

# Classical phase space

## Phase space and probability density

We consider a system of  $N$  particles in a  $d$ -dimensional space. Canonical coordinates and momenta

$$\begin{aligned} q &= (q_1, \dots, q_{dN}) \\ p &= (p_1, \dots, p_{dN}) \end{aligned}$$

determine exactly the microscopic state of the system. The *phase space* is the  $2dN$ -dimensional space  $\{(p, q)\}$ , whose every point  $P = (p, q)$  corresponds to a possible state of the system.

A *trajectory* is such a curve in the phase space along which the point  $P(t)$  as a function of time moves. Trajectories are determined by the classical equations of motion

$$\begin{aligned} \frac{dq_i}{dt} &= \frac{\partial H}{\partial p_i} \\ \frac{dp_i}{dt} &= -\frac{\partial H}{\partial q_i}, \end{aligned}$$

where

$$\begin{aligned} H &= H(q_1, \dots, q_{dN}, p_1, \dots, p_{dN}, t) \\ &= H(q, p, t) = H(P, t) \end{aligned}$$

is the Hamiltonian function of the system.

The trajectory is *stationary*, if  $H$  does not depend on time: trajectories starting from the same initial point  $P$  are identical.

Let  $F = F(q, p, t)$  be a property of the system. Now

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F, H\},$$

where  $\{F, G\}$  stands for Poisson brackets

$$\{F, G\} \equiv \sum_i \left( \frac{\partial F}{\partial q_i} \frac{\partial G}{\partial p_i} - \frac{\partial G}{\partial q_i} \frac{\partial F}{\partial p_i} \right).$$

We define the *volume measure of the phase space*

$$d\Gamma = \prod_{i=1}^{dN} \frac{dq_i dp_i}{h} = h^{-dN} dq_1 \dots dq_{dN} dp_1 \dots dp_{dN}.$$

Here  $h = 6.62608 \cdot 10^{-34}$  Js is the Planck constant.

**Note**  $[dq dp] = \text{Js}$ , so  $d\Gamma$  is dimensionless.

**Note**  $\Delta_0 \Gamma = 1$  corresponds to the smallest possible volume element of the phase space where a point representing the system can be localized in accordance with the uncertainty principle. The volume  $\Delta \Gamma = \int d\Gamma$  is then roughly equal to the number of quantum states in the part of the space under consideration.

The *ensemble* or *statistical set* consists, at a given moment, of all those phase space points which correspond to identical macroscopic systems.

Corresponding to a *macro state* of the system there are thus sets of *micro states* which belong to the ensemble with the probability  $\rho(P) d\Gamma$ .  $\rho(P)$  is the *probability density* which satisfies the condition

$$\int d\Gamma \rho(P) = 1.$$

The statistical average, or the ensemble expectation value, of a measurable quantity  $f = f(P)$  is

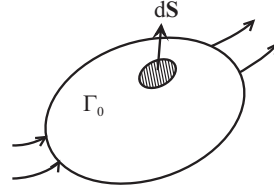
$$\langle f \rangle = \int d\Gamma f(P) \rho(P).$$

We associate every phase space point with the velocity field

$$\mathbf{V} = (\dot{q}, \dot{p}) = \left( \frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q} \right).$$

The probability current is then  $\mathbf{V}\rho$ . The probability weight of an element  $\Gamma_0$  evolves then like

$$\frac{\partial}{\partial t} \int_{\Gamma_0} \rho d\Gamma = - \int_{\partial \Gamma_0} \mathbf{V}\rho \cdot d\mathbf{S}.$$



Because

$$\int_{\partial \Gamma_0} \mathbf{V}\rho \cdot d\mathbf{S} = \int_{\Gamma_0} \nabla \cdot (\mathbf{V}\rho) d\Gamma,$$

we get in the limit  $\Gamma_0 \rightarrow 0$  the *continuity equation*

$$\frac{\partial}{\partial t} \rho + \nabla \cdot (\mathbf{V}\rho) = 0.$$

According to the equations of motion

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} \end{aligned}$$

we have

$$\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0,$$

so we end up with the *incompressibility condition*

$$\nabla \cdot \mathbf{V} = \sum_i \left[ \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right] = 0.$$

From the continuity equation we get then

$$\begin{aligned} 0 &= \frac{\partial \rho}{\partial t} + \nabla \cdot (\mathbf{V}\rho) \\ &= \frac{\partial \rho}{\partial t} + \rho \nabla \cdot \mathbf{V} + \mathbf{V} \cdot \nabla \rho \\ &= \frac{\partial \rho}{\partial t} + \mathbf{V} \cdot \nabla \rho. \end{aligned}$$

When we employ the *convective time derivative*

$$\begin{aligned}\frac{d}{dt} &= \frac{\partial}{\partial t} + \mathbf{V} \cdot \nabla \\ &= \frac{\partial}{\partial t} + \sum_i \left( \dot{q}_i \frac{\partial}{\partial q_i} + \dot{p}_i \frac{\partial}{\partial p_i} \right),\end{aligned}$$

the continuity equation can be written in the form known as the *Liouville theorem*

$$\frac{d}{dt} \rho(P(t), t) = 0.$$

The points in the phase space move like an incompressible fluid which carries with it the constant probability describing the ensemble.

## Flow in phase space

The *energy surface*  $\Gamma_E$  is the manifold determined by the equation

$$H(q, p) = E.$$

Since the energy is a constant of motion every phase point  $P^i(t)$  moves on a certain energy surface  $\Gamma_{E_i}$ . The expectation value of the energy of the system

$$E = \langle H \rangle = \int d\Gamma H \rho$$

is also a constant of motion.

The volume of the energy surface is

$$\Sigma_E = \int d\Gamma_E = \int d\Gamma \delta(H(P) - E).$$

The volume of the phase space is

$$\int d\Gamma = \int_{-\infty}^{\infty} dE \Sigma_E.$$

Let us consider the element  $\Delta\Gamma_E$  of an energy surface.

**Non ergodic flow:** In the course of time the element  $\Delta\Gamma_E$  traverses only a part of the energy surface  $\Gamma_E$ .

**Ergodic flow:** Almost all points of the surface  $\Gamma_E$  are sometimes arbitrarily close to any point in  $\Delta\Gamma_E$

$\Leftrightarrow$

The flow is ergodic if  $\forall f(P)$ ,  $f(P)$  "smooth enough",

$$\bar{f} = \langle f \rangle_E$$

holds. Here  $\bar{f}$  is the time average

$$\bar{f} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt f(P(t))$$

and  $\langle f \rangle_E$  the energy surface expectation value

$$\langle f \rangle_E = \frac{1}{\Sigma_E} \int d\Gamma_E f(P).$$

We define the *microcanonical ensemble* so that its density distribution is

$$\rho_E(P) = \frac{1}{\Sigma_E} \delta(H(P) - E).$$

Every point of the energy surface belongs with the same probability to the microcanonical ensemble.

The microcanonical ensemble is stationary, i.e.  $\frac{\partial \rho_E}{\partial t} = 0$  and the expectation values over it temporal constants.

The *mixing flow* is such an ergodic flow where the points of an energy surface element  $d\Gamma_E$  disperse in the course of time all over the energy surface.

If  $\hat{\rho}_E(P, t)$  is an arbitrary non stationary density distribution at the moment  $t = t_0$ , then

$$\lim_{t \rightarrow \infty} \hat{\rho}_E(P, t) = \frac{1}{\Sigma_E} \delta(H(P) - E) = \rho_E(P)$$

and

$$\begin{aligned}\lim_{t \rightarrow \infty} \langle f \rangle &= \lim_{t \rightarrow \infty} \int d\Gamma \hat{\rho}_E(P, t) f(P) \\ &= \int d\Gamma f(P) \rho_E(P)\end{aligned}$$

i.e. the density describing an arbitrary (non equilibrium) state evolves towards a microcanonical ensemble.

## Microcanonical ensemble and entropy

If the total energy of a macroscopic system is known exactly its equilibrium state can be described by a microcanonical ensemble. The corresponding probability density is

$$\rho_E(P) = \frac{1}{\Sigma_E} \delta(H(P) - E).$$

For a convenience we allow the energy to have some "tolerance" and define

$$\rho_{E, \Delta E}(P) = \frac{1}{Z_{E, \Delta E}} \theta(E + \Delta E - H(P)) \theta(H(P) - E).$$

Here the normalization constant

$$Z_{E, \Delta E} = \int d\Gamma \theta(E + \Delta E - H(P)) \theta(H(P) - E)$$

is the *microcanonical state sum* or *partition function*.

$Z_{E, \Delta E}$  is the number of states contained in the energy slice  $E < H < E + \Delta E$  (see the volume measure of the phase space). In the microcanonical ensemble the probability is distributed evenly in every allowed part of the phase space.

## Entropy

We define the *Gibbs entropy* as

$$S = -k_B \int d\Gamma \rho(P) \ln \rho(P).$$

Let  $\Delta\Gamma_i$  the volume of the phase space element  $i$  and  $\rho_i$  the average probability density in  $i$ . The state of the system is, with the probability

$$p_i = \rho_i \Delta\Gamma_i,$$

in the element  $i$  and

$$\sum p_i = 1.$$

We choose the sizes of all elements to be smallest possible, i.e.  $\Delta\Gamma_i = 1$ . Then

$$\begin{aligned} S &= -k_B \sum_i \Delta\Gamma_i \rho_i \ln \rho_i = -k_B \sum_i \rho_i \Delta\Gamma_i \ln \rho_i \Delta\Gamma_i \\ &= -k_B \sum_i p_i \ln p_i, \end{aligned}$$

since  $\ln \Delta\Gamma_i = 0$ .

If  $\rho$  is constant in the range  $\Delta\Gamma = W$  we have

$$\rho = \frac{1}{W},$$

so that

$$S = -k_B \frac{1}{W} \ln \frac{1}{W} \int d\Gamma.$$

We end up with the *Boltzmann entropy*

$$S = k_B \ln W.$$

Here  $W$  is the *thermodynamic probability*: the number of all those states that correspond to the macroscopical properties of the system.

One can show that the entropy is *additive*, i.e. if the system is composed of two partial systems 1 and 2 its entropy is

$$S_{1+2} = S_1 + S_2.$$

If we require that the entropy has a maximum under the condition

$$\int d\Gamma \rho(P) = 1,$$

$\rho$  takes the form

$$\rho(P) = \rho_0 \quad \forall P \in \Gamma_E.$$

The maximum principle of the entropy leads thus to the microcanonical distribution.

### Entropy and disorder

The maximum of entropy

$\Leftrightarrow$

Microcanonical ensemble

$\Leftrightarrow$

Every microscopic state which satisfies

$$E < H < E + \Delta E,$$

is present with the same probability, i.e. there is a complete lack of information

$\Leftrightarrow$

Disorder is at maximum.

## Quantum mechanical ensembles

### Systems of identical particles

Let  $\mathcal{H}^1$  be a Hilbert space for one particle. Then the Hilbert space for  $N$  identical particles is

$$\mathcal{H}^N = \underbrace{\mathcal{H}^1 \otimes \mathcal{H}^1 \otimes \dots \otimes \mathcal{H}^1}_{N \text{ copies}}.$$

If, for example,  $|\mathbf{x}_i\rangle \in \mathcal{H}^1$  is a position eigenstate the  $N$ -particle state can be written as

$$|\Psi\rangle = \int \int \dots \int d\mathbf{x}_1 \dots d\mathbf{x}_N |\mathbf{x}_1, \dots, \mathbf{x}_N\rangle \psi(\mathbf{x}_1, \dots, \mathbf{x}_N),$$

where

$$|\mathbf{x}_1, \dots, \mathbf{x}_N\rangle = |\mathbf{x}_1\rangle \otimes |\mathbf{x}_2\rangle \otimes \dots \otimes |\mathbf{x}_N\rangle.$$

There are two kinds of particles:

**Bosons** The wave function is symmetric with respect to the exchange of particles.

**Fermions** The wave function is antisymmetric with respect to the exchange of particles.

**Note** If the number of translational degrees of freedom is less than 3, e.g. the system is confined to a two dimensional plane, the phase gained by the many particle wave function under the exchange of particles can be other than  $\pm 1$ . Those kind of particles are called *anyons*. The Hilbert space of a many particle system is not the whole  $\mathcal{H}^N$  but its subspace:

$$\mathcal{H} = \begin{cases} \mathcal{S}\mathcal{H}^N & = \mathcal{S}(\mathcal{H}^1 \otimes \dots \otimes \mathcal{H}^1) \quad \text{symm.} \\ \mathcal{A}\mathcal{H}^N & = \mathcal{A}(\mathcal{H}^1 \otimes \dots \otimes \mathcal{H}^1) \quad \text{antisymm.} \end{cases}$$

### Dimension of space and statistics

Let us consider two identical particles in an  $n$ -dimensional Euclidean space  $\mathcal{E}_n$ .

We separate the center of mass and relative coordinates:

$$\begin{aligned} \mathbf{X} &= \frac{1}{2}(\mathbf{x}_1 + \mathbf{x}_2) \in \mathcal{E}_n \\ \mathbf{x} &= (\mathbf{x}_1 - \mathbf{x}_2) \in \mathcal{E}_n. \end{aligned}$$

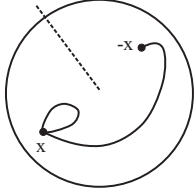
Since the particles are identical we identify the points

$$\begin{aligned} \mathbf{x} &= \mathbf{x}_1 - \mathbf{x}_2 \\ -\mathbf{x} &= \mathbf{x}_2 - \mathbf{x}_1 \end{aligned}$$

in the space  $\mathcal{E}_n$  of the relative motion. Let us call the resulting space  $r(n, 2)$ . The point  $\mathbf{o} \in r(n, 2)$  is the singular point in this space.

### Two dimensional space

The space  $r(2, 2)$  is a circular cone with the vertex aperture  $60^\circ$ .



A closed curve that does not circulate the vertex

- corresponds in the original space  $\mathcal{E}_n$  to a closed curve which connects a point  $\mathbf{x}$  to the same point  $\mathbf{x}$ .
- can be continuously squeezed to a point without crossing the singular point.

A closed curve that goes around the vertex

- corresponds in the original space  $\mathcal{E}_n$  to a curve which connects points  $\mathbf{x}$  and  $-\mathbf{x}$ , i.e. corresponds to particle exchange.
- cannot be continuously squeezed to a point without crossing the singular point, no matter how many times the curve circulates the vertex.

