 0$, but the magnetic field is non-zero, so its renormalization group flow diverges

$$B' = s^{D-\Delta} B = 1 \implies s = B^{-\frac{1}{D-\Delta}}$$

from which

$$M(0, \dots, B) = B^{\frac{\Delta}{D-\Delta}} M(0, \dots, 1)$$

Therefore, at the critical temperature, the behaviour of the magnetization is

$$M \sim B^{\frac{\Delta}{D-\Delta}} \sim B^{\frac{1}{\delta}}, \quad T = T_c \implies \boxed{\delta = \frac{D-\Delta}{\Delta}}$$

Below the critical temperature, $T < T_c$, and for $B = 0$, the renormalization group flow is

$$t'_1 = s^{\Delta_1} t_1 = -1 \implies s = (-t_1)^{-\frac{1}{\Delta_1}}$$

from which

$$M(t_1, \dots, 0) = (-t_1)^{\frac{\Delta}{\Delta_1}} M(-1, \dots, 0)$$

Therefore, the behaviour is

$$M(t_1) \sim (-t_1)^{\frac{\Delta}{\Delta_1}} \sim (T_c - T)^{\frac{\Delta}{\Delta_1}} \sim (T_c - T)^\beta \implies \boxed{\beta = \frac{\Delta}{\Delta_1}}$$

The only important quantities needed to study a system are the relevant couplings. To study each relevant coupling, one tunes all the others to zero and studies how the renormalization group acts.

Lecture 19

8.2 Triangular Ising model

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See Le Bellac, §3.3. Consider a two-dimensional Ising model on a triangular lattice. The scale parameter is $s = \sqrt{3}$. The number of spins in each spin block is

$$s^D = (\sqrt{3})^2 = 3$$

Each block is composed of the three vertices of a triangle. The block spin transformation is

$$S'_\alpha = \text{sign}(S_\alpha^{(1)} + S_\alpha^{(2)} + S_\alpha^{(3)}) = f(S_\alpha^{(i)})$$

One may split the Hamiltonian into

$$H = H_0 + V$$

where H_0 describes the interactions among the spins within the same block and V describes the interactions between spins belonging to different blocks. The transformed, effective Hamiltonian is

$$\begin{aligned} e^{-G} e^{-H'(S')} &= \sum_{\{S_i\}} \prod_{\alpha} \delta(S'_\alpha - f(S_\alpha^{(i)})) e^{-H(S_i)} \\ &= \frac{1}{Z_0} \sum_{\{S_i\}} \prod_{\alpha} \delta(S'_\alpha - f(S_\alpha^{(i)})) e^{-H_0 - V} Z_0 = \langle e^{-V} \rangle_0 Z_0 \end{aligned}$$

where G is a normalization constant and

$$Z_0 \equiv \sum_{\{S_i\}} \prod_{\alpha} \delta(S'_\alpha - f(S_\alpha^{(i)})) e^{-H_0} = [(Z_0)_{\text{single block}}]^{\frac{N}{3}}$$

Partition function. The Hamiltonian of each block is

$$H_0 = -k(S_\alpha^{(1)} S_\alpha^{(2)} + S_\alpha^{(1)} S_\alpha^{(3)} + S_\alpha^{(2)} S_\alpha^{(3)})$$

One may compute the partition function of a single block. Recalling the block spin transformation used in this case, there are four configurations with $S'_\alpha = 1$

$$\uparrow\uparrow\uparrow, \quad \uparrow\uparrow\downarrow, \quad \uparrow\downarrow\uparrow, \quad \downarrow\uparrow\uparrow$$

Therefore

$$(Z_0)_{\text{s.b. w/ } S'_\alpha=1} = \sum_{\{S_\alpha^{(i)}\} | S'_\alpha=1} \delta(1 - f(S_\alpha^{(i)})) e^{-H_0} = e^{3k} + 3e^{-k}$$

Similarly, for $S'_\alpha = -1$ one finds

$$(Z_0)_{\text{s.b. w/ } S'_\alpha=-1} = e^{3k} + 3e^{-k}$$

Thus the partition function is

$$Z_0 = [(Z_0)_{\text{s.b.}}]^{\frac{N}{3}} = (e^{3k} + 3e^{-k})^{\frac{N}{3}}$$

Average value. One would like to compute the average value $\langle e^{-V} \rangle_0$. One assumes that the interaction V is small enough so that¹⁶

$$\langle e^{-V} \rangle_0 \sim \langle 1 - V \rangle_0 \sim 1 - \langle V \rangle_0 \sim e^{-\langle V \rangle_0}$$

One needs to evaluate the average $\langle V \rangle_0$. Consider a two-block interaction of the type

$$V_{\alpha\beta} = -kS_\alpha^{(1)}(S_\beta^{(2)} + S_\beta^{(3)})$$

Since the Hamiltonian H_0 contains no interactions between different blocks, then one may factorize the average values

$$\langle V_{\alpha\beta} \rangle_0 = -k\langle S_\alpha^{(1)} \rangle_0 [\langle S_\beta^{(2)} \rangle_0 + \langle S_\beta^{(3)} \rangle_0]$$

In this way one just needs to compute one term

$$\langle S_\alpha^{(1)} \rangle_0 = \frac{1}{(Z_0)_{\text{s.b.}}} \sum_{\{S_\alpha^{(i)}\}} S_\alpha^{(1)} \delta(S'_\alpha - f(S_\alpha^{(i)})) e^{-H_0}$$

For $S'_\alpha = 1$ one finds the contribution

$$\sum_{\{S_\alpha^{(i)}\}} S_\alpha^{(1)} \delta(1 - f(S_\alpha^{(i)})) e^{-H_0} = e^{3k} + e^{-k}$$

while for $S'_\alpha = -1$ one finds the opposite

$$\sum_{\{S_\alpha^{(i)}\}} S_\alpha^{(1)} \delta(1 + f(S_\alpha^{(i)})) e^{-H_0} = -(e^{3k} + e^{-k})$$