The space  $r(2, 2) - \{\mathbf{o}\}$  is said to be *infinitely connected*.

### Three dimensional space

The vectors in the space  $r(3, 2)$  can be specified by telling their

- length and
- direction identifying, however, the opposite directions.

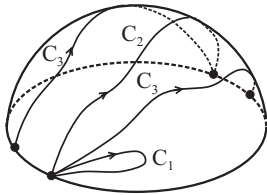
The space of the relative motion can be represented as the product

$$r(3, 2) - \{\mathbf{o}\} = (0, \infty) \times \mathcal{P}_2,$$

where  $\mathcal{P}_2$  is a surface of a three dimensional hemisphere where the opposite points on the equator are identified.

A closed curve that does not circulate the singular point

- is closed on the hemisphere.
- corresponds to a closed curve from the point  $\mathbf{x}$  to the same point  $\mathbf{x}$  in the original space  $\mathcal{E}_3$ .
- can be squeezed continuously to a point without crossing the singular point.



A closed curve that circulates the singular point *once*

- is a curve on the sphere connecting opposite points and, consequently, opposite points on a hemisphere with the equator passing through these points.

- corresponds to a curve connecting points  $\mathbf{x}$  and  $-\mathbf{x}$  in the original space  $\mathcal{E}_n$ , i.e. corresponds to the exchange of the particles.
- cannot be squeezed continuously to a point without crossing the singular point.

A closed curve that circulates the singular point *twice*

- corresponds to the double exchange.
- can be squeezed continuously to a point without crossing the singular point.

The space  $r(3, 2) - \{\mathbf{o}\}$  is said to be *doubly connected*.

### Quantization

- The configuration space of two identical particles is flat with the exception of the singular point  $\mathbf{x} = \mathbf{o}$ .
- In general, the configuration space of  $N$  identical particles is flat with the exception of a finite number of singular points.
- The dynamics of classical systems is governed by *local* equations of motion; occasional singular points have no effect.
- Quantum mechanical description is *global*; the topology of the configuration space is essential.
- In the quantum mechanics of identical particles the configuration space must be treated (somewhat) warped.

Proceeding formally

- At every point  $\mathbf{x}$  we set a one dimensional Hilbert space  $h_{\mathbf{x}}$ .
- The physical state of the system is described by the vectors  $|\Psi(\mathbf{x})\rangle \in h_{\mathbf{x}}$ .
- In every Hilbert space  $h_{\mathbf{x}}$  we specify the normalized base vector  $|\chi_{\mathbf{x}}\rangle$ . The set  $\{|\chi_{\mathbf{x}}\rangle\}$  is called a *gauge*.
- A wave function  $\psi$  is the coordinate of a state vector with respect to the base:

$$|\Psi(\mathbf{x})\rangle = \psi(\mathbf{x}) |\chi_{\mathbf{x}}\rangle.$$

- The transformation  $\{|\chi_{\mathbf{x}}\rangle\} \rightarrow \{|\chi'_{\mathbf{x}}\rangle\}$  from a base to another causes the gauge transformation

$$\psi(\mathbf{x}) \rightarrow \psi'(\mathbf{x}) = e^{i\phi(\mathbf{x})} \psi(\mathbf{x}).$$

Physics is independent on the gauge.

- We employ a linear unitary operator  $P(\mathbf{x}', \mathbf{x})$ , which moves vectors from the space  $h_{\mathbf{x}}$  parallelly to the space  $h_{\mathbf{x}'}$ .

- The gauge can be chosen so that

$$P(\mathbf{x} + d\mathbf{x}, \mathbf{x}) \left| \chi_{\mathbf{x}} \right\rangle = (1 + i\mathbf{b}_k(\mathbf{x})d\mathbf{x}^k) \left| \chi_{\mathbf{x}+d\mathbf{x}} \right\rangle.$$

- Because the derivative operators

$$D_k = \frac{\partial}{\partial x_k} - ib_k(\mathbf{x})$$

are invariant in the gauge transform the Hamiltonian must be written using them.

- The commutator

$$f_{kl} = i[D_k, D_l] = \frac{\partial b_l}{\partial x_k} - \frac{\partial b_k}{\partial x_l}$$

is independent of the gauge.

Due to the gauge invariance a vector potential  $\mathbf{b}(\mathbf{x})$  shows up in the Hamiltonian.

- $\mathbf{b}(\mathbf{x})$  is a consequence of the topology.
- The force field related to the potential is  $f_{kl}$
- We can set  $f_{kl} = 0$  everywhere in the configuration space except the singular points.
- Moving an arbitrary vector  $|\Psi(\mathbf{x})\rangle \in h_{\mathbf{x}}$  along a closed curve it
  - remains invariant provided that we are not circulating a singular point.
  - maps to the vector  $|\Psi'\rangle = P_{\mathbf{x}}|\Psi\rangle \in h_{\mathbf{x}}$  if we circulate a singular point.
- Because  $h_{\mathbf{x}}$  is one dimensional we must have

$$P_{\mathbf{x}} = e^{i\xi}.$$

- Since

$$P_{\mathbf{x}'} = P(\mathbf{x}', \mathbf{x})P_{\mathbf{x}}P(\mathbf{x}', \mathbf{x})^{-1} = P_{\mathbf{x}},$$

the parameter  $\xi$  is independent on the point  $\mathbf{x}$ ;  $\xi$  is characteristic to the two particle system.

- A route circulating a singular point once corresponds in the two particle configuration space to a curve connecting points  $(\mathbf{x}_1, \mathbf{x}_2)$   $(\mathbf{x}_2, \mathbf{x}_1)$ :  $P_{\mathbf{x}}$  exchanges the particles.
- In two dimensional space there is no reason to restrict the values of  $\xi$  to 0 (bosons) or  $\pi$  (fermions).
- In three dimensional space the extra condition  $P_{\mathbf{x}}^2 = 1$  forces the condition  $\xi = 0$  or  $\pi$ .

## Density operator and entropy

Let  $\mathcal{H}$  be the Hilbert space of a many particle system. *The probability measure* tells us the weight that a state  $|\psi\rangle \in \mathcal{H}$  represents a system with given macroscopical properties.

*The apriory probability*: when there is no knowledge of the actual state of the system every state in  $\mathcal{H}$  can taken with equal weight.

We define *the density operator*  $\rho$  so that

$$\rho = \frac{1}{\mathcal{N}} \sum_{n=1}^{\mathcal{N}} |n\rangle \langle n|,$$

where  $\mathcal{N} = \dim \mathcal{H}$  and  $|n\rangle \in \mathcal{H}$  are the base vectors of  $\mathcal{H}$ . *The expectation value* of an operator  $A$  is

$$\langle A \rangle = \text{Tr } \rho A,$$

which is also called as *the statistical expectation value*. Here  $\text{Tr } B$  is *the trace* of the operator  $B$

$$\text{Tr } B = \sum_{n=1}^{\mathcal{N}} \langle n|B|n\rangle.$$

Now

$$\begin{aligned} \text{Tr } \rho &= \sum_{n=1}^{\mathcal{N}} \langle n|\rho|n\rangle = \frac{1}{\mathcal{N}} \sum_{n'} \sum_n \langle n|n'\rangle \langle n'|n\rangle \\ &= \frac{1}{\mathcal{N}} \sum_n 1 = 1, \end{aligned}$$

so, for example,

$$\langle I \rangle = \text{Tr } \rho I = 1$$

and

$$\langle P_n \rangle = \frac{1}{\mathcal{N}}, \text{ when } P_n = |n\rangle \langle n|.$$

Let  $|\psi\rangle \in \mathcal{H}$  be an arbitrary normalized state. The probability for the state  $|\psi\rangle$  is

$$\begin{aligned} \langle P_{\psi} \rangle &= \text{Tr } \rho |\psi\rangle \langle \psi| = \sum_n \langle n|\rho|\psi\rangle \langle \psi|n\rangle \\ &= \sum_n \langle \psi| \underbrace{|n\rangle \langle n|}_{I} \rho |\psi\rangle = \langle \psi|\rho|\psi\rangle \\ &= \frac{1}{\mathcal{N}} \sum_n \langle \psi|n\rangle \langle n|\psi\rangle = \frac{1}{\mathcal{N}} \sum_n |\psi_n|^2 \\ &= \frac{1}{\mathcal{N}}. \end{aligned}$$

So, we can write

$$\rho = \frac{1}{\mathcal{N}} I.$$

## Ensemble

*Macrostate* is the state determined by macroscopical parameters.

**Microstate** is a particular state in a Hilbert space.

Let us choose a set of identical macrostates. We perform complete measurements whose results are the states  $\psi^i$ ,  $i = 1, \dots, \mathcal{M}$ . We define the density operator of this set, ensemble, as

$$\rho_{\mathcal{M}} = \frac{1}{\mathcal{M}} \sum_{i=1}^{\mathcal{M}} |\psi^i\rangle \langle \psi^i|.$$

Then

$$\text{Tr } \rho_{\mathcal{M}} = 1.$$

The ensemble expectation values of operators are

$$\begin{aligned} \langle A \rangle &= \text{Tr } \rho_{\mathcal{M}} A = \frac{1}{\mathcal{M}} \sum_{i=1}^{\mathcal{M}} \langle \psi^i | A | \psi^i \rangle \\ &= \frac{1}{\mathcal{M}} \sum_{i=1}^{\mathcal{M}} \langle A \rangle^i, \end{aligned}$$

where

$$\langle A \rangle^i = \langle \psi^i | A | \psi^i \rangle$$

is the expectation value of  $A$  in the quantum state  $|\psi^i\rangle$ . In an ideal case there exists the limit

$$\rho = \lim_{\mathcal{M} \rightarrow \infty} \frac{1}{\mathcal{M}} \sum_{i=1}^{\mathcal{M}} |\psi^i\rangle \langle \psi^i|,$$

defining the macrostate of the system.

**Note** In practice the method is unrealistic since it depends on the employed measurements.

*Pure state:* When the state of the system is known "quantum mechanically" accurately we can set

$$\rho = |\psi\rangle \langle \psi|.$$

In the corresponding ensemble every state  $|\psi^i\rangle = |\psi\rangle$ . The statistical mechanics of a pure state reduces to ordinary quantum mechanics, e.g.

$$\langle A \rangle = \text{Tr } \rho A = \langle \psi | A | \psi \rangle.$$

Other states are known as mixed states.

### Properties of the density operator

$$\begin{aligned} \rho^\dagger &= \rho \\ \langle \psi | \rho | \psi \rangle &\geq 0 \quad \forall |\psi\rangle \in \mathcal{H} \\ \text{Tr } \rho &= 1. \end{aligned}$$

The density operator associates with every normalized  $|\psi\rangle \in \mathcal{H}$  the probability

$$p_\psi = \text{Tr } \rho P_\psi = \langle \psi | \rho | \psi \rangle.$$

Since  $\rho$  is hermitean there exists an orthonormal basis  $\{|\alpha\rangle\}$  for  $\mathcal{H}$ , where  $\rho$  is diagonal

$$\rho = \sum_{\alpha} p_{\alpha} |\alpha\rangle \langle \alpha|.$$

Here

$$0 \leq p_{\alpha} \leq 1$$

and

$$\sum p_{\alpha} = 1.$$

In this basis

$$\langle A \rangle = \text{Tr } \rho A = \sum_{\alpha} p_{\alpha} \langle \alpha | A | \alpha \rangle.$$

### The equation of motion

Let us fix the probabilities  $p_{\alpha}$  corresponding to the states  $|\alpha\rangle$ . Now

$$\rho(t) = \sum_{\alpha} p_{\alpha} |\alpha(t)\rangle \langle \alpha(t)|.$$

Since the state vectors satisfy the Schrödinger equations

$$\begin{aligned} i\hbar \frac{d}{dt} |\alpha(t)\rangle &= H |\alpha(t)\rangle \\ -i\hbar \frac{d}{dt} \langle \alpha(t)| &= \langle \alpha(t)| H, \end{aligned}$$

we end up with the equation of motion

$$i\hbar \frac{d}{dt} \rho(t) = [H, \rho(t)].$$

In a *stationary ensemble* the expectation values are independent on time, so  $\dot{\rho} = 0$  or

$$[H, \rho] = 0.$$

This is possible e.g. when  $\rho = \rho(H)$ .

### Entropy

The entropy is defined by

$$S = -k_B \text{Tr } \rho \ln \rho.$$

In the base where  $\rho$  is diagonal,

$$S = -k_B \sum_{\alpha} p_{\alpha} \ln p_{\alpha}.$$

Entropy has the properties

1.  $S \geq 0$ , because  $0 \leq p_{\alpha} \leq 1$ .
2.  $S = 0$  corresponds to a pure state, i.e.  $\exists \alpha : p_{\alpha} = 1$  and  $p_{\alpha'} = 0 \quad \forall \alpha' \neq \alpha$ .
3. If the dimension  $\mathcal{N}$  of the Hilbert space  $\mathcal{H}$  is finite the entropy has a maximum when

$$\rho = \frac{1}{\mathcal{N}} I$$

or  $p_{\alpha} = \frac{1}{\mathcal{N}} \quad \forall |\alpha\rangle \in \mathcal{H}$ . Then

$$S = k_B \ln \mathcal{N}.$$

4. The entropy is additive

Let the total Hilbert space be

$$\mathcal{H}_{1+2} = \mathcal{H}_1 \otimes \mathcal{H}_2$$

and correspondingly

$$\rho_{1+2} = \rho_1 \otimes \rho_2.$$

If  $\rho_i |\alpha^{(i)}\rangle = p_\alpha^{(i)} |\alpha^{(i)}\rangle$ , then

$$\rho_{1+2} \left| \alpha^{(1)}, \beta^{(2)} \right\rangle = p_\alpha^{(1)} p_\beta^{(2)} \left| \alpha^{(1)}, \beta^{(2)} \right\rangle.$$

Now

$$\text{Tr}_{1+2} A = \sum_{\alpha, \beta} \langle \alpha^{(1)}, \beta^{(2)} | A | \alpha^{(1)}, \beta^{(2)} \rangle,$$

so that

$$\begin{aligned} S_{1+2} &= -k_B \text{Tr}_{1+2} \rho_{1+2} \ln \rho_{1+2} \\ &= -k_B \sum_{\alpha, \beta} p_\alpha^{(1)} p_\beta^{(2)} (\ln p_\alpha^{(1)} + \ln p_\beta^{(2)}) \\ &= -k_B \sum_{\alpha} p_\alpha^{(1)} \ln p_\alpha^{(1)} - k_B \sum_{\beta} p_\beta^{(2)} \ln p_\beta^{(2)} \\ &= S_1 + S_2. \end{aligned}$$

## Density of states

Let us denote

$$H |n\rangle = E_n |n\rangle,$$

so that

$$H = \sum_n E_n |n\rangle \langle n|.$$

If the volume  $V$  of the system is finite the spectrum is discrete and the states can be normalized like

$$\langle n|m\rangle = \delta_{n,m}.$$

*Thermodynamic limit:*

$$V \rightarrow \infty \text{ and } N \rightarrow \infty$$

so that  $N/V$  remains constant.

The state cumulant (function) is defined as

$$J(E) = \sum_n \theta(E - E_n),$$

i.e. the value of  $J$  at the point  $E$  is the number of those states whose energy is less than  $E$ .

The state density (function) is defined as

$$\omega(E) = \frac{dJ(E)}{dE} = \sum_n \delta(E - E_n),$$

since  $d\theta(x)/dx = \delta(x)$ .

Now

$$J(E + \Delta E) - J(E) \approx \omega(E) \Delta E$$

is the number of those states whose energy lies between  $(E, E + \Delta E)$ . We can also write

$$\begin{aligned} J(E) &= \text{Tr} \theta(E - H) \\ \omega(E) &= \text{Tr} \delta(H - E). \end{aligned}$$

$\omega(E)$  corresponds to the volume  $\Gamma_E$  of the energy surface of the classical phase space. When the system is large the energy spectrum is almost continuous and  $\omega(E)$  can be smoothed to continuous functions.

**Example 1.** Free particle

The Hamiltonian is

$$H = \frac{p^2}{2m}.$$

The eigenfunctions are the plane waves

$$\psi_{\mathbf{k}} = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}},$$

where the wave vector can acquire the values

$$\mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z), \quad n_i \in \mathcal{I}, \quad V = L^3.$$

The corresponding energies are

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}.$$

In the limit of large volume the summation can be transformed to the integration over the wave vector, like

$$\sum_{\mathbf{k}} = \int dN_{\mathbf{k}} = g \frac{V}{(2\pi)^3} \int d^3\mathbf{k} = g \frac{V}{h^3} \int d^3\mathbf{p},$$

where  $g = 2S + 1$  and  $S$  is the spin of the particle. Then

$$\begin{aligned} J_1(E) &= \int dN_{\mathbf{k}} \theta \left( E - \frac{p^2}{2m} \right) = g \frac{V}{h^3} 4\pi \int_0^p dp' p'^2 \\ &= g \frac{V}{h^3} \frac{4\pi}{3} p^3. \end{aligned}$$

So we get

$$\begin{aligned} J_1(E) &= \frac{2}{3} C_1 V E^{3/2} \\ \omega_1(E) &= C_1 V E^{1/2} \\ C_1 &= 2\pi g \left( \frac{2m}{h} \right)^{3/2}. \end{aligned}$$

**Example 2.** Maxwell-Boltzmann gas

Let us consider  $N$  free particles. The total energy is

$$E = \sum_j \frac{p_j^2}{2m}$$



and the state cumulant

$$\begin{aligned}
J_N(E) &= \int dN_{\mathbf{k}_1} \cdots \int dN_{\mathbf{k}_N} \theta \left( E - \frac{p_1^2}{2m} - \cdots - \frac{p_N^2}{2m} \right) \\
&= \int dE_1 \cdots \int dE_N \omega_1(E_1) \cdots \omega_1(E_N) \\
&\quad \times \theta(E - E_1 - \cdots - E_N).
\end{aligned}$$

Thus the corresponding state density is

$$\begin{aligned}
\omega_N(E) &= \frac{dJ_N(E)}{dE} \\
&= \int dE_1 \cdots dE_N \omega_1(E_1) \cdots \omega_1(E_N) \\
&\quad \times \delta(E - E_1 - \cdots - E_N).
\end{aligned}$$

We define the Laplace transformations

$$\begin{aligned}
\Omega_1(s) &= \int_0^\infty dE e^{-sE} \omega_1(E) \\
\Omega_N(s) &= \int_0^\infty dE e^{-sE} \omega_N(E).
\end{aligned}$$

Now

$$\begin{aligned}
\Omega_N(s) &= \int_0^\infty dE_1 \cdots dE_N \omega_1(E_1) \cdots \omega_1(E_N) \\
&\quad \times \int_0^\infty dE e^{-sE} \delta(E - E_1 - \cdots - E_N) \\
&= \int_0^\infty dE_1 \cdots dE_N \omega_1(E_1) e^{-sE_1} \cdots \omega_1(E_N) e^{-sE_N} \\
&= [\Omega_1(s)]^N.
\end{aligned}$$

Since

$$\Omega_1(s) = \int_0^\infty dE e^{-sE} C_1 V E^{1/2} = C_1 V \frac{1}{2} \sqrt{\pi} s^{-3/2},$$

we have

$$\Omega_N(s) = (C_2 V)^N s^{-3N/2},$$

where

$$C_2 = \frac{1}{2} \sqrt{\pi} C_1 = g \left( \frac{2\pi m}{h^2} \right)^{3/2}.$$

Performing the inverse Laplace transformations we get

$$\omega_N(E) = \frac{1}{\Gamma(\frac{3}{2}N)} (C_2 V)^N E^{3/2N-1}.$$

**Note** The permutation symmetry was ignored! An approximative correction can be obtained when the state density is divided by  $N!$ :

$$\omega_N(E) = \frac{1}{N! \Gamma(\frac{3}{2}N)} (C_2 V)^N E^{3/2N-1}.$$

**Note** Neither the multiple occupation of bosons nor the Pauli exclusion principle have been taken into account.

## Energy, entropy and temperature

### Microcanonical ensemble

We require, that

1. with full certainty the energy lies between  $(E, E + \Delta E)$ .
2. the entropy has its maximum.

Then the density operator is

$$\rho_E = \frac{1}{Z_E} \theta(E + \Delta E - H) \theta(H - E),$$

where (supposing  $\Delta E > 0$ )

$$\begin{aligned}
Z_E &= \text{Tr} \theta(E + \Delta E - H) \theta(H - E) \\
&= \text{Tr} [\theta(E + \Delta E - H) - \theta(E - H)] \\
&= J(E + \Delta E) - J(E)
\end{aligned}$$

is the number of states between  $(E, E + \Delta E)$ . When  $\Delta E$  is small, we have

$$Z_E \approx \omega(E) \Delta E.$$

Entropy is

$$S_E = k_B \ln Z_E.$$

Since  $Z_E$  is a positive integer,  $S_E \geq 0$  holds. Furthermore we get

$$\begin{aligned}
S_E &= k_B \ln[\omega(E) \Delta E] \\
&= k_B \ln \omega(E) + S_0,
\end{aligned}$$

so, we can write

$$S_E = k_B \ln \omega(E).$$

**Note** As a matter of fact

$$\omega = \omega(E, V, N).$$

In the definition of the density operator we have applied quantum mechanical "ergodicity hypothesis": all allowed states in the Hilbert space are equally probable.

### Temperature

According to thermodynamics we have

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N}.$$

In the microcanonical ensemble we define the temperature  $T$  so that

$$\frac{1}{T} = k_B \frac{\partial}{\partial E} \ln \omega(E, V, N).$$



Denoting

$$\beta = \frac{1}{k_B T},$$

we have

$$\beta = \frac{\partial \ln \omega}{\partial E}.$$

**Example** Maxwell-Boltzmann gas  
Now

$$\omega_N \propto E^{3/2N-1},$$

so

$$\ln \omega_N = \frac{3}{2} N \ln E + \dots$$

and

$$\beta = \frac{3N}{2E}$$

or we end up with the equation of state for 1-atomic ideal gas:

$$E = \frac{3}{2} k_B T N.$$

The thermodynamics of a quantum mechanical system can be derived from the density of states  $\omega(E, V, N)$ . In practice the state density of a microcanonical ensemble ( $E$  and  $N$  constant) is difficult to calculate.

## Equilibrium distributions

### Canonical ensembles

We maximise the entropy under the conditions

$$\begin{aligned} \langle H \rangle &= \text{Tr } \rho H = E = \text{constant} \\ \langle I \rangle &= \text{Tr } \rho = 1. \end{aligned}$$

So, we require that

$$\delta(S - \lambda \langle H \rangle - \lambda' \langle I \rangle) = 0,$$

where  $\lambda$  and  $\lambda'$  are Lagrange multipliers. We get

$$\begin{aligned} \delta \text{Tr} (-k_B \rho \ln \rho - \lambda \rho H - \lambda' \rho) = \\ \text{Tr} (-k_B \ln \rho - k_B - \lambda H - \lambda' I) \delta \rho = 0. \end{aligned}$$

Since  $\delta \rho$  is an arbitrary variation, we end up with the *canonical* or *Gibbs distribution*

$$\rho = \frac{1}{Z} e^{-\beta H},$$

where  $Z$  is the *canonical sum over states* (or *partition function*)

$$Z = \text{Tr} e^{-\beta H} = \sum_n e^{-\beta E_n} = \int dE \omega(E) e^{-\beta E}.$$

**Note** In the canonical ensemble the number of particles is constant, i.e.

$$Z = Z(p, V, N, \dots).$$

The probability for the state  $\psi$  is

$$p_\psi = \text{Tr } \rho P_\psi = \frac{1}{Z} \langle \psi | e^{-\beta H} | \psi \rangle.$$

Particularly, in the case of an eigenstate of the Hamiltonian,

$$H |n\rangle = E_n |n\rangle,$$

we have

$$p_n = \frac{1}{Z} e^{-\beta E_n}.$$

For one particle system we get *Boltzmann distribution*

$$p_\nu = \frac{1}{Z} e^{-\beta \epsilon_\nu}; \quad Z = \sum_\nu e^{-\beta \epsilon_\nu}.$$

Here  $\epsilon_\nu$  is the one particle energy.

Because in the canonical ensemble we have

$$\ln \rho = -\beta H - \ln Z,$$

the entropy will be

$$\begin{aligned} S &= -k_B \text{Tr } \rho \ln \rho = -k_B \langle \ln \rho \rangle \\ &= k_B \beta E + k_B \ln Z. \end{aligned}$$

We recall that  $E$  is the expectation value of the energy

$$E = \langle H \rangle = \frac{1}{Z} \text{Tr } H e^{-\beta H}.$$

The variation of the partition function is

$$\begin{aligned}\delta Z &= \text{Tr} \delta(e^{-\beta H}) = -\delta\beta \text{Tr} H e^{-\beta H} \\ &= -\delta\beta E Z.\end{aligned}$$

The variation of the entropy is then

$$\begin{aligned}\delta S &= k_B \left( E \delta\beta + \beta \delta E + \frac{\delta Z}{Z} \right) \\ &= k_B \beta \delta E.\end{aligned}$$

According to thermodynamics the temperature will be

$$T = \left( \frac{\delta E}{\delta S} \right)_{V,N} = \frac{1}{k_B \beta},$$

or

$$\beta = \frac{1}{k_B T}.$$

### Free energy

Since

$$\frac{\partial}{\partial \beta} Z = -\text{Tr} e^{-\beta H} H = -Z \langle H \rangle$$

or

$$E = -\frac{\partial}{\partial \beta} \ln Z = k_B T^2 \frac{\partial \ln Z}{\partial T},$$

we can write

$$S = k_B \frac{\partial}{\partial T} (T \ln Z).$$

The Helmholtz free energy  $F = E - TS$  can be expressed as

$$F = -k_B T \ln Z.$$

With the help of this the density operator takes the form

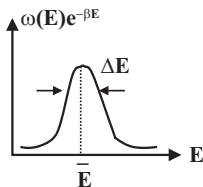
$$\rho = e^{\beta(F-H)}.$$

### Fluctuations

Let us write the sum over states as

$$Z = \int dE \omega(E) e^{-\beta E} = \int dE e^{-\beta E + \ln \omega(E)}.$$

We suppose that the function  $\omega(E) e^{-\beta E}$  has a sharp maximum at  $E = \bar{E}$  and that  $\omega(E) \approx$  microcanonical state density.



Now

$$\ln \omega(E) = \frac{1}{k_B} S(E)$$

and

$$\begin{aligned}\ln \omega(E) - \beta E &= \\ &= \ln \omega(\bar{E}) - \beta \bar{E} \\ &= 0, \text{ maximum} \\ &+ \left( \frac{1}{k_B} \frac{\partial S}{\partial E} \Big|_{E=\bar{E}} - \beta \right) (E - \bar{E}) \\ &+ \frac{1}{2k_B} \frac{\partial^2 S}{\partial E^2} \Big|_{E=\bar{E}} (E - \bar{E})^2 + \dots\end{aligned}$$

At the point of maximum  $E = \bar{E}$  we have

$$\begin{aligned}k_B \beta &= \frac{\partial S}{\partial E} \Big|_{E=\bar{E}} = \frac{1}{T(\bar{E})} \\ &= \frac{1}{\text{average temperature}}.\end{aligned}$$

So  $T$  is the average temperature. In the Taylor series

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E} \left( \frac{1}{T} \right) = -\frac{1}{T^2} \frac{\partial T}{\partial E} = -\frac{1}{T^2 C_V},$$

so

$$Z \approx \omega(\bar{E}) e^{-\beta \bar{E}} \int dE \underbrace{e^{-\frac{1}{2k_B T^2 C_V} (E - \bar{E})^2}}_{\text{normal distribution}}.$$

As the variance of the normal distribution in the integrand we can pick up

$$(\Delta E)^2 = k_B T^2 C_V$$

or

$$\Delta E = \sqrt{k_B T^2 C_V} = \mathcal{O}(\sqrt{N}),$$

because  $C_V$ , as well as  $E$ , is extensive ( $\mathcal{O}(N)$ ). Thus the fluctuation of the energy is

$$\frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}}.$$

**Note** Fluctuations can be obtained more straightforwardly from the free energy:

$$\langle (H - \langle H \rangle)^2 \rangle = -\frac{\partial^2 (\beta F)}{\partial \beta^2}.$$

### Grand canonical ensemble

Let's consider a system where both the energy and the number of particles are allowed to fluctuate. The Hilbert space of the system is then the direct sum

$$\mathcal{H} = \mathcal{H}^{(0)} \oplus \mathcal{H}^{(1)} \oplus \dots \oplus \mathcal{H}^{(N)} \oplus \dots$$

and the Hamiltonian operator the sum

$$H = H^{(0)} + H^{(1)} + \dots + H^{(N)} + \dots$$

We define the (particle) number operator  $\hat{N}$  so that

$$\hat{N} |\psi\rangle = N |\psi\rangle \quad \forall |\psi\rangle \in \mathcal{H}^{(N)}.$$