Therefore

$$\langle S_\alpha^{(1)} \rangle_0 = \frac{1}{(Z_0)_{\text{s.b.}}} (e^{3k} + e^{-k}) S'_\alpha$$

So, the average interaction is

$$\begin{aligned} -\langle V_{\alpha\beta} \rangle_0 &= k\langle S_\alpha^{(1)} \rangle_0 [\langle S_\beta^{(2)} \rangle_0 + \langle S_\beta^{(3)} \rangle_0] = 2k\langle S_\alpha^{(1)} \rangle_0 \langle S_\beta^{(2)} \rangle_0 \\ &= \frac{2k}{[(Z_0)_{\text{s.b.}}]^2} (e^{3k} + e^{-k})^2 S'_\alpha S'_\beta = 2k \frac{(e^{3k} + e^{-k})^2}{(e^{3k} + 3e^{-k})^2} S'_\alpha S'_\beta = k' S'_\alpha S'_\beta \end{aligned}$$

The relationship between the block spin coupling and the original coupling is non-linear

$$k' = 2k \left[\frac{e^{3k} + e^{-k}}{e^{3k} + 3e^{-k}} \right]^2$$

¹⁶The proper argument uses the cumulant expansion. See Le Bellac, after eq. (3.3.3).

Transformed Hamiltonian. From this, one may identify the normalization constant and the block spin Hamiltonian

$$e^{-G} e^{-H'(S')} = [(Z_0)_{\text{s.b.}}]^{\frac{N}{3}} e^{-\langle V \rangle_0} = [(Z_0)_{\text{s.b.}}]^{\frac{N}{3}} \exp \left[k' \sum_{\langle \alpha \beta \rangle} S'_\alpha S'_\beta \right]$$

as

$$G = -\frac{N}{3} \ln(Z_0)_{\text{s.b.}} = -\frac{N}{3} \ln(e^{3k} + 3e^{-k}), \quad H'(S') = -k' \sum_{\langle \alpha \beta \rangle} S'_\alpha S'_\beta$$

Due to the approximations performed, the block spin transformation does not add any new interactions and the only effect is the non-trivial renormalization of the coupling. The fixed point satisfies

$$k^* = 2k^* \left[\frac{e^{3k^*} + e^{-k^*}}{e^{3k^*} + 3e^{-k^*}} \right]^2 \implies k^* = \frac{1}{4} \ln(1 + 2\sqrt{2}) \approx 0.336$$

One may determine the scaling dimension from

$$s^{\Delta_1} = d_k k'|_{k^*} \approx 1.634$$

and also the critical exponent

$$\boxed{\nu = \frac{1}{\Delta_1} \approx 1.118}, \quad s = \sqrt{3}$$

These can be compared to the exact results

$$k^* = 0.275, \quad \nu = 1$$

and one may notice an improvement over the mean-field approximation

$$k^* = \frac{1}{6}, \quad \nu = \frac{1}{2}$$

9 General facts about critical phenomena

A list of general facts about critical phenomena is the following.

- Spontaneous symmetry breaking is related to the presence of phase transitions of second and higher orders¹⁷.
- Phase transitions are signaled by discontinuities in the derivatives of a thermodynamic free energy. These discontinuities can only happen in the thermodynamic limit $N, V \rightarrow \infty$.
- For any transition, one may define some order parameters (e.g. $m, \bar{v}_{\text{gas}} - \bar{v}_{\text{liquid}}$).
- One may describe how a system approaches its critical point by a set of critical exponents. For example, for spins systems

$$m \sim (T_c - T)^\beta, \quad m \sim B^{\frac{1}{\delta}}, \quad \chi \sim (T - T_c)^{-\gamma}$$

where the first is at $T < T_c$ and the second at $T = T_c$; also

$$C \sim (T - T_c)^\alpha, \quad \xi \sim (T - T_c)^{-\nu}, \quad \langle \delta m(x) \delta m(0) \rangle \sim (x^{D-2+\eta})^{-1}$$

where the last is for $x \leq \xi$. Only two exponents are independent, typically one works with η and ν . Another example are liquid-gas systems

$$(v_{\text{gas}} - v_{\text{liquid}}) \sim (T_c - T)^\beta, \quad \bar{p} \sim \bar{v}^\delta, \quad \kappa \sim (T - T_c)^{-\gamma}$$

¹⁷The logical statement is: second and higher orders imply spontaneous symmetry breaking. The liquid-to-solid transition is symmetry breaking, but first order.

- Universality: systems with the same set of critical exponents belong to the same class of universality. For example, the Ising model in three dimensions is in the same universality class as liquid-gas systems.
- The systems possess a correlation length ξ . The number of degrees of freedom that are correlated is ξ^D . The correlation length diverges at the critical point

$$\xi \sim (T - T_c)^{-\nu}$$

At the critical point, all parts of a system are correlated: the system has a collective behaviour. On the other hand, at infinite temperature, the correlation length is zero. In both extreme cases, the system exhibits scale invariance.

- In systems at their critical point, scale invariance emerges. Typically, this symmetry is enhanced to conformal invariance. Critical points correspond to second and higher order phase transition and also to conformal invariance.
- By linearizing and diagonalizing the renormalization group transformation around a fixed point, one discovers three types of couplings: relevant, irrelevant and marginal.
- Four dimensions is the upper critical dimension. The Gaussian approximation in the mean-field approximation and in the Ginzburg–Landau theory gives exact results in dimensions $D \geq 4$. This is because in higher dimensions, the fluctuations beyond Gaussian order have irrelevant couplings (this is the equivalent of positive mass dimension in quantum field theory).