We maximize the entropy  $S$  under constraints

$$\begin{aligned}\langle H \rangle &= \bar{E} = \text{given energy} \\ \langle \hat{N} \rangle &= \bar{N} = \text{given particle number} \\ \langle I \rangle &= 1.\end{aligned}$$

With the help of Lagrange multipliers we start with

$$\delta(S - \lambda \langle H \rangle - \lambda' \langle \hat{N} \rangle - \lambda'' \langle I \rangle) = 0,$$

and end up with the *grand canonical distribution*

$$\rho = \frac{1}{Z_G} e^{-\beta(H - \mu \hat{N})}.$$

Here

$$Z_G = \text{Tr} e^{-\beta(H - \mu \hat{N})}$$

is the *grand canonical partition function*. In the base where the Hamiltonian is diagonal this is

$$Z_G = \sum_N \sum_n e^{-\beta(E_n^{(N)} - \mu N)},$$

where

$$H |N; n\rangle = H^{(N)} |N; n\rangle = E_n^{(N)} |N; n\rangle,$$

when  $|N; n\rangle \in \mathcal{H}^{(N)}$  is a state of  $N$  particles, i.e.

$$\hat{N} |N; n\rangle = N |N; n\rangle.$$

### Number of particles and energy

Now

$$\begin{aligned}\frac{\partial \ln Z_G}{\partial \mu} &= \frac{1}{Z_G} \text{Tr} e^{-\beta(H - \mu \hat{N})} \beta \hat{N} \\ &= \beta \langle \hat{N} \rangle = \beta \bar{N}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial \ln Z_G}{\partial \beta} &= -\frac{1}{Z_G} \text{Tr} e^{-\beta(H - \mu \hat{N})} (H - \mu \hat{N}) \\ &= -\langle H \rangle + \mu \langle \hat{N} \rangle = -\bar{E} + \mu \bar{N},\end{aligned}$$

so

$$\begin{aligned}\bar{N} &= k_B T \frac{\partial \ln Z_G}{\partial \mu} \\ \bar{E} &= k_B T^2 \frac{\partial \ln Z_G}{\partial T} + k_B T \mu \frac{\partial \ln Z_G}{\partial \mu}.\end{aligned}$$

### Entropy

According to the definition we have

$$S = -k_B \text{Tr} \rho \ln \rho = -k_B \langle \ln \rho \rangle.$$

Now

$$\ln \rho = -\beta H + \beta \mu \hat{N} - \ln Z_G,$$

so

$$S = \frac{\bar{E}}{T} - \mu \frac{\bar{N}}{T} + k_B \ln Z_G.$$

### Grand potential

In thermodynamics we defined

$$\Omega = E - TS - \mu N,$$

so in the grand canonical ensemble the *grand potential* is

$$\Omega = -k_B T \ln Z_G.$$

With the help of this the density operator can be written as

$$\rho = e^{\beta(\Omega - H + \mu \hat{N})}.$$

**Note** The grand canonical state sum depends on the variables  $T$ ,  $V$  and  $\mu$ , i.e.

$$Z_G = Z_G(T, V, \mu).$$

### Fluctuations

Now

$$\begin{aligned}\frac{\partial^2 Z_G}{\partial \mu^2} &= \frac{\partial^2}{\partial \mu^2} \text{Tr} e^{-\beta(H - \mu \hat{N})} \\ &= \text{Tr} e^{-\beta(H - \mu \hat{N})} \beta^2 \hat{N}^2 = Z_G \beta^2 \langle \hat{N}^2 \rangle,\end{aligned}$$

so

$$\begin{aligned}(\Delta N)^2 &= \langle (\hat{N} - \bar{N})^2 \rangle = \langle \hat{N}^2 \rangle - \bar{N}^2 \\ &= (k_B T)^2 \frac{\partial^2 \ln Z_G}{\partial \mu^2} = k_B T \frac{\partial \bar{N}}{\partial \mu} = \mathcal{O}(\bar{N}).\end{aligned}$$

Thus the particle number fluctuates like

$$\frac{\Delta N}{\bar{N}} = \mathcal{O}\left(\frac{1}{\sqrt{\bar{N}}}\right).$$

A corresponding expression is valid also for the fluctuations of the energy. For a mole of matter the fluctuations are  $\propto 10^{-12}$  or the accuracy  $\approx$  the accuracy of the microcanonical ensemble.

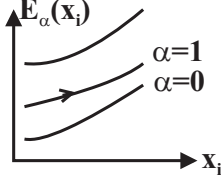
### Connection with thermodynamics

Let us suppose that the Hamiltonian  $H$  depends on external parameters  $\{x_i\}$ :

$$H(x_i) |\alpha(x_i)\rangle = E_\alpha(x_i) |\alpha(x_i)\rangle.$$

### Adiabatic variation

A system in the state  $|\alpha(x_i)\rangle$  stays there provided that the parameters  $x_i(t)$  are allowed to vary slowly enough.



Then the probabilities for the states remain constant and the change in the entropy

$$S = -k_B \sum_{\alpha} p_{\alpha} \ln p_{\alpha}$$

is zero. Now

$$\begin{aligned} \frac{\partial E_{\alpha}}{\partial x_i} &= \frac{\partial}{\partial x_i} \langle \alpha | H | \alpha \rangle = \left\langle \alpha \left| \frac{\partial H}{\partial x_i} \right| \alpha \right\rangle + E_{\alpha} \frac{\partial}{\partial x_i} \langle \alpha | \alpha \rangle \\ &= \left\langle \alpha \left| \frac{\partial H}{\partial x_i} \right| \alpha \right\rangle, \end{aligned}$$

since  $\langle \alpha | \alpha \rangle = 1$ .

Let  $F_i$  be the generalized force

$$F_i = - \left\langle \alpha \left| \frac{\partial H}{\partial x_i} \right| \alpha \right\rangle = - \frac{\partial E_{\alpha}}{\partial x_i}$$

and  $\delta x_i$  the related displacement. Then

$$\delta \langle H \rangle = - \sum_i F_i \delta x_i.$$

### Statistical study

Let us consider the density operator in an equilibrium state ( $[H, \rho] = 0$ ). In the base  $\{|\alpha\rangle\}$ , where the Hamiltonian is diagonal,

$$H |\alpha\rangle = E_{\alpha} |\alpha\rangle,$$

we have

$$\rho = \sum_{\alpha} p_{\alpha} P_{\alpha},$$

where

$$P_{\alpha} = |\alpha\rangle \langle \alpha|.$$

We divide the variation of the density operator into two parts:

$$\begin{aligned} \delta \rho &= \overbrace{\sum_{\alpha} p_{\alpha} \delta P_{\alpha}}^{\text{adiabatic}} + \overbrace{\sum_{\alpha} \delta p_{\alpha} P_{\alpha}}^{\text{nonadiabatic}} \\ &= \delta \rho^{(1)} + \delta \rho^{(2)}. \end{aligned}$$

Then

$$\begin{aligned} \delta \langle H \rangle &= \text{Tr } \delta \rho H + \text{Tr } \rho \delta H \\ &= \text{Tr } \delta \rho^{(1)} H + \text{Tr } \delta \rho^{(2)} H + \sum_i \delta x_i \text{Tr } \rho \frac{\partial H}{\partial x_i} \\ &= \sum_{\alpha} p_{\alpha} \text{Tr } H \delta P_{\alpha} + \text{Tr } \delta \rho^{(2)} H - \sum_i F_i \delta x_i. \end{aligned}$$

Now

$$\begin{aligned} \text{Tr } H \delta P_{\alpha} &= \sum_{\beta} \langle \beta | H (|\alpha\rangle \langle \delta \alpha| + |\delta \alpha\rangle \langle \alpha|) | \beta \rangle \\ &= E_{\alpha} \delta \langle \alpha | \alpha \rangle = 0, \end{aligned}$$

so

$$\delta \langle H \rangle = \text{Tr } \delta \rho^{(2)} H - \sum_i F_i \delta x_i.$$

Since

$$\begin{aligned} \int dE \omega(E) f(E) &= \sum_{\alpha} \int dE \delta(E - E_{\alpha}) f(E) \\ &= \sum_{\alpha} f(E_{\alpha}), \end{aligned}$$

we can write the nonadiabatic term as

$$\begin{aligned} \text{Tr } \delta \rho^{(2)} H &= \sum_{\alpha} \delta p_{\alpha} E_{\alpha} \\ &= \int dE \omega(E) E \delta p(E). \end{aligned}$$

According to the definition the statistical entropy is

$$S^{\text{stat}} = -k_B \sum_{\alpha} p_{\alpha} \ln p_{\alpha}.$$

Its variation is

$$\begin{aligned} \delta S^{\text{stat}} &= -k_B \sum_{\alpha} \delta p_{\alpha} \ln p_{\alpha} - k_B \overbrace{\sum_{\alpha} \delta p_{\alpha}}^{=0} \\ &= -k_B \sum_{\alpha} \delta p_{\alpha} \ln p_{\alpha} \\ &= -k_B \int dE \omega(E) \delta p(E) \ln p(E). \end{aligned}$$

In the microcanonical ensemble

$$p(E) \propto \frac{1}{Z_{E, \Delta E}} \propto \frac{1}{\omega(E)},$$

holds, so

$$-k_B \ln p(E) = k_B \ln \omega(E) = S^{\text{stat}}(E),$$

where  $S^{\text{stat}}(E)$  is the microcanonical entropy. The variation of the entropy can be written as

$$\delta S^{\text{stat}} = \int dE \omega(E) S^{\text{stat}}(E) \delta p(E).$$

We expand  $S^{\text{stat}}(E)$  as a Taylor series in a neighborhood of the point  $E = \bar{E}$ :

$$\begin{aligned} S^{\text{stat}}(E) &= S^{\text{stat}}(\bar{E}) \\ &\quad + \left. \frac{\partial S^{\text{stat}}(E)}{\partial E} \right|_{E=\bar{E}} (E - \bar{E}) + \dots \\ &= S^{\text{stat}}(\bar{E}) + \frac{E - \bar{E}}{T^{\text{stat}}(\bar{E})} + \dots \end{aligned}$$

Since

$$\int dE \omega(E) \delta p(E) = \sum_{\alpha} \delta p_{\alpha} = 0,$$

we get

$$\begin{aligned} \delta S^{\text{stat}} &= \frac{1}{T^{\text{stat}}(\bar{E})} \int dE \omega(E) E \delta p(E) \\ &= \frac{1}{T^{\text{stat}}(\bar{E})} \text{Tr} \delta \rho^{(2)} H \end{aligned}$$

or

$$\delta \langle H \rangle = T^{\text{stat}} \delta S^{\text{stat}} - \sum_i F_i \delta x_i.$$

This is equivalent to the first law of the thermodynamics,

$$\delta U = T^{\text{therm}} \delta S^{\text{therm}} - \delta W,$$

provided we identify

$$\begin{aligned} \langle H \rangle &= \bar{E} = U = \text{internal energy} \\ T^{\text{stat}} &= T^{\text{therm}} \\ S^{\text{stat}} &= S^{\text{therm}} \\ \sum_i F_i \delta x_i &= \delta W = \text{work.} \end{aligned}$$

## Einstein's theory of fluctuations

We divide a large system into macroscopical partial systems whose mutual interactions are weak.

$\Rightarrow \exists$  operators  $\{\hat{X}_i\}$  corresponding to the extensive properties of the partial systems so that

$$\begin{aligned} [\hat{X}_i, \hat{X}_j] &\approx 0 \\ [\hat{X}_i, H] &\approx 0. \end{aligned}$$

$\Rightarrow \exists$  a mutual eigenstate  $|E, X_1, \dots, X_n\rangle$ , which is one of the macrostates of the system, i.e. corresponding to the parameter set  $(E, X_1, \dots, X_n)$  there is a macroscopical number of microstates. Let  $\Gamma(E, X_1, \dots, X_n)$  be the number of the microstates corresponding to the macrostate  $|E, X_1, \dots, X_n\rangle$  (the volume of the phase space).

The total number of the states is

$$\Gamma(E) = \sum_{\{X_i\}} \Gamma(E, X_1, \dots, X_n)$$

and the relative probability of the macrostate  $|E, X_1, \dots, X_n\rangle$

$$f(E, X_1, \dots, X_n) = \frac{\Gamma(E, X_1, \dots, X_n)}{\Gamma(E)}.$$

The entropy of the state  $|E, X_1, \dots, X_n\rangle$  is

$$S(E, X_1, \dots, X_n) = k_B \ln \Gamma(E, X_1, \dots, X_n)$$

or

$$f(E, X_1, \dots, X_n) = \frac{1}{\Gamma(E)} e^{\frac{1}{k_B} S(E, X_1, \dots, X_n)}.$$

In the thermodynamic equilibrium the entropy  $S$  has its maximum

$$S^0 = S(E, X_1^{(0)}, \dots, X_n^{(0)}).$$

Let us denote by

$$x_i = X_i - X_i^{(0)}$$

deviations from the equilibrium positions.

The Taylor series of the entropy will be

$$S = S^0 - \frac{1}{2} k_B \sum_{i,j} g_{ij} x_i x_j + \dots,$$

where

$$g_{ij} = \frac{1}{k_B} \left( \frac{\partial^2 S}{\partial X_i \partial X_j} \right) \Big|_{\{X_i^{(0)}\}}.$$

We use notation

$$x = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix} \text{ and } g = (g_{ij}).$$

Then

$$f(x) = C e^{-\frac{1}{2} x^T g x},$$

where

$$C = (2\pi)^{-n/2} \sqrt{\det g}.$$

*Correlation functions* can be written as

$$\begin{aligned} \langle x_p \cdots x_r \rangle &\equiv \int dx f(x) x_p \cdots x_r \\ &= \left[ \frac{\partial}{\partial h_p} \cdots \frac{\partial}{\partial h_r} F(h) \right]_{h=0}, \end{aligned}$$

where

$$dx = dx_1 \cdots dx_n$$

and

$$F(h) = e^{\frac{1}{2} h^T g^{-1} h}.$$

### pVT-system

When studying the stability conditions of matter we found out that

$$\Delta S = -\frac{1}{2T} \sum_i (\Delta T_i \Delta S_i - \Delta p_i \Delta V_i + \Delta \mu_i \Delta N_i).$$

Supposing that there is only one volume element in the system we get

$$f = C e^{-\frac{1}{2k_B T} (\Delta T \Delta S - \Delta p \Delta V + \Delta \mu \Delta N)}.$$

We suppose that the system is not allowed to exchange particles, i.e.  $\Delta N = 0$ . Employing the definitions of the heat capacity and compressibility we can write

$$f(\Delta T, \Delta V) \propto e^{-\frac{1}{2} \left[ \frac{C_V}{k_B T^2} (\Delta T)^2 + \frac{1}{V k_B T \kappa_T} (\Delta V)^2 \right]}.$$

We can now read out the matrix  $g$ :

$$g = \begin{matrix} T & V \\ \left( \begin{array}{cc} \frac{C_V}{k_B T^2} & 0 \\ 0 & \frac{1}{V k_B T \kappa_T} \end{array} \right) \end{matrix}.$$

The variances are then

$$\begin{aligned} \langle (\Delta T)^2 \rangle &= \frac{k_B T^2}{C_V} \\ \langle (\Delta V)^2 \rangle &= V k_B T \kappa_T. \end{aligned}$$

### Reversibel minimum work

Let  $x = X - X^{(0)}$  be the fluctuation of the variable  $X$ . For one variable we have

$$f(x) \propto e^{-\frac{1}{2} g x^2}.$$

Now  $S = S(U, X, \dots)$  holds and

$$dU = T dS - F dX - dW_{\text{other}}.$$

We get the partial derivative

$$\frac{\partial S}{\partial X} = \frac{F}{T}.$$

On the other hand we had

$$\begin{aligned} S &= S^0 - \frac{1}{2} k_B \sum_{i,j} g_{ij} x_i x_j \\ &= S^0 - \frac{1}{2} k_B g x^2, \end{aligned}$$

so

$$\frac{\partial S}{\partial X} = -k_B g x$$

and

$$F = -k_B T g x.$$

When there is no action on  $X$  from outside, the deviation  $x$  fluctuates spontaneously. Let us give rise to the same deviation  $x$  by applying *reversible* external work:

$$dU = -F dx = k_B T g x dx.$$

Integrating this we get

$$(\Delta U)_{\text{rev}} \equiv \Delta R = \frac{1}{2} k_B T g x^2,$$

where  $\Delta R$  is the minimum reversible work required for the fluctuation  $\Delta X$ . We can write

$$f(\Delta X) \propto e^{-\frac{\Delta R}{k_B T}}.$$

## Ideal systems

### System of free spins

Let us consider  $N$  particles with spin  $\frac{1}{2}$ :

$$\begin{aligned} S_i &= \frac{1}{2} \hbar \\ S_{iz} &= \pm \frac{1}{2} \hbar \quad i = 1, \dots, N. \end{aligned}$$

The  $z$  component of the total spin is

$$S_z = \sum_i S_{iz} = \frac{1}{2} \hbar (N^+ - N^-),$$

where

$$\begin{aligned} N^+ &= +\frac{1}{2} \hbar \text{ spin count} \\ N^- &= -\frac{1}{2} \hbar \text{ spin count.} \end{aligned}$$

$S_z$  determines the macrostate of the system. Denoting  $S_z = \hbar \nu$  we have

$$\begin{aligned} N^+ &= \frac{1}{2} N + \nu \\ N^- &= \frac{1}{2} N - \nu \end{aligned}$$

and

$$\nu = -\frac{1}{2} N, -\frac{1}{2} N + 1, \dots, \frac{1}{2} N.$$

Let  $W(\nu)$  be the number of those microstates for which  $S_z = \hbar \nu$ , i.e.  $W(\nu)$  tells us, how many ways there are to distribute  $N$  particles into groups of  $N^+$  and  $N^-$  particles so that  $N^+ + N^- = N$  and  $N^+ - N^- = 2\nu$ . From combinatorics we know that

$$\begin{aligned} W(\nu) &= \binom{N}{N^+} = \frac{N!}{N^+! N^-!} \\ &= \frac{N!}{(\frac{1}{2} N + \nu)! (\frac{1}{2} N - \nu)!}. \end{aligned}$$

$W(\nu)$  the *degeneracy* of the state  $S_z = \hbar \nu$ .

The Boltzmann entropy is

$$S = k_B \ln W(\nu).$$

Using Stirling's formula

$$\ln N! \approx N \ln N - N$$

we get

$$\begin{aligned} \ln W(\nu) &\approx N \ln N - N \\ &\quad - \left[ \left( \frac{1}{2} N + \nu \right) \ln \left( \frac{1}{2} N + \nu \right) - \left( \frac{1}{2} N + \nu \right) \right] \\ &\quad - \left[ \left( \frac{1}{2} N - \nu \right) \ln \left( \frac{1}{2} N - \nu \right) - \left( \frac{1}{2} N - \nu \right) \right] \\ &= \frac{1}{2} N \ln \frac{N^2}{\frac{1}{4} N^2 - \nu^2} - \nu \ln \frac{\frac{1}{2} N + \nu}{\frac{1}{2} N - \nu}. \end{aligned}$$

We look for the extremum of  $W(\nu)$ :

$$\begin{aligned}\frac{\partial \ln W(\nu)}{\partial \nu} &= \frac{1}{2} N \frac{\frac{1}{4} N^2 - \nu^2}{N^2} \frac{N^2}{\left(\frac{1}{4} N^2 - \nu^2\right)^2} 2\nu \\ &\quad - \ln \frac{\frac{1}{2} N + \nu}{\frac{1}{2} N - \nu} \\ &\quad - \nu \frac{\frac{1}{2} N - \nu}{\frac{1}{2} N + \nu} \frac{\frac{1}{2} N - \nu + \frac{1}{2} N + \nu}{\left(\frac{1}{2} N - \nu\right)^2} \\ &= -\ln \frac{\frac{1}{2} N + \nu}{\frac{1}{2} N - \nu} = 0.\end{aligned}$$

We can see that  $\nu = 0$ .  
Now

$$\begin{aligned}\left. \frac{\partial^2 \ln W(\nu)}{\partial \nu^2} \right|_{\nu=0} &= \left. \frac{N}{\frac{1}{4} N^2 - \nu^2} \right|_{\nu=0} \\ &= -\frac{4}{N} < 0,\end{aligned}$$

so  $\nu = 0$  is a maximum.  
Let us expand  $\ln W(\nu)$  as a Taylor series in the vicinity of its maximum:

$$\ln W(\nu) = \ln W(0) - \frac{2}{N} \nu^2 + \mathcal{O}(\nu^3),$$

so  $W(\nu)$  obeys the normal distribution

$$W(\nu) \approx W(0) e^{-\frac{2}{N} \nu^2},$$

whose deviation is

$$\Delta \nu = \frac{1}{2} \sqrt{N}.$$

In this distribution

$$\ln W(0) \approx N \ln 2$$

or

$$W(0) \approx 2^N.$$

### Total number of states

We have exactly

$$\begin{aligned}W_{\text{tot}} &= \sum_{N^+} \binom{N}{N^+} = (1+1)^N \\ &= 2^N.\end{aligned}$$

According to the previous treatment we can write approximatively

$$\begin{aligned}W_{\text{tot}}^{\text{appr}} &\approx \sum_{\nu} W(0) e^{-\frac{2}{N} \nu^2} \approx W(0) \int_{-\infty}^{\infty} d\nu e^{-\frac{2}{N} \nu^2} \\ &\approx 2^N \sqrt{\frac{\pi}{2} N}.\end{aligned}$$

On the other hand we have

$$\begin{aligned}\ln W_{\text{tot}}^{\text{appr}} &= \overbrace{N \ln 2}^{\text{extensive}} + \overbrace{\frac{1}{2} \ln \left( \frac{\pi}{2} N \right)}^{\text{non extensive}} \\ &= \ln W_{\text{tot}} + \text{non extensive}\end{aligned}$$

### Energy

Let's put the system in the external magnetic field

$$\mathbf{B} = \mu_0 \mathbf{H},$$

where

$$\mathbf{H} = H \hat{z}$$

is the magnetizing field.

The potential energy is

$$E = -\mu_0 \sum_i \boldsymbol{\mu}_i \cdot \mathbf{H} = -\mu_0 H \sum_i \mu_{iz},$$

where  $\boldsymbol{\mu}_i$  is the magnetic moment of the particle  $i$ .  
Now

$$\boldsymbol{\mu} = \gamma \mathbf{S},$$

where  $\gamma$  is the gyromagnetic ratio. For electrons we have

$$\gamma = 2\gamma_0 = -\frac{e}{m},$$

where  $\gamma_0$  is the classical value  $\frac{e}{2m}$ .  
For electrons we can further write

$$\mu_z^e = -\mu_B \sigma_z = \mp \mu_B.$$

Here  $\sigma_z$  is the Pauli spin matrix and

$$\mu_B = \frac{e\hbar}{2m} = 5.79 \cdot 10^{-5} \frac{\text{eV}}{\text{T}}$$

the Bohr magneton.

Thus the energy is

$$E = -\mu_0 H \sum \mu_{iz} = -\mu_0 \gamma H S_z = \epsilon \nu,$$

where

$$\epsilon = -\hbar \gamma \mu_0 H$$

is the energy/particle. For electrons we have

$$\epsilon = 2\mu_0 \mu_B H.$$

Now

$$\Delta E = \epsilon \Delta \nu,$$

so from the condition

$$\omega(E) \Delta E = W(\nu) \Delta \nu$$

we get as the density of states

$$\omega(E) = \frac{1}{|\epsilon|} W \left( \frac{E}{\epsilon} \right).$$



### 1) Microcanonical ensemble

Denoting

$$E_0 = \frac{1}{2} \epsilon N,$$

the total energy will lie between  $-E_0 \leq E \leq E_0$ .

With the help of the energy the degeneracy can be written as

$$\begin{aligned} \ln W(\nu) &= \frac{1}{2} N \ln \frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{\epsilon} \ln \frac{E_0 + E}{E_0 - E} \\ &= \ln \omega(E) + \ln |\epsilon|. \end{aligned}$$

As the entropy we get

$$\begin{aligned} S(E) &= k_B \ln \omega(E) \\ &= Nk_B \left[ \frac{1}{2} \ln \frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{2E_0} \ln \frac{E_0 + E}{E_0 - E} \right] \\ &\quad + \text{non extensive term.} \end{aligned}$$

The temperature was defined like

$$\frac{1}{T} = \frac{\partial S}{\partial E},$$

so

$$\beta(E) = \frac{1}{k_B T(E)} = -\frac{N}{2E_0} \ln \frac{E_0 + E}{E_0 - E}.$$

We can solve for the energy:

$$\begin{aligned} E &= -E_0 \tanh \frac{\beta E_0}{N} \\ &= -\frac{1}{2} N \mu_0 \hbar \gamma H \tanh \left( \frac{\mu_0 \hbar \gamma H}{2k_B T} \right). \end{aligned}$$

The *magnetization* or the *magnetic polarization* means the magnetic moment per the volume element, i.e.

$$\mathbf{M} = \frac{1}{V} \sum_i \boldsymbol{\mu}_i.$$

The  $z$  component of the magnetization is

$$\begin{aligned} M_z &= -\frac{1}{V} \frac{\epsilon \nu}{\mu_0 H} = \frac{1}{V} \frac{\hbar \gamma \mu_0 H \nu}{\mu_0 H} \\ &= \frac{1}{V} \gamma \hbar \nu. \end{aligned}$$

Now

$$E = -\mu_0 H V M_z,$$

so we get for our system as the equation of state

$$M = \frac{1}{2} \rho \hbar \gamma \tanh \left( \frac{\mu_0 \hbar \gamma H}{2k_B T} \right),$$

where  $\rho = N/V$  is the particle density.

**Note** The relations derived above

$$\begin{aligned} E &= E(T, H, N) \\ M &= M(T, H, N) \end{aligned}$$

determine the thermodynamics of the system.

### 2) Canonical ensemble

The canonical partition function is

$$Z = \sum_n e^{-\beta E_n}.$$

Here

$$E_n = -\mu_0 H \sum_{i=1}^N \mu_{iz}$$

the energy of a single microstate.

Denote

$$\mu_{iz} = \hbar \gamma \nu_i, \quad \nu_i = \pm \frac{1}{2}.$$

Now

$$\begin{aligned} Z &= \sum_{\text{all microstates}} e^{\beta \mu_0 H \sum_i \mu_{iz}} \\ &= \sum_{\nu_1 = -\frac{1}{2}}^{\frac{1}{2}} \dots \sum_{\nu_N = -\frac{1}{2}}^{\frac{1}{2}} e^{\beta \mu_0 \hbar \gamma H \sum_i \nu_i} \\ &= \left[ \sum_{\nu = -\frac{1}{2}}^{\frac{1}{2}} e^{\beta \mu_0 H \gamma \hbar \nu} \right]^N = Z_1^N, \end{aligned}$$

where  $Z_1$  the one particle state sum

$$\begin{aligned} Z_1 &= e^{-\frac{1}{2} \beta \mu_0 H \gamma} + e^{\frac{1}{2} \beta \mu_0 H \gamma} \\ &= 2 \cosh \frac{\mu_0 H \gamma}{2k_B T}. \end{aligned}$$

The same result can be obtained using the degeneracy:

$$\begin{aligned} Z &= \sum_{\nu} W(\nu) e^{-\beta E(\nu)} \\ &= \sum_{\nu} W(\nu) e^{-\beta \epsilon \nu} \\ &= \sum_{N^+} \binom{N}{N^+} e^{-\beta \epsilon (N^+ - \frac{1}{2} N)} \\ &= e^{-\frac{1}{2} \beta \epsilon N} (1 + e^{-\beta \epsilon})^N. \end{aligned}$$

The free energy  $F$  is

$$\begin{aligned} F &= F(T, \mathbf{H}) = -k_B T \ln Z \\ &= -k_B T N \left[ \ln 2 + \ln \cosh \frac{\mu_0 H \gamma \hbar}{2k_B T} \right]. \end{aligned}$$

The entropy is

$$\begin{aligned} S &= - \left( \frac{\partial F}{\partial T} \right)_{\mathbf{H}} \\ &= Nk_B \left[ \ln 2 + \ln \cosh \frac{\mu_0 H \gamma \hbar}{2k_B T} \right. \\ &\quad \left. - \frac{\mu_0 \hbar \gamma H}{2k_B T} \tanh \frac{\mu_0 \hbar \gamma H}{2k_B T} \right]. \end{aligned}$$

Differentiating the free energy with respect to the field  $\mathbf{H}$  we get

$$\begin{aligned} -\left(\frac{\partial F}{\partial H_z}\right)_T &= k_B T \frac{1}{Z} \frac{\partial}{\partial H} \sum_{\nu} W(\nu) e^{-\beta \epsilon \nu} \\ &= \mu_0 \gamma \hbar \frac{1}{Z} \sum_{\nu} \nu W(\nu) e^{-\beta \epsilon \nu} \\ &= \mu_0 \gamma \hbar \langle \nu \rangle = \mu_0 V M_z. \end{aligned}$$

Since the differential of the free energy is

$$dF = -S dT - \mu_0 V \mathbf{M} \cdot d\mathbf{H},$$

the magnetization is

$$\begin{aligned} M &= -\frac{1}{\mu_0 V} \left(\frac{\partial F}{\partial H}\right)_T \\ &= -\frac{1}{2} \rho \hbar \gamma \tanh\left(\frac{\mu_0 \hbar \gamma H}{2k_B T}\right). \end{aligned}$$

This is identical with the result we obtained in the microcanonical ensemble.