Part IV

Kinetic theory

See Tong, Kinetic Theory, §2.

10 Kinetic theory of gases

At the beginning of the course one has assumed the existence of an equilibrium distribution function. In the following, one may study such existence. Consider the probability distribution of N particles in a gas

$$\rho(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N, t)$$

This distribution satisfies the Liouville equation

$$0 = \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\}$$

where the Hamiltonian is

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + V(\mathbf{q}_i) + \sum_{i<j} U(|\mathbf{q}_i - \mathbf{q}_j|)$$

where V is an external potential while U is the potential due to a two-body short-range interaction between particles, meaning that one has assumed that the gas is diluted. So far, one has assumed that there exists an equilibrium distribution¹⁸

$$\frac{\partial \rho_{\text{eq}}}{\partial t} = 0 \iff \{\rho_{\text{eq}}, H\} = 0$$

¹⁸The following if and only if should be interpreted in this sense. By definition, an equilibrium distribution does explicitly depend on time. So, if it satisfies the Liouville equation, then its Poisson bracket with the Hamiltonian is zero. Viceversa, if the Poisson bracket is zero, and the distribution satisfies the Liouville equation, then it is an equilibrium distribution.

However, the validity of this assumption is not trivial and must be carefully studied. Let

$$\rho_1(\mathbf{q}_1, \mathbf{p}_1, t) = \int \left[\prod_{i=2}^N d^3 q_i d^3 p_i \right] \rho(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N, t)$$

then the one-particle distribution is

$$f_1(\mathbf{q}, \mathbf{p}, t) = N \rho_1(\mathbf{q}, \mathbf{p}, t)$$

It describes the number of particles with momentum \mathbf{p} and position \mathbf{q} . Knowing this distribution, one may compute

- the density of particles

$$n(\mathbf{q}, t) = \int d\mathbf{p} f_1(\mathbf{q}, \mathbf{p}, t)$$

- the average velocity

$$\mathbf{u}(\mathbf{q}, t) = \int d\mathbf{p} \frac{\mathbf{p}}{m} f_1(\mathbf{q}, \mathbf{p}, t)$$

- the average kinetic energy

$$\mathcal{E}(\mathbf{q}, t) = \int d\mathbf{p} \frac{\mathbf{p}^2}{2m} f_1(\mathbf{q}, \mathbf{p}, t)$$

One would like to find an equation describing how f_1 behaves. Its behaviour in time is

$$\begin{aligned} \frac{\partial f_1}{\partial t} &= N \int \left[\prod_{i=2}^N d^3 q_i d^3 p_i \right] \partial_t \rho(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N, t) = N \int \left[\prod_{i=2}^N d^3 q_i d^3 p_i \right] \{H, \rho\} \\ &= N \int \left[\prod_{i=2}^N d^3 q_i d^3 p_i \right] \left[\sum_{j=1}^N \frac{\partial \rho}{\partial \mathbf{p}_j} \cdot \frac{\partial V}{\partial \mathbf{q}_j} - \sum_{j=1}^N \frac{\partial \rho}{\partial \mathbf{q}_j} \cdot \frac{\mathbf{p}_j}{m} + \sum_{j=1}^N \sum_{k < l} \frac{\partial U(|\mathbf{q}_k - \mathbf{q}_l|)}{\partial \mathbf{q}_j} \cdot \frac{\partial \rho}{\partial \mathbf{p}_j} \right] \\ &= N \int \left[\prod_{i=2}^N d^3 q_i d^3 p_i \right] \left[\frac{\partial \rho}{\partial \mathbf{p}_1} \cdot \frac{\partial V}{\partial \mathbf{q}_1} - \frac{\partial \rho}{\partial \mathbf{q}_1} \cdot \frac{\mathbf{p}_1}{m} + \sum_{k=2}^N \frac{\partial U(|\mathbf{q}_1 - \mathbf{q}_k|)}{\partial \mathbf{q}_1} \cdot \frac{\partial \rho}{\partial \mathbf{p}_1} \right] \\ &= \{H_1, f_1\} + \int d^3 q_2 d^3 p_2 \frac{\partial U(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_1} \cdot \frac{\partial f_2}{\partial \mathbf{p}_1} \end{aligned}$$

At the third line, one has noted that, for $j = 2, \dots, N$, one may integrate by parts to move the derivatives from ρ to the other terms. Since

$$\frac{\partial \mathbf{p}_j}{\partial \mathbf{q}_j} = 0, \quad \frac{\partial^2 V}{\partial \mathbf{p}_j \partial \mathbf{q}_j} = 0, \quad \frac{\partial^2 U}{\partial \mathbf{p}_j \partial \mathbf{q}_j} = 0$$

all the terms with $j = 2, \dots, N$ vanish.

The first addendum is the streaming term, where the Hamiltonian is a one-particle Hamiltonian

$$H_1 = \frac{\mathbf{p}_1^2}{2m} + V(\mathbf{q}_1)$$

This addendum describes how the particles move in the absence of collisions. The second addendum is the collision integral $(\partial_t f_1)_{\text{coll}}$. In the integral appears the two-particle distribution function

$$f_2(\mathbf{q}_1, \mathbf{p}_1, \mathbf{q}_2, \mathbf{p}_2, t) = N(N-1) \int \left[\prod_{i=3}^N d^3 q_i d^3 p_i \right] \rho(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N, t)$$

where the factor of $N-1$ comes from summing over k , since the argument does not distinguish between particles. Thus, to find the one-particle distribution function f_1 one needs the two-particle f_2 .

Lecture 20

In general, the n -particle distribution function

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$$f_n(\mathbf{q}_1, \dots, \mathbf{q}_n, \mathbf{p}_1, \dots, \mathbf{p}_n, t) = \frac{N!}{(N-n)!} \int \left[\prod_{i=n+1}^N d^3 q_i d^3 p_i \right] \rho(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N, t)$$

obeys the equation

$$\partial_t f_n = \{H_n, f_n\} + \sum_{i=1}^n \int d^3 q_{n+1} d^3 p_{n+1} \frac{\partial U(|\mathbf{q}_i - \mathbf{q}_{n+1}|)}{\partial \mathbf{q}_i} \cdot \frac{\partial f_{n+1}}{\partial \mathbf{p}_i}$$

where the effective n -body Hamiltonian includes the external force and any interactions between the n particles but neglects interactions with any particles outside of this set

$$H_n = \sum_{i=1}^n \left[\frac{\mathbf{p}_i^2}{2m} + V(\mathbf{q}_i) \right] + \sum_{i < j \leq n} U(|\mathbf{q}_i - \mathbf{q}_j|)$$

The set of equations above for f_n is known as the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy. One starts from one equation (Liouville's) for ρ , which is a function of $6N \sim 6 \times 10^{23}$ variables, and one obtains $N \sim 10^{23}$ coupled equations. The advantage of the hierarchy of equations is that they isolate the interesting, simple variables, namely f_1 and other lower f_n . Given a particular problem, one may decide which terms are important and, ideally, which terms are so small that they can be ignored, truncating the hierarchy to be more manageable.

Boltzmann equation. Some useful approximations to truncate the hierarchy are:

- assuming the system is diluted, at most two particles can interact (and scatter) at a time;
- the external potential $V(\mathbf{q})$, and the associated force, vary slowly on atomic and scattering scales;
- the time between collisions τ is much greater than the time for a collision to occur τ_{coll} .

Most of the time, particles evolve according to the single particle Hamiltonian H_1 and occasionally scatter with each other.

One may model the collision integral as the difference between the number of collisions per unit time such that the final particle has position and momentum within $\mathbf{q} + [0, d\mathbf{q}]$ and $\mathbf{p} + [0, d\mathbf{p}]$, and the number of collisions per unit time such that the initial particle has position and momentum within $\mathbf{q} + [0, d\mathbf{q}]$ and $\mathbf{p} + [0, d\mathbf{p}]$. Assume that the scattering process is elastic

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}'_1 + \mathbf{p}'_2, \quad \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} = \frac{\mathbf{p}'_1{}^2}{2m} + \frac{\mathbf{p}'_2{}^2}{2m}$$

and let $\omega(\mathbf{p}_1, \mathbf{p}_2 \mid \mathbf{p}'_1, \mathbf{p}'_2)$ be the scattering function which contains the dynamics; the first arguments denote the initial particles, while the second denotes the final particles. The collision integral is therefore

$$(\partial_t f_1)_{\text{coll}} = \int d^3 p_2 d^3 p'_1 d^3 p'_2 \times [\omega(\mathbf{p}'_1, \mathbf{p}'_2 \mid \mathbf{p}_1, \mathbf{p}_2) f_2(\mathbf{q}_1, \mathbf{q}_1, \mathbf{p}'_1, \mathbf{p}'_2, t) - \omega(\mathbf{p}_1, \mathbf{p}_2 \mid \mathbf{p}'_1, \mathbf{p}'_2) f_2(\mathbf{q}_1, \mathbf{q}_1, \mathbf{p}_1, \mathbf{p}_2, t)]$$

The first term captures scattering into the state \mathbf{p}_1 , the second scattering out of the state \mathbf{p}_1 .

The scattering function has a few properties under the discrete symmetries of space-time. It is time-reversal invariant

$$\mathbf{p} \rightarrow -\mathbf{p} \implies \omega(\mathbf{p}, \mathbf{p}_2 \mid \mathbf{p}'_1, \mathbf{p}'_2) = \omega(-\mathbf{p}'_1, -\mathbf{p}'_2 \mid -\mathbf{p}, -\mathbf{p}_2)$$

and parity invariant

$$\mathbf{p} \rightarrow -\mathbf{p}, \quad \mathbf{q} \rightarrow -\mathbf{q} \implies \omega(\mathbf{p}, \mathbf{p}_2 \mid \mathbf{p}'_1, \mathbf{p}'_2) = \omega(-\mathbf{p}, -\mathbf{p}_2 \mid -\mathbf{p}'_1, -\mathbf{p}'_2)$$

The combination of the two implies that the scattering function is invariant under exchange of ingoing and outgoing momenta¹⁹

$$\omega(\mathbf{p}, \mathbf{p}_2 | \mathbf{p}'_1, \mathbf{p}'_2) = \omega(\mathbf{p}'_1, \mathbf{p}'_2 | \mathbf{p}, \mathbf{p}_2)$$

The collision integral becomes

$$(\partial_t f_1)_{\text{coll}} = \int d^3 p_2 d^3 p'_1 d^3 p'_2 \omega(\mathbf{p}'_1, \mathbf{p}'_2 | \mathbf{p}_1, \mathbf{p}_2) [f_2(\mathbf{q}_1, \mathbf{q}_1, \mathbf{p}'_1, \mathbf{p}'_2, t) - f_2(\mathbf{q}_1, \mathbf{q}_1, \mathbf{p}_1, \mathbf{p}_2, t)]$$

One would like to express the integrand in terms of the one-particle distribution function instead of the two-particle. To this end, one assumes a molecular chaos, meaning that the velocities of two particles are uncorrelated

$$f_2(\mathbf{q}_1, \mathbf{q}_1, \mathbf{p}_1, \mathbf{p}_2) = f_1(\mathbf{q}_1, \mathbf{p}_1) f_1(\mathbf{q}_1, \mathbf{p}_2)$$

In particular, one assumes that the velocities are uncorrelated before the collision²⁰. This seems reasonable: during the collision process, the velocities between two particles become correlated, but there is then a long time, τ , before one of these particles undergoes another collision. This next collision is typically with a completely different particle and it seems entirely plausible that the velocity of this new particle has nothing to do with the velocity of the first. The particles lose the memory of the interaction by the time they scatter again.