Also, the microcanonical entropy = the canonical entropy + a non extensive term.

### Energy

a)

$$\begin{aligned} E &= \langle E(\nu) \rangle = \epsilon \bar{\nu} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z \\ &= -\frac{1}{2} N \epsilon \tanh\left(\frac{1}{2} \beta \epsilon\right) \\ &= \text{the energy of the microcanonical ensemble.} \end{aligned}$$

b) According to thermodynamics

$$F = E - TS$$

or

$$\begin{aligned} E &= F + TS = F - T \frac{\partial F}{\partial T} \\ &= F + \beta \frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta} (\beta F) \\ &= -\frac{\partial}{\partial \beta} \ln Z \\ &= \text{the energy given at a).} \end{aligned}$$

### Susceptibility

According to the definition the susceptibility is

$$\begin{aligned} \chi &= \left(\frac{\partial M}{\partial H}\right)_T = -\frac{1}{\mu_0 V} \left(\frac{\partial^2 F}{\partial H^2}\right) \\ &= \frac{\mu_0 \rho}{k_B T} \frac{\left(\frac{1}{2} \hbar \gamma\right)^2}{\cosh^2\left(\frac{\hbar \gamma \mu_0 H}{2k_B T}\right)}. \end{aligned}$$

When  $H \rightarrow 0$  we end up with *Curie's law*

$$\chi = \frac{C}{T},$$

where

$$C = \frac{\mu_0 \rho}{k_B T} \left(\frac{1}{2} \hbar \gamma\right)^2.$$

### Thermodynamical identifications

Earlier we identified

$$E^{\text{stat}} \equiv E = \langle H \rangle = U^{\text{term}} = \text{internal energy,}$$

so

$$\begin{aligned} F &= E - TS = F^{\text{therm}} \\ &= \text{the Helmholtz free energy} \\ &= U - TS. \end{aligned}$$

Now

$$\begin{aligned} dF &= -S dT - \mu_0 V \mathbf{M} \cdot d\mathbf{H} \\ &= dF^{\text{therm}} = -S dT - dW, \end{aligned}$$

so

$$dW = \mu_0 V \mathbf{M} \cdot d\mathbf{H}.$$

*Another possibility*

Let us identify

$$E = \text{enthalpy} = H^{\text{therm}} = H.$$

Then

$$\begin{aligned} F &= E - TS = H^{\text{therm}} - TS = G^{\text{therm}} \\ &= \text{the Gibbs free energy} = G \end{aligned}$$

and

$$\begin{aligned} dG &= -S dT - \mu_0 V \mathbf{M} \cdot d\mathbf{H} \\ dH &= T dS - \mu_0 V \mathbf{M} \cdot d\mathbf{H}, \end{aligned}$$

so

$$\begin{aligned} G &= G(T, \mathbf{H}) \\ H &= H(S, \mathbf{H}). \end{aligned}$$

In the thermodynamics we had for a  $pVT$  system

$$dH = T dS + V dp,$$

from which we get the analogies

$$\begin{aligned} p &\longleftrightarrow -\mu_0 \mathbf{H} \quad (\text{intensive}) \\ V &\longleftrightarrow V \mathbf{M} \quad (\text{extensive}). \end{aligned}$$

On the other hand we had

$$U = H - pV$$

and

$$dU = T dS - p dV = T dS - dW,$$

so now

$$U = H + \mu_0 V \mathbf{M} \cdot \mathbf{H}$$

and

$$dU = T dS + \mu_0 V \mathbf{H} \cdot d\mathbf{M},$$

from which

$$dW = -\mu_0 V \mathbf{H} \cdot d\mathbf{M}.$$

**Example** *Adiabatic demagnetization* Now

$$\frac{S}{Nk_B} = \ln 2 + \ln \cosh x - x \tanh x,$$

where

$$x = \frac{\mu_0 \hbar H \gamma}{2k_B T}.$$

When  $T \rightarrow 0$ , then  $x \rightarrow \infty$ , so that

$$\begin{aligned} \ln \cosh x &= \ln \frac{1}{2} e^x (1 + e^{-2x}) \\ &= x - \ln 2 + e^{-2x} + \dots \end{aligned}$$

and

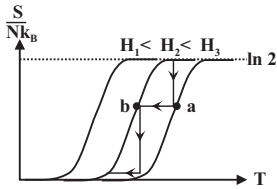
$$\begin{aligned} \tanh x &= \frac{e^x (1 - e^{-2x})}{e^x (1 + e^{-2x})} \\ &= 1 - 2e^{-2x} + \dots \end{aligned}$$

Hence

$$\frac{S}{Nk_B} \rightarrow 2xe^{-2x} + \dots$$

When  $T \rightarrow \infty$ , then  $x \rightarrow 0$ , and

$$\frac{S}{Nk_B} \rightarrow \ln 2.$$



We decrease the field adiabatically within the interval  $a \rightarrow b$ . Now  $S = S(H/T)$ , so that

$$S_a = S\left(\frac{H_a}{T_a}\right) = S_b = S\left(\frac{H_b}{T_b}\right)$$

or

$$\frac{T_b}{T_a} = \frac{H_b}{H_a}.$$

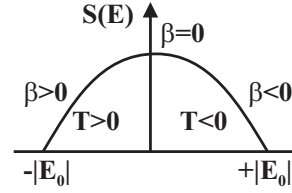
### Negative temperature

The entropy of the spin system is

$$S(E) = Nk_B \left[ \frac{1}{2} \ln \frac{4E_0^2}{E_0^2 - E^2} - \frac{E}{2E_0} \ln \frac{E_0 + E}{E_0 - E} \right],$$

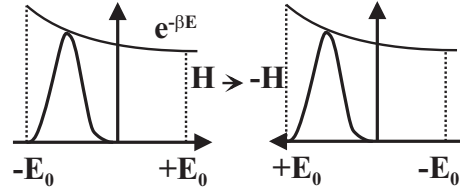
where

$$E_0 = \mu_0 \mu_B H N \text{ ja } -|E_0| < E < |E_0|.$$



Now

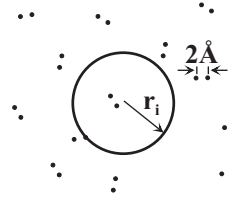
$$\beta(E) = \frac{1}{k_B} \frac{\partial S}{\partial E} = -\frac{N}{2E_0} \ln \frac{E + E_0}{E - E_0}.$$



Originally the maximum of  $\omega(E)e^{-\beta E}/Z$  is at a negative value  $E$ . Reversing the magnetic field abruptly  $E \rightarrow -E$  and correspondingly  $\beta \rightarrow -\beta$ .

The temperature can be negative if the energy is bounded both above and below.

### Classical ideal gas (Maxwell-Boltzmann gas)



We define  $r_i$  so that

The volume occupied by one molecule =

$$v_i = \frac{4}{3} \pi r_i^3 = \frac{V}{N} = \frac{1}{\rho}$$

or

$$r_i = \sqrt[3]{\frac{3}{4\pi\rho}}.$$

Typically

- the diameter of an atom or a molecule  $d \approx 2\text{\AA}$ .
- the range of the interaction  $2-4\text{\AA}$ .
- the free path (collision interval)  $l \approx 600\text{\AA}$ .
- at STP ( $T = 273\text{K}$ ,  $p = 1\text{atm}$ )  $r_i \approx 20\text{\AA}$ .

or

$$\frac{d}{2} \ll r_i \ll \frac{l}{600 \text{ \AA}}$$

The most important effect of collisions is that the system *thermalizes* i.e. attains an equilibrium, which corresponds to a statistical ensemble. Otherwise we can forget the collisions.

Let us consider a system of *one molecule* which can exchange energy (heat) with its surroundings. Then the

suitable ensemble is the canonical ensemble and the distribution the Boltzmann distribution

$$\rho_l = \langle l | \rho | l \rangle = \frac{1}{Z} e^{-\beta \epsilon_l},$$

where the canonical partition function is

$$Z = \sum_l e^{-\beta \epsilon_l}.$$

Since in the  $k$ -space the density of 1 particle states is constant, in the *velocity space*, where

$$d^3v = \frac{1}{m^3} d^3p = \left(\frac{\hbar}{m}\right)^3 d^3k,$$

the density of states is also constant.

Because the system is translationally invariant we have

$$\epsilon_k = \langle \mathbf{k} | H | \mathbf{k} \rangle = \frac{\hbar^2 k^2}{2m} = \frac{1}{2} m v^2,$$

so that the velocity distribution is

$$f(\mathbf{v}) \propto \langle \mathbf{k} | \rho | \mathbf{k} \rangle = e^{-\frac{m v^2}{2k_B T}}$$

or

$$f(\mathbf{v}) = C e^{-\frac{m v^2}{2k_B T}}.$$

$C$  can be determined from the condition

$$\begin{aligned} 1 &= \int f(\mathbf{v}) d^3v = C \left[ \int_{-\infty}^{\infty} dv_x e^{-\frac{m v_x^2}{2k_B T}} \right]^3 \\ &= C \left( \frac{2\pi k_B T}{m} \right)^{3/2}. \end{aligned}$$

Thus the velocity obeys *Maxwell's distribution*

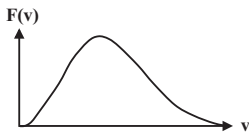
$$f(\mathbf{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m v^2}{2k_B T}}.$$

From the relation

$$\int d^3v = \int_0^{\infty} 4\pi v^2 dv$$

we can obtain for the *speed* (the absolute value of the velocity  $v = |\mathbf{v}|$ ) the distribution  $F(v)$

$$F(v) = 4\pi v^2 f(v).$$



- The most probable speed

$$v_m = \sqrt{\frac{2k_B T}{m}}.$$

- The average of the speed

$$\langle v \rangle = \int_0^{\infty} dv v F(v) = \sqrt{\frac{8k_B T}{\pi m}}.$$

- The average of the square of the speed

$$\langle v^2 \rangle = \int_0^{\infty} dv v^2 F(v) = \frac{3k_B T}{m}.$$

**Note**

$$\left\langle \frac{1}{2} m v_x^2 \right\rangle = \left\langle \frac{1}{2} m v_y^2 \right\rangle = \left\langle \frac{1}{2} m v_z^2 \right\rangle = \frac{1}{2} k_B T$$

and

$$\left\langle \frac{1}{2} m v^2 \right\rangle = 3 \left\langle \frac{1}{2} m v_x^2 \right\rangle = \frac{3}{2} k_B T,$$

i.e. the energy is evenly distributed among the 3 (translational) degrees of freedom: the *equipartition* of the energy.

### Partition function and thermodynamics

The single particle partition function is

$$\begin{aligned} Z_1(\beta) &= \int dE \omega(E) e^{-\beta E} \\ &= g \sum_{\mathbf{k}} e^{-\beta \frac{\hbar^2 k^2}{2m}} = g \frac{V}{h^3} \int d^3p e^{-\frac{p^2}{2mk_B T}} \\ &= g \frac{V}{h^3} (2\pi m k_B T)^{3/2}. \end{aligned}$$

Here  $g$  is the spin degeneracy.

When we denote the *thermal de Broglie wave length* by

$$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

we can write the one body partition function as

$$Z_1(\beta) = g \frac{V}{\lambda_T^3}.$$

In the  $N$  particle system the canonical partition function takes the form

$$\begin{aligned} Z_N &= \frac{1}{N!} g^N \sum_{\mathbf{k}_1} \dots \sum_{\mathbf{k}_N} e^{-\beta(\epsilon_{\mathbf{k}_1} + \dots + \epsilon_{\mathbf{k}_N})} \\ &= \frac{1}{N!} g^N \left( \sum_{\mathbf{k}} e^{-\beta \epsilon_{\mathbf{k}}} \right)^N \\ &= \frac{1}{N!} Z_1^N. \end{aligned}$$

Here  $N!$  takes care of the fact that each state

$$|\mathbf{k}_1, \dots, \mathbf{k}_N\rangle$$

is counted only once. Neither the multiple occupation nor the Pauli exclusion principle has been taken into account.

Using Stirling's formula  $\ln N! \approx N \ln N - N$  the free energy can be written as

$$\begin{aligned} F_N &= \\ &= -k_B T \ln Z_N \\ &= N k_B T \left[ \ln \frac{N}{V} - 1 - \ln g + \ln \lambda_T^3 \right] \\ &= N k_B T \left[ \ln \frac{N}{V} - \frac{3}{2} \ln T - 1 - \ln g + \frac{3}{2} \ln \frac{h^2}{2\pi m k_B} \right]. \end{aligned}$$

Since

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

the pressure will be

$$p = -\frac{\partial F}{\partial V} = N k_B T \frac{1}{V}$$

i.e. we end up with the *ideal gas equation of state*

$$pV = N k_B T.$$

With the help of the entropy

$$S = -\frac{\partial F}{\partial T} = -\frac{F}{T} + \frac{3}{2} N k_B$$

the internal energy is

$$U = F + TS = \frac{3}{2} N k_B T$$

i.e. the *ideal gas internal energy*.

The heat capacity is

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{2} N k_B.$$

Comparing this with

$$C_V = \frac{1}{2} f k_B N$$

we see that the number of degrees of freedom is  $f = 3$ .

### Grand canonical partition function

According to the definition we have

$$Z_G = \sum_N \sum_n e^{-\beta(E_n^{(N)} - \mu N)} = \sum_N z^N Z_N,$$

where

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

is called the *fugacity* and  $Z_N$  is the partition function of  $N$  particles.

So we get

$$\begin{aligned} Z_G &= \sum_N \frac{1}{N!} z^N Z_1^N = e^{z Z_1} \\ &= \exp \left[ e^{\beta\mu} \frac{gV}{\lambda_T^3} \right]. \end{aligned}$$

The grand potential is

$$\Omega(T, V, \mu) = -k_B T \ln Z_G = -k_B T e^{\beta\mu} \frac{gV}{\lambda_T^3}.$$

Since

$$d\Omega = -S dT - p dV - \bar{N} d\mu,$$

we get

$$p = -\frac{\partial \Omega}{\partial V} = -\frac{\Omega}{V} = k_B T e^{\beta\mu} \frac{g}{\lambda_T^3}$$

and

$$\bar{N} = -\frac{\partial \Omega}{\partial \mu} = e^{\beta\mu} \frac{gV}{\lambda_T^3} = \frac{pV}{k_B T}$$

or we end up with the *ideal gas equation of state*

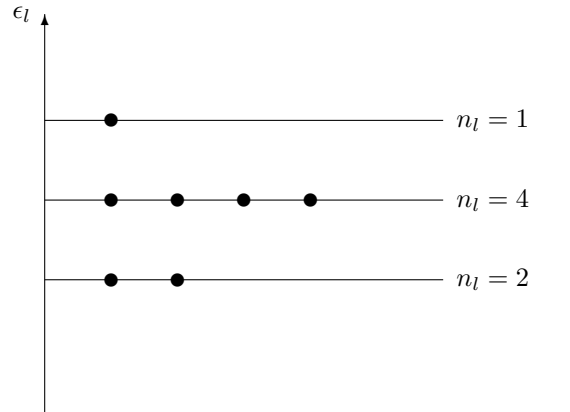
$$pV = \bar{N} k_B T.$$

Here

$$\begin{aligned} \bar{N} &= \langle N \rangle = \frac{\sum_N N z^N Z_N}{\sum_N z^N Z_N} \\ &= \frac{1}{Z_G} z \frac{\partial Z_G}{\partial z} = \frac{\partial \ln Z_G}{\partial \ln z}. \end{aligned}$$

*Another way*

We distribute  $N$  particles among the 1 particle states so that in the state  $l$  there are  $n_l$  particles.



Now

$$N = \sum_l n_l \text{ and } E = \sum_l \epsilon_l n_l.$$

The number of possible distributions is

$$W = W(n_1, n_2, \dots, n_l, \dots) = \frac{N!}{n_1! n_2! \dots n_l! \dots}.$$

Since in every distribution  $(n_1, n_2, \dots)$  everyone of the  $N!$  permutations of the particles gives an identical state the partition function is

$$\begin{aligned} Z_G &= \text{Tr} e^{-\beta(H - \mu \hat{N})} \\ &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \frac{1}{N!} W e^{-\beta(E - \mu N)} \end{aligned}$$

$$\begin{aligned}
&= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \frac{1}{n_1! n_2! \cdots} e^{-\beta \sum_l n_l (\epsilon_l - \mu)} \\
&= \prod_l \left[ \sum_{n=0}^{\infty} \frac{1}{n!} e^{-\beta n (\epsilon_l - \mu)} \right] \\
&= \prod_l \exp \left[ e^{-\beta (\epsilon_l - \mu)} \right] \\
&= \exp \left[ \sum_l e^{-\beta (\epsilon_l - \mu)} \right] \\
&= \exp \left[ e^{\beta \mu} Z_1 \right]
\end{aligned}$$

or exactly as earlier.

Now

$$\begin{aligned}
\frac{\partial \ln Z_G}{\partial \epsilon_l} &= \frac{-\beta \sum_{n=0}^{\infty} n \frac{1}{n!} e^{-\beta n (\epsilon_l - \mu)}}{\prod_l \left[ \sum_{n=0}^{\infty} \frac{1}{n!} e^{-\beta n (\epsilon_l - \mu)} \right]} \\
&= -\beta \langle n_l \rangle
\end{aligned}$$

so the *occupation number*  $\bar{n}_l$  of the state  $l$  is

$$\begin{aligned}
\bar{n}_l &= \langle n_l \rangle = -\frac{1}{\beta} \frac{\partial \ln Z_G}{\partial \epsilon_l} = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_l} e^{-\beta (\epsilon_l - \mu)} \\
&= e^{-\beta (\epsilon_l - \mu)}.
\end{aligned}$$

The Boltzmann distribution gives a wrong result if the 1 particle states are multiply occupied. Our approximation is therefore valid only if

$$\bar{n}_l \ll 1 \quad \forall l$$

or

$$e^{\beta \mu} \ll e^{\beta \epsilon_l} \quad \forall l.$$

Now  $\min \epsilon_l = 0$ , so that

$$e^{\beta \mu} \ll 1.$$

On the other hand

$$e^{\beta \mu} = \frac{\bar{N}}{V} \lambda_T^3, \quad \text{when } g = 1$$

and

$$\frac{\bar{N}}{V} = \frac{1}{v_i} = \frac{3}{4\pi r_i^3},$$

so we must have

$$\lambda_T \ll r_i.$$

Now

$$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

is the minimum diameter of the wave packet of a particle with the typical thermal energy ( $\bar{\epsilon}_l = k_B T$ ) so in other words:

The Maxwell-Boltzmann approximation is valid when the wave packets of individual particles do not overlap.

## Occupation number representation

Let us consider a system of  $N$  non interacting particles. Denote by

$$|n_1, n_2, \dots, n_i, \dots\rangle$$

the quantum state where there are  $n_i$  particles in the one particle state  $i$ . Let the energy of the state  $i$  be  $\epsilon_i$ . Then

$$\begin{aligned}
H |n_1, n_2, \dots\rangle &= \left( \sum_i n_i \epsilon_i \right) |n_1, n_2, \dots\rangle \\
N &= \sum_i n_i.
\end{aligned}$$

We define the *creation operator*  $a_i^\dagger$  so that

$$a_i^\dagger |n_1, n_2, \dots, n_i, \dots\rangle = C |n_1, n_2, \dots, n_i + 1, \dots\rangle$$

i.e.  $a_i^\dagger$  creates one particle into the state  $i$ .

Correspondingly the *destruction operator*  $a_i$  obeys:

$$a_i |n_1, n_2, \dots, n_i, \dots\rangle = C' |n_1, n_2, \dots, n_i - 1, \dots\rangle,$$

i.e.  $a_i$  removes one particle from the state  $i$ .

The basis  $\{|n_1, n_2, \dots\rangle\}$  is complete, i.e.

$$\sum_{\{n_i\}} |n_1, n_2, \dots\rangle \langle n_1, n_2, \dots| = 1$$

and orthonormal or

$$\langle n'_1, n'_2, \dots | n_1, n_2, \dots \rangle = \delta_{n_1 n'_1} \delta_{n_2 n'_2} \cdots$$

### Bosons

For bosons the creation and destruction operators obey the commutation relations

$$\begin{aligned}
[a_i, a_j^\dagger] &= \delta_{ij} \\
[a_i, a_j] &= [a_i^\dagger, a_j^\dagger] = 0.
\end{aligned}$$

It can be shown that

$$\begin{aligned}
a_i |n_1, \dots, n_i, \dots\rangle &= \sqrt{n_i} |n_1, \dots, n_i - 1, \dots\rangle \\
a_i^\dagger |n_1, \dots, n_i, \dots\rangle &= \sqrt{n_i + 1} |n_1, \dots, n_i + 1, \dots\rangle.
\end{aligned}$$

The (*occupation*) *number operator*

$$\hat{n}_i = a_i^\dagger a_i$$

obeys the relation

$$\begin{aligned}
\hat{n}_i |n_1, \dots, n_i, \dots\rangle &= a_i^\dagger a_i |n_1, \dots, n_i, \dots\rangle \\
&= n_i |n_1, \dots, n_i, \dots\rangle
\end{aligned}$$

and  $n_i = 0, 1, 2, \dots$

An arbitrary one particle operator, i.e. an operator  $O^{(1)}$ , which in the configuration space operates only on the

coordinates on one particle, can be written in the occupation number representation as

$$\hat{O}^{(1)} = \sum_{i,j} \langle i | O^{(1)} | j \rangle a_i^\dagger a_j.$$

A two body operator  $O^{(2)}$  can be written as

$$\hat{O}^{(2)} = \sum_{ijkl} \langle ij | O^{(2)} | kl \rangle a_i^\dagger a_j^\dagger a_l a_k.$$

**Example Hamiltonian**

$$H = \sum_i -\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} V(\mathbf{r}_i, \mathbf{r}_j)$$

takes in the occupation representation the form

$$H = \sum_{i,j} \langle i | -\frac{\hbar^2}{2m} \nabla^2 | j \rangle a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} \langle ij | V | kl \rangle a_i^\dagger a_j^\dagger a_l a_k,$$

where

$$\langle i | -\frac{\hbar^2}{2m} \nabla^2 | j \rangle = -\frac{\hbar^2}{2m} \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_j(\mathbf{r}) d^3r$$

and

$$\langle ij | V | kl \rangle = \int \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) V(\mathbf{r}_1, \mathbf{r}_2) \phi_k(\mathbf{r}_2) \phi_l(\mathbf{r}_1) d^3r_1 d^3r_2.$$

**Fermions**

The creation and destruction operators of fermions satisfy the *anticommutation* relations

$$\begin{aligned} \{a_i, a_j^\dagger\} &= a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} \\ \{a_i, a_j\} &= \{a_i^\dagger, a_j^\dagger\} = 0. \end{aligned}$$

It can be shown that

$$\begin{aligned} a_i |n_1, \dots, n_i, \dots\rangle &= \begin{cases} (-1)^{S_i} \sqrt{n_i} |n_1, \dots, n_i - 1, \dots\rangle, & \text{if } n_i = 1 \\ 0, & \text{otherwise} \end{cases} \\ a_i^\dagger |n_1, \dots, n_i, \dots\rangle &= \begin{cases} (-1)^{S_i} \sqrt{n_i + 1} |n_1, \dots, n_i + 1, \dots\rangle, & \text{if } n_i = 0 \\ 0, & \text{otherwise} \end{cases} \end{aligned}$$

Here

$$S_i = n_1 + n_2 + \dots + n_{i-1}.$$

The number operator satisfies

$$\hat{n}_i |n_1, \dots, n_i, \dots\rangle = n_i |n_1, \dots, n_i, \dots\rangle$$

and  $n_i = 0, 1$ .

One and two body operators take the same form as in the case of bosons.

**Note** Since  $a_i$  and  $a_j$  *anticommute* one must be careful with the order of the creation and destruction operators in  $O^{(2)}$ .

In the case of non interacting particles the Hamiltonian operator in the configuration space is

$$H = \sum_i H_1(\mathbf{r}_i),$$

where 1 body Hamiltonian  $H_1$  is

$$H_1(\mathbf{r}_i) = -\frac{\hbar^2}{2m} \nabla_i^2 + U(\mathbf{r}_i).$$

Let  $\phi_j$  be eigenfunctions of  $H_1$  i.e.

$$H_1 \phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r}).$$

In the occupation space we have then

$$\hat{H} = \sum_j \epsilon_j a_j^\dagger a_j = \sum_j \epsilon_j \hat{n}_j$$

and

$$\hat{N} = \sum_j a_j^\dagger a_j = \sum_j \hat{n}_j.$$

The grand canonical partition function is now

$$Z_G = \text{Tr} e^{-\beta(\hat{H} - \mu \hat{N})} = \sum_{n_1} \sum_{n_2} \dots e^{-\beta \sum_l n_l (\epsilon_l - \mu)}.$$

**Bose-Einstein ideal gas**

In bosonic systems the occupations of one particle states are  $n_l = 0, 1, 2, \dots$ . The grand canonical state sum is

$$\begin{aligned} Z_{G, \text{BE}} &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots e^{-\beta \sum_l n_l (\epsilon_l - \mu)} \\ &= \prod_l \left[ \sum_{n=0}^{\infty} e^{-\beta n (\epsilon_l - \mu)} \right] \\ &= \prod_l \frac{1}{1 - e^{-\beta (\epsilon_l - \mu)}}. \end{aligned}$$

The grand potential is

$$\Omega_{\text{BE}} = k_B T \sum_l \ln \left[ 1 - e^{-\beta (\epsilon_l - \mu)} \right].$$

The occupation number of the state  $l$  is

$$\begin{aligned} \bar{n}_l &= \langle n_l \rangle = \frac{1}{Z_G} \sum_{n_1} \sum_{n_2} \dots n_l e^{-\beta \sum_m n_m (\epsilon_m - \mu)} \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_l} \ln Z_G = \frac{\partial \Omega}{\partial \epsilon_l}, \end{aligned}$$



and for the *Bose-Einstein occupation number* we get

$$\bar{n}_l = \frac{1}{e^{\beta(\epsilon_l - \mu)} - 1}.$$

### Entropy

Since  $d\Omega = -S dT - p dV - N d\mu$  we have

$$\begin{aligned} S &= \left( \frac{\partial \Omega}{\partial T} \right)_\mu \\ &= -k_B \sum_l \ln \left[ 1 - e^{-\beta(\epsilon_l - \mu)} \right] \\ &\quad - k_B T \sum_l \frac{1}{1 - e^{-\beta(\epsilon_l - \mu)}} (\epsilon_l - \mu) e^{-\beta(\epsilon_l - \mu)} \frac{-1}{k_B T^2}. \end{aligned}$$

Now

$$e^{\beta(\epsilon_l - \mu)} = 1 + \frac{1}{\bar{n}_l}$$

and

$$\beta(\epsilon_l - \mu) = \ln(1 + \bar{n}_l) - \ln \bar{n}_l,$$

so

$$\begin{aligned} S &= -k_B \sum_l \ln \left( 1 - \frac{\bar{n}_l}{\bar{n}_l + 1} \right) \\ &\quad + k_B \sum_l \bar{n}_l [\ln(\bar{n}_l + 1) - \ln \bar{n}_l] \end{aligned}$$

or

$$S = k_B \sum_l [(\bar{n}_l + 1) \ln(\bar{n}_l + 1) - \bar{n}_l \ln \bar{n}_l].$$