The evolution of the one-particle distribution function is given by the Boltzmann equation

$$\partial_t f_1 = \{H_1, f_1\} + (\partial_t f_1)_{\text{coll}}$$

where the collision integral is

$$\begin{aligned} (\partial_t f_1)_{\text{coll}} = & \int d^3 p_2 d^3 p'_1 d^3 p'_2 \omega(\mathbf{p}'_1, \mathbf{p}'_2 | \mathbf{p}_1, \mathbf{p}_2) \\ & \times [f_1(\mathbf{q}_1, \mathbf{p}'_1, t) f_1(\mathbf{q}_1, \mathbf{p}'_2, t) - f_1(\mathbf{q}_1, \mathbf{p}_1, t) f_1(\mathbf{q}_1, \mathbf{p}_2, t)] \end{aligned}$$

The equation contains only the one-particle distribution function and it can be solved.

Equilibrium. One may study the Boltzmann equation at equilibrium. At equilibrium it holds

$$\partial_t f_1^{\text{eq}} = 0$$

If f_1 is any function of the energy or, indeed, any function that Poisson commutes with the Hamiltonian, then it holds

$$\{H_1, f_1\} = 0$$

Assuming no external potential V and the Hamiltonian to be

$$H_1 = \frac{\mathbf{p}_1^2}{2m}$$

the above condition is satisfied for f_1 being any function of the momentum \mathbf{p}_1 only. At this point, the collision integral is the last term needed to vanish. One way to make it vanish is by finding a distribution which obeys the detailed balance condition

$$f_1(\mathbf{q}, \mathbf{p}'_1, t) f_1(\mathbf{q}, \mathbf{p}'_2, t) = f_1(\mathbf{q}, \mathbf{p}_1, t) f_1(\mathbf{q}, \mathbf{p}_2, t)$$

which can be rewritten in terms of logarithms

$$\ln f_1(\mathbf{q}, \mathbf{p}'_1, t) + \ln f_1(\mathbf{q}, \mathbf{p}'_2, t) = \ln f_1(\mathbf{q}, \mathbf{p}_1, t) + \ln f_1(\mathbf{q}, \mathbf{p}_2, t)$$

¹⁹There is a further assumption of translational invariance, since the scattering rate at position $-\mathbf{q}$ should be equivalent to the scattering rate at position \mathbf{q} .

²⁰This also introduces an arrow of time. Emphasis on *before*.

This equation implies that the sum of logarithms is a conserved quantity in the collision. Recall that in an elastic collision, both momentum and energy are conserved. Therefore, one may write

$$\ln f_1(\mathbf{q}, \mathbf{p}, t) = \beta[\alpha - E(\mathbf{p}) + \mathbf{u} \cdot \mathbf{p}]$$

where α, β are constants, \mathbf{u} is a constant drift velocity and E is the energy of the particle. From this, one obtains the Maxwell–Boltzmann distribution as the equilibrium solution

$$f_1(\mathbf{q}, \mathbf{p}, t) = e^{\beta[\alpha - E(\mathbf{p}) + \mathbf{u} \cdot \mathbf{p}]} = C \exp \left[-\beta \frac{(\mathbf{p} - \mathbf{p}_0)^2}{2m} \right] = \frac{N}{V} \left(\frac{\beta}{2\pi m} \right)^{\frac{3}{2}} \exp \left[-\frac{1}{2} \beta m (\mathbf{v} - \mathbf{u})^2 \right]$$

where one uses the non-relativistic kinematic relations for the energy and the momentum

$$E = \frac{\mathbf{p}^2}{2m}, \quad \mathbf{p} = m\mathbf{v}$$

If one relaxes (ignores) the condition of the streaming term $\{H_1, f_1\} = 0$, the solutions to the detailed balance condition are many more. These solutions are

$$f_1^{\text{local}}(\mathbf{q}, \mathbf{p}, t) = n(\mathbf{q}, t) \left(\frac{\beta(\mathbf{q}, t)}{2\pi m} \right)^{\frac{3}{2}} \exp \left[-\frac{1}{2} \beta(\mathbf{q}, t) m [\mathbf{v} - \mathbf{u}(\mathbf{q}, t)]^2 \right], \quad \beta = \frac{1}{kT}$$

Its collision integral vanishes, but the streaming term does not. These distributions are in local equilibrium, with the particle density, temperature and drift velocity varying over space.

Boltzmann H-theorem. Even if the Maxwell–Boltzmann distribution is the equilibrium distribution, one has to prove that a system with a generic distribution approaches the above distribution at equilibrium. The H-theorem²¹ states that systems evolve irreversibly to equilibrium. In other words, the quantity

$$H = -\frac{1}{k_B} S$$

is monotonically decreasing in time and so there is an irreversible flow to equilibrium.

Proof. Such quantity is defined as

$$H(t) \equiv \int d^3q d^3p f_1(\mathbf{q}, \mathbf{p}, t) \ln f_1(\mathbf{q}, \mathbf{p}, t)$$

Its temporal behaviour is given by the time derivative

$$\begin{aligned} \frac{dH}{dt} &= \int d^3q_1 d^3p_1 [\partial_t f_1 \ln f_1 + \partial_t f_1] = \int d^3q_1 d^3p_1 (1 + \ln f_1) \partial_t f_1 \\ &= \partial_t \int d^3q_1 d^3p_1 f_1 + \int d^3q_1 d^3p_1 \partial_t f_1 \ln f_1 = 0 + \int d^3q_1 d^3p_1 \ln f_1 \partial_t f_1 \\ &= \int d^3p_1 d^3q_1 \ln f_1 [\{H_1, f_1\} + (\partial_t f_1)_{\text{coll}}] \\ &= \int d^3p_1 d^3q_1 \ln f_1 \left(\frac{\partial f_1}{\partial \mathbf{p}_1} \cdot \frac{\partial V}{\partial \mathbf{q}_1} - \frac{\partial f_1}{\partial \mathbf{q}_1} \cdot \frac{\mathbf{p}_1}{m} \right) \\ &\quad + \int d^3p_1 d^3q_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\mathbf{p}'_1, \mathbf{p}'_2 | \mathbf{p}_1, \mathbf{p}_2) \ln f_1(\mathbf{q}_1, \mathbf{p}_1, 1) \\ &\quad \times [f_1(\mathbf{q}_1, \mathbf{p}'_1, t) f_1(\mathbf{q}_1, \mathbf{p}'_2, t) - f_1(\mathbf{q}_1, \mathbf{p}_1, t) f_1(\mathbf{q}_1, \mathbf{p}_2, t)] \end{aligned}$$

At the second line, the first integral gives the number of particles N .

The first integral vanishes. In fact, one may integrate by parts twice each addendum. For the first, one integrates in the momentum and finds

$$\int d^3p_1 d^3q_1 \ln f_1 \frac{\partial f_1}{\partial \mathbf{p}_1} \cdot \frac{\partial V}{\partial \mathbf{q}_1} = - \int d^3p_1 d^3q_1 \frac{1}{f_1} \frac{\partial f_1}{\partial \mathbf{p}_1} \cdot f_1 \frac{\partial V}{\partial \mathbf{q}_1} = \int d^3p_1 d^3q_1 f_1 \frac{\partial^2 V}{\partial \mathbf{p}_1 \partial \mathbf{q}_1} = 0$$

²¹Notice that H is the Greek letter uppercase eta η .

Notice that the derivative of the potential behaves as a constant due to being independent of the momentum. Similarly happens for the second addendum by integrating in the position. Therefore, one has

$$\begin{aligned} \frac{dH}{dt} = & \int d^3p_1 d^3q_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\mathbf{p}'_1, \mathbf{p}'_2 | \mathbf{p}_1, \mathbf{p}_2) \ln f_1(\mathbf{q}_1, \mathbf{p}_1, t) \\ & \times [f_1(\mathbf{q}_1, \mathbf{p}'_1, t) f_1(\mathbf{q}_1, \mathbf{p}'_2, t) - f_1(\mathbf{q}_1, \mathbf{p}_1, t) f_1(\mathbf{q}_1, \mathbf{p}_2, t)] \end{aligned}$$

Now, since the scattering function $\omega(\mathbf{p}_1, \mathbf{p}_2 | \mathbf{p}'_1, \mathbf{p}'_2)$ is invariant under the exchange of ingoing and outgoing momenta

$$\mathbf{p}_1, \mathbf{p}_2 \leftrightarrow \mathbf{p}'_1, \mathbf{p}'_2$$

one may write four times the same contribution using the above property to arrive at

$$\begin{aligned} \frac{dH}{dt} = & -\frac{1}{4} \int d^3p_1 d^3q_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\mathbf{p}'_1, \mathbf{p}'_2 | \mathbf{p}_1, \mathbf{p}_2) \\ & \times [f_1(\mathbf{p}'_1) f_1(\mathbf{p}'_2) - f_1(\mathbf{p}_1) f_1(\mathbf{p}_2)] \{ \ln[f_1(\mathbf{p}'_1) f_1(\mathbf{p}'_2)] - \ln[f_1(\mathbf{p}_1) f_1(\mathbf{p}_2)] \} \\ \leq & 0 \end{aligned}$$

where one notices that the second line is a function of the type

$$(x - y)(\ln x - \ln y) \geq 0, \quad \forall x, y$$

□

This proves the H-theorem

$$\boxed{\frac{dH}{dt} \leq 0}$$

and at equilibrium one finds $d_t H = 0$ which gives the Maxwell-Boltzmann distribution.

Arrow of time. The kinetic theory of gases employs Hamiltonian mechanics (meaning reversibility in time), but one finds a quantity that grows monotonically and the system irreversibly flows to equilibrium. The step which is not compatible with Hamiltonian evolution is the assumption that the velocities of the particles are uncorrelated *before* the collision, which then leads to the Boltzmann equation.

Lecture 21

11 Hydrodynamics*

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No exam. See Tong, KT, §§2.4, 2.5, 2.6, Huang, §5. Hydrodynamics deals with systems in local equilibrium with parameters that vary slowly in space and time. One works with quantities like density, temperature and velocity

$$\rho(\mathbf{r}, t), \quad T(\mathbf{r}, t), \quad \mathbf{u}(\mathbf{r}, t)$$

Conserved quantities. The average value of a phase space variable $A(\mathbf{r}, \mathbf{p})$ is defined as

$$\langle A(\mathbf{r}, t) \rangle \equiv \frac{\int d^3p A(\mathbf{r}, \mathbf{p}) f_1(\mathbf{r}, \mathbf{p}, t)}{\int d^3p f_1(\mathbf{r}, \mathbf{p}, t)} = \frac{1}{n(\mathbf{r}, t)} \int d^3p A(\mathbf{r}, \mathbf{p}) f_1(\mathbf{r}, \mathbf{p}, t)$$

The request that the average value $\langle A(\mathbf{q}, t) \rangle$ varies slowly motivates

$$\int d^3p A(\mathbf{r}, \mathbf{p}) (\partial_t f_1)_{\text{coll}} = 0$$

which means that A satisfies the detailed balance

$$A(\mathbf{r}, \mathbf{p}_1) + A(\mathbf{r}, \mathbf{p}_2) = A(\mathbf{r}, \mathbf{p}'_1) + A(\mathbf{r}, \mathbf{p}'_2)$$