## Fermi-Dirac ideal gas

The Hamiltonian operator is

$$\hat{H} = \sum_l \epsilon_l a_l^\dagger a_l$$

and the number operator

$$\hat{N} = \sum_l a_l^\dagger a_l.$$

Now

$$\{a_l, a_{l'}^\dagger\} = \delta_{ll'}$$

and

$$\{a_l, a_{l'}\} = \{a_l^\dagger, a_{l'}^\dagger\} = 0.$$

The eigenvalues of the number operator related to the state  $l$ ,

$$\hat{n}_l = a_l^\dagger a_l,$$

are

$$n_l = 0, 1.$$

The *state sum* in the grand canonical ensemble is

$$\begin{aligned} Z_{G,FD} &= \text{Tr} e^{-\beta(\hat{H} - \mu \hat{N})} \\ &= \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \left\langle n_1 n_2 \dots \left| e^{-\beta(\hat{H} - \mu \hat{N})} \right| n_1 n_2 \dots \right\rangle \\ &= \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots e^{-\beta \sum_l n_l (\epsilon_l - \mu)} \\ &= \prod_l \left\{ \sum_{n=0}^1 e^{-\beta n (\epsilon_l - \mu)} \right\} \\ &= \prod_l \left[ 1 + e^{-\beta(\epsilon_l - \mu)} \right]. \end{aligned}$$

The *grand potential* is

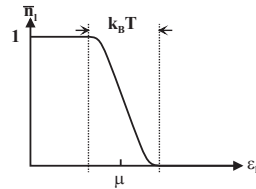
$$\Omega_{FD} = -k_B T \sum_l \ln \left[ 1 + e^{-\beta(\epsilon_l - \mu)} \right].$$

The average occupation number of the state  $l$  is

$$\begin{aligned} \bar{n}_l &= \langle n_l \rangle = \frac{1}{Z_{G,FD}} \text{Tr} \hat{n}_l e^{-\beta(\hat{H} - \mu \hat{N})} \\ &= \frac{1}{Z_{G,FD}} \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots n_l e^{-\beta \sum_{l'} n_{l'} (\epsilon_{l'} - \mu)} \\ &= -\frac{1}{\beta} \frac{\partial \ln Z_{G,FD}}{\partial \epsilon_l} = \frac{\partial \Omega_{FD}}{\partial \epsilon_l} \\ &= \frac{e^{-\beta(\epsilon_l - \mu)}}{1 + e^{-\beta(\epsilon_l - \mu)}}. \end{aligned}$$

Thus the *Fermi-Dirac occupation number* can be written as

$$\bar{n}_l = \frac{1}{e^{\beta(\epsilon_l - \mu)} + 1}.$$



The expectation value of the square of the occupation number will be

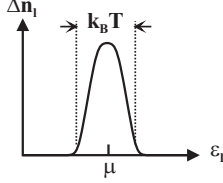
$$\begin{aligned} \langle n_l^2 \rangle &= \frac{1}{Z_{G,FD}} \text{Tr} \hat{n}_l^2 e^{-\beta(\hat{H} - \mu \hat{N})} \\ &= \frac{1}{Z_{G,FD}} \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots n_l^2 e^{-\beta \sum_{l'} n_{l'} (\epsilon_{l'} - \mu)} \\ &= \frac{1}{\beta^2} \frac{1}{Z_{G,FD}} \frac{\partial^2 Z_{G,FD}}{\partial \epsilon_l^2} \\ &= -\frac{1}{\beta} \frac{1}{Z_{G,FD}} \left( \prod_{l' \neq l} \left[ 1 + e^{-\beta(\epsilon_{l'} - \mu)} \right] \right) \\ &\quad \times \frac{\partial}{\partial \epsilon_l} e^{-\beta(\epsilon_l - \mu)} \end{aligned}$$

$$= \frac{e^{-\beta(\epsilon_l - \mu)}}{1 + e^{-\beta(\epsilon_l - \mu)}} = \bar{n}_l.$$

This is natural, since  $n_l^2 = n_l$ .

For the variance we get

$$\begin{aligned} (\Delta n_l)^2 &= \langle n_l^2 \rangle - \langle n_l \rangle^2 = \bar{n}_l - \bar{n}_l^2 \\ &= \bar{n}_l(1 - \bar{n}_l). \end{aligned}$$



There are fluctuations only in the vicinity of the chemical potential  $\mu$ .

The *entropy* is

$$\begin{aligned} S &= -\frac{\partial \Omega}{\partial T} \\ &= k_B \sum_l \ln \left[ 1 + e^{-\beta(\epsilon_l - \mu)} \right] \\ &\quad + \frac{1}{T} \sum_l \overbrace{\frac{e^{-\beta(\epsilon_l - \mu)}}{1 + e^{-\beta(\epsilon_l - \mu)}}}^{=\bar{n}_l} (\epsilon_l - \mu). \end{aligned}$$

Now  $\beta(\epsilon_l - \mu) = \ln \frac{1 - \bar{n}_l}{\bar{n}_l}$  and  $1 + e^{-\beta(\epsilon_l - \mu)} = \frac{1}{1 - \bar{n}_l}$ , so

$$S = -k_B \sum_l [(1 - \bar{n}_l) \ln(1 - \bar{n}_l) + \bar{n}_l \ln \bar{n}_l].$$

## Bosonic systems

### Bose condensate

#### Number of particles

The average number of particles is

$$\begin{aligned} \bar{N} &= \langle N \rangle = - \left( \frac{\partial \Omega}{\partial \mu} \right)_T \\ &= \sum_l \frac{1}{e^{\beta(\epsilon_l - \mu)} - 1} \end{aligned}$$

or

$$\bar{N} = \sum_l \bar{n}_l.$$

We denote

$$z = e^{\beta\mu} = \text{fugacity},$$

so

$$\bar{n}_l = \frac{1}{e^{\beta\epsilon_l} z^{-1} - 1}.$$

Let us consider a free non interacting gas. Then

$$\epsilon_l = \frac{\hbar^2 k_l^2}{2m} = \frac{\mathbf{p}_l^2}{2m}.$$

Now

$$1 \leq e^{\beta\epsilon_l} < \infty.$$

Since  $\bar{n}_l \geq 0$ , the fugacity is restricted to lie between

$$0 < z < 1$$

or  $\mu < 0$ .

We treat the state  $\mathbf{p} = 0$  separately, since the corresponding occupation number  $\bar{n}_0$  can become macroscopic:

$$\bar{n}_0 = \frac{z}{1 - z} \rightarrow_{z \rightarrow 1} \infty.$$

We write the grand potential as

$$\begin{aligned} \Omega_{\text{BE}} &= k_B T \ln [1 - e^{\beta\mu}] \\ &\quad + k_B T \sum_{\mathbf{k} \neq 0} \ln \left[ 1 - e^{\beta\mu} e^{-\beta \frac{\hbar^2 k^2}{2m}} \right]. \end{aligned}$$

Let us define functions  $g_\alpha(z)$  so that

$$g_\alpha(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^\alpha}.$$

Then

$$\Omega_{\text{BE}} = k_B T \ln(1 - z) - \frac{V k_B T}{\lambda_T^3} g_{5/2}(z).$$

For the number of particles we get

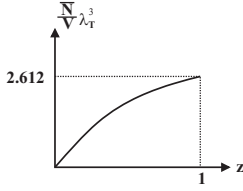
$$\bar{N} = \bar{n}_0 + \frac{V}{\lambda_T^3} g_{3/2}(z).$$

When the temperature is high or the density low, the term  $\frac{\bar{n}_0}{V}$  is negligible as compared with  $\frac{g_{3/2}(z)}{\lambda_T^3}$ , i.e.

$$\frac{\bar{N}}{V} \lambda_T^3 = g_{3/2}(z).$$

Now  $g_{3/2}(z)$  is a positive monotonically increasing function and

$$\begin{aligned} \left(\frac{\bar{N}}{V} \lambda_T^3\right)_{z=0} &= g_{3/2}(0) = 0 \\ \left(\frac{\bar{N}}{V} \lambda_T^3\right)_{z=1} &= g_{3/2}(1) = \zeta(3/2) = 2.612. \end{aligned}$$



Let us choose the density  $\rho = \frac{\bar{N}}{V}$  and  $T$  so that

$$\frac{\bar{N}}{V} \lambda_T^3 = 2.612,$$

and  $z = 1$ . If we still increase the density or decrease the temperature the increase of the term  $\frac{\bar{N}}{V} \lambda_T^3$  must originate from  $\frac{\bar{n}_0}{V} \lambda_T^3$ , since  $z \leq 1$ , i.e.

$$\frac{\bar{N}}{V} \lambda_T^3 = g_{3/2}(z), \quad \text{when } \frac{\bar{N}}{V} \lambda_T^3 < 2.612$$

$$\frac{\bar{N}}{V} \lambda_T^3 = \frac{\bar{n}_0}{V} \lambda_T^3 + g_{3/2}(1), \quad \text{when } \frac{\bar{N}}{V} \lambda_T^3 \geq 2.612.$$

When

$$\lambda_T^3 \geq 2.612 \frac{V}{\bar{N}},$$

the state  $\mathbf{p} = 0$  will be occupied macroscopically forming the *Bose-Einstein condensate*. The formation starts when the temperature is less than the *critical temperature*

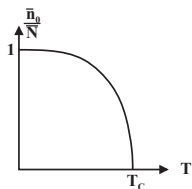
$$T_c = \left(\frac{2\pi\hbar^2}{mk_B}\right) \left(\frac{\rho}{2.612}\right)^{2/3}$$

or the density greater than the *critical density*

$$\rho_c = 2.612 \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}.$$

When  $T < T_c$ , the relative fraction of the condensate is

$$\frac{\bar{n}_0}{\bar{N}} = 1 - \frac{2.612}{\lambda_T^3} \frac{V}{\bar{N}} = 1 - \left(\frac{T}{T_c}\right)^{3/2}.$$



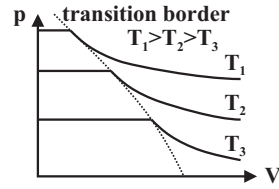
## Pressure

With the help of the grand potential the pressure is

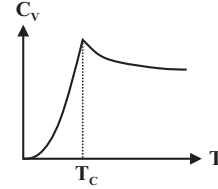
$$\begin{aligned} p &= -\left(\frac{\partial\Omega}{\partial V}\right)_{T,N} = -\frac{\Omega_{BE}}{V} \\ &= \frac{k_B T}{\lambda_T^3} g_{5/2}(z), \end{aligned}$$

so

$$p = \begin{cases} \frac{k_B T}{\lambda_T^3} g_{5/2}(z) & \text{above the critical point} \\ \frac{k_B T}{\lambda_T^3} g_{5/2}(1) = 1.342 \frac{k_B T}{\lambda_T^3} & \text{below the critical point.} \end{cases}$$



We are dealing with a 1st order phase transition.

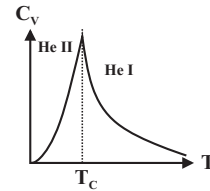


## <sup>4</sup>He liquid

A *second order* phase transition to a *super liquid state* at the temperature  $T_c = 2.17\text{K}$ . The expression given above,

$$T_c = \frac{2\pi\hbar^2}{mk_B} \left(\frac{\rho}{2.612}\right)^{2/3},$$

results  $T_c = 3.13\text{K}$ .



This is called a  $\lambda$ -transition.

## Two liquid model

When  $T < T_c$ , we suppose that <sup>4</sup>He is composed of two components: super and normal components. Then

$$\begin{aligned} \rho &= \rho_s + \rho_n \\ \mathbf{j} &= \mathbf{j}_s + \mathbf{j}_n \\ &\vdots \end{aligned}$$

When  $T \rightarrow 0$ , then  $\frac{\rho_s}{\rho} \rightarrow 1$ , but  $\frac{\bar{n}_0}{N} \rightarrow \sim 0.1$ .

This is due to the fact that <sup>4</sup>He is *not* an ideal liquid: between <sup>4</sup>He atoms there is

- a strong repulsion at short distances,
- an attraction at longer distances.

## Black body radiation (photon gas)

The *photon* is a relativistic massless *boson*, whose spin is  $S = 1$ , so  $g = 2S + 1 = 3$ . In the vacuum only transversal polarization exists, so  $g = 2$ .

The energy of a photon is

$$\begin{aligned}\epsilon(p) &= \sqrt{(m_0 c^2)^2 + (pc)^2} \\ &= pc = \hbar kc.\end{aligned}$$

With the help of the frequency  $f$  or of the angular velocity  $\omega$  the energy is

$$\epsilon = \hbar\omega = \hbar 2\pi f = hf.$$

Since the wave length  $\lambda$  is

$$\lambda = \frac{2\pi}{k},$$

we have

$$\begin{aligned}f &= \frac{c}{\lambda} \\ \omega &= ck.\end{aligned}$$

### Density of states

Employing the periodic boundary conditions the wave vector is

$$\mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z),$$

so the number of states in the vicinity of  $\mathbf{k}$  is

$$\begin{aligned}dN_{\mathbf{k}} &= g \left( \frac{L}{2\pi} \right)^3 d\mathbf{k} \\ &= g \frac{V}{(2\pi)^3} 4\pi k^2 dk.\end{aligned}$$

With the help of the angular velocity this is

$$\begin{aligned}dN_{\mathbf{k}} &= dN_{\omega} = g \frac{V}{(2\pi)^3} 4\pi \frac{\omega^2}{c^2} \frac{d\omega}{c} \\ &= g \frac{V \omega^2 d\omega}{2\pi^2 c^3}.\end{aligned}$$

We denote now

$$dN_{\omega} = f(\omega) d\omega,$$

so

$$f(\omega) d\omega = V \frac{\omega^2 d\omega}{\pi^2 c^3}.$$

The sum over quantum states can be replaced by the integration like

$$\sum_l \dots = \sum_{\mathbf{k}, \lambda} \dots = \int_0^{\infty} d\omega f(\omega) \dots$$

Here  $\mathbf{k}$  is the wave vector and

$$\lambda = \begin{cases} L, & \text{left} \\ R, & \text{right} \end{cases}$$

is the polarization.

Photons obey the *Bose-Einstein statistics*

Let's consider  $n$  photons each with the angular velocity  $\omega$ . The total energy of this system is

$$\epsilon_n(\omega) = n\hbar\omega,$$

so the system is equivalent with a *single harmonic oscillator*,

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = n\hbar\omega + 0\text{-point motion}.$$

Thus we can consider a system of one harmonic