This can be seen by employing the properties of the scattering function ω . Quantities which obey this equation are called collisional invariants: the quantity A remains unchanged before and after the collision. To find an equation for the evolution of the average value $\langle A(\mathbf{r}, t) \rangle$, one starts from the Boltzmann equation

$$\partial_t f_1 = \{f_1, H_1\} + (\partial_t f_1)_{\text{coll}}$$

and multiplies it by

$$\int d^3p A(\mathbf{r}, \mathbf{p})$$

to obtain the equation describing how a collisional invariant changes in time

$$0 = \frac{\partial}{\partial t} \langle nA \rangle - n \left\langle \mathbf{F} \cdot \frac{\partial A}{\partial \mathbf{p}} \right\rangle + \frac{\partial}{\partial \mathbf{r}} \cdot \left\langle nA \frac{\mathbf{p}}{m} \right\rangle - n \left\langle \frac{\mathbf{p}}{m} \cdot \frac{\partial A}{\partial \mathbf{r}} \right\rangle, \quad \mathbf{F} = -\frac{\partial V}{\partial \mathbf{r}}$$

notice the $n(\mathbf{r}, t)$ does not depend on the momentum, so it can be brought inside or outside an average.

There are three collisional invariants of interest. The density is the trivial invariant $A = 1$, for which one obtains the particle number conservation

$$\frac{\partial}{\partial t} n + \frac{\partial}{\partial \mathbf{r}} \cdot (n\mathbf{u}) = 0$$

The next invariant is the momentum $A = m\mathbf{v}$. Let the pressure tensor be

$$P_{ij} = P_{ji} = \rho \langle (v_j - u_j)(v_i - u_i) \rangle, \quad \rho(\mathbf{r}, t) \equiv mn(\mathbf{r}, t)$$

then one finds momentum conservation

$$\rho \left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) u_i = \frac{\rho}{m} F_i - \frac{\partial}{\partial r_j} P_{ij}$$

where the parenthesis is the material derivative

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j}$$

The last invariant is the kinetic energy

$$A = \frac{1}{2} m(\mathbf{v} - \mathbf{u})^2$$

One may define three quantities. The temperature

$$\frac{3}{2} kT(\mathbf{r}, t) \equiv \frac{1}{2} m \langle (\mathbf{v} - \mathbf{u}(\mathbf{r}, t))^2 \rangle$$

the heat flux

$$\mathbf{q} \equiv \frac{1}{2} m \rho \langle (\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u})^2 \rangle$$

and the rate of strain

$$U_{ij} \equiv \frac{1}{2} \left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right)$$

With these quantities, the time evolution of the kinetic energy is

$$\rho \left(\frac{\partial}{\partial t} + u_i \frac{\partial}{\partial r_i} \right) kT(\mathbf{r}, t) + \frac{2}{3} \frac{\partial q_i}{\partial r_i} + \frac{2}{3} m U_{ij} P_{ij} = 0$$

The three equations found describe how density, velocity and temperature vary in space and time, for any distribution $f_1(\mathbf{r}, \mathbf{p}, t)$. However the equations depend on \mathbf{u} , P_{ij} and \mathbf{q} which require the distribution f_1 to be computed by solving the Boltzmann equation.

Zeroth order — ideal fluids. The zeroth order approximation to the solution of the Boltzmann equation leads to the concept of ideal fluids. One may start by simply guessing a form of the distribution function f_1 . As a first guess, consider the local equilibrium distribution $f_1^{(0)}$ whose collision integral vanishes (but not the Poisson bracket)

$$\left(\frac{\partial f_1^{(0)}}{\partial t} \right)_{\text{coll}} = 0$$

From it one may find

$$\mathbf{q} = \mathbf{0}, \quad P_{ij} = kn(\mathbf{r}, t)T(\mathbf{r}, t)\delta_{ij} \equiv P(\mathbf{r}, t)\delta_{ij}$$

Then the three equations above become

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{r}}(\rho \mathbf{u}) &= 0 \\ \rho \left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) u_i &= \frac{\rho}{m} F_i - \frac{\partial P}{\partial r_i} \\ \left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) T + \frac{2}{3} T \frac{\partial u_i}{\partial r_i} &= 0 \end{aligned}$$

Combining the first and the last, one finds

$$\left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) (\rho T^{-\frac{3}{2}}) = 0$$

This equation implies that the quantity $\rho T^{-3/2}$ is constant along the streamlines of the fluid, and knowing that

$$\rho = mn = m \frac{N}{V}$$

also means that $VT^{3/2}$ is constant: this is the requirement that motion along streamlines is (locally) adiabatic (by definition of adiabatic process). In fact, recall that for an adiabatic process, one has

$$dQ = 0, \quad dE = -p dV$$

Knowing that

$$dE = C_V dT, \quad P = \frac{NkT}{V}, \quad C_V = \frac{3}{2}Nk$$

one finds

$$-P dV = C_V dT \implies -\frac{dV}{V} = \frac{3}{2} \frac{dT}{T} \implies VT^{\frac{3}{2}} = \text{const.}$$

Sound waves. Linearizing the three equations above around the ideal fluid at rest

$$\mathbf{u} = \mathbf{0}, \quad \rho = \text{const.}, \quad T = \text{const.}$$

gives the wave equation

$$\nabla^2 \rho - \frac{1}{c_s^2} \frac{\partial^2 \rho}{\partial t^2} = 0$$

where the speed is the speed of sound

$$c_s = \sqrt{\frac{5}{3} \frac{kT}{m}}$$

First order — transport with collisions. An ideal fluid has no dissipation nor irreversible flow to equilibrium. In fact, $f_1^{(0)}$ is not a solution of the Boltzmann equation at equilibrium, since

$$\{H_1, f_1^{(0)}\} \neq 0$$

This distribution is almost a solution. One may add a correction term

$$f_1 = f_1^{(0)} + \delta f_1$$

One should study how this term contributes to the collision integral and apply the Chapman–Enskog expansion. However, there is an easier way to make progress: the collision integral is replaced with a simpler function that captures the relevant physics. This is the relaxation time approximation

$$\left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} \approx -\frac{\delta f_1}{\tau}$$

where τ is the collision time (or also called relaxation time). The correction δf_1 can be found from the Boltzmann equation. Once the full distribution f_1 has been obtained, one may compute some previous quantities. The heat flux becomes

$$\mathbf{q} = -\kappa \nabla T$$

where the thermal conductivity is

$$\kappa = \frac{5}{2} \tau n k^2 T = C_p \tau n k T, \quad C_p = \frac{5}{2} k$$

where C_p is the heat capacity at constant pressure [r]²². The pressure tensor can be written as

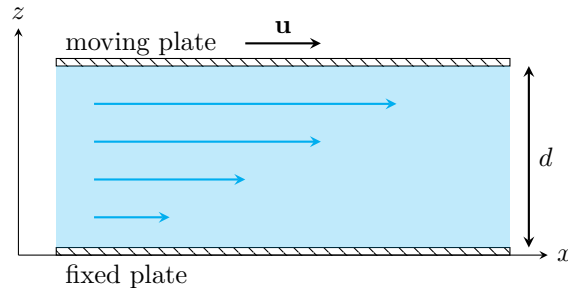
$$P_{ij} = P \delta_{ij} + \Pi_{ij}$$

The stress tensor Π_{ij} contains the shear viscosity η . In fact, if there is a fluid gradient, one finds

$$\frac{\partial u_x}{\partial z} \neq 0 \implies \Pi_{xz} = -\eta \frac{\partial u_x}{\partial z}, \quad \eta = \tau n k T$$

Consider for example the situation in the figure, where the upper plate is moving to the right with a velocity \mathbf{u} . The moving plate creates a gradient of velocity in the fluid

$$u_x(0) = 0, \quad u_x(d) = u$$



The force applied to the upper plate by the fluid per unit area in order to resist the motion is

$$\frac{F}{A} = \eta \frac{u}{d} \approx \eta \frac{\partial u_x}{\partial z}$$

²²There is something going on with the physical units. After eq. (2.54), and also before section 2.5.3, Tong says that the definition of heat flux includes an overall factor of m . This means that the extra unit of mass is then passed into the thermal conductivity κ and so into the heat capacity C_p . Without the overall m , one should have the specific heat capacity c_p instead. In this way the units also match with Wikipedia. Huang defines the heat flux in both ways on pp. 99 and 100, but uses the second (see also eqs. 5.68, 5.69).

With the corrected distribution function f_1 , the equations of the three collisional invariants are as follows. The equation of motion for density fluctuations remains the same

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$

The equation for momentum has an extra contribution from the stress tensor. Moreover one assumes that, to leading order, variations in the viscosity can be neglected, $\nabla \eta = 0$. This leads to the Navier–Stokes equation

$$\left(\frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right) \mathbf{u} = \frac{\mathbf{F}}{m} - \frac{1}{\rho} \nabla \left(P - \frac{\eta}{3} \nabla \cdot \mathbf{u} \right) + \frac{\eta}{\rho} \nabla^2 \mathbf{u}$$

Finally, the heat conduction equation is

$$\left(\frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right) kT = -\frac{2}{3} kT (\nabla \cdot \mathbf{u}) + \frac{2\kappa}{3\rho} \nabla^2 T$$

equivalently

$$\rho \left(\frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right) kT = -\frac{2}{3} mP (\nabla \cdot \mathbf{u}) + \frac{2}{3} \kappa \nabla^2 T$$

where one recalls

$$\rho = mn, \quad P = nkT, \quad \kappa = \frac{5}{2} \tau n k^2 T$$

These three equations have been derived in the dilute gas approximation, but they work well also for liquids.

Prandtl numbers. Since the scattering time τ appears both in the thermal conductivity and the viscosity, one may define a dimensionless number, the Prandtl number

$$\text{Pr} = \frac{C_p \eta}{\kappa} = \frac{C_p \tau n k_B T}{C_p \tau n k_B T} = 1$$

Experimentally, for monatomic gases, the Prandtl number is $\text{Pr} \approx 2/3$. This discrepancy is due to the relaxation time approximation.

Intuitive derivation of the Navier–Stokes equation. The Navier–Stokes equation can be intuitively derived as follows. One may write Newton’s equation for a volume of fluid

$$\mathbf{F} = m \frac{d\mathbf{u}}{dt}, \quad m = \rho dx_1 dx_2 dx_3$$

The force is a sum of external forces and a force due to the other volumes of fluid

$$\mathbf{F} = (\mathbf{F}_1 + \mathbf{G}_1) dx_1 dx_2 dx_3$$

Therefore, one may rewrite Newton’s second equation as

$$\rho \left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial x_j} \right) = \frac{\rho}{m} F_i - \frac{\partial P_{ij}}{\partial x_j}$$

The term due to the other volumes is

$$-\frac{\partial P_{ij}}{\partial x_j} = -\frac{1}{\rho} \nabla P - \frac{\eta}{3} (\nabla \cdot \mathbf{u}) + \frac{\eta}{\rho} \nabla^2 u$$

The first term is the pressure, while the other two are the viscous forces.

Reynolds number. One may define the Reynolds number

$$\text{Re} = \frac{\rho u L}{\eta}$$

For small Re , the viscosity is dominant and there is laminar flow. For large Re , the turbulent inertia is dominant, which is complicated to describe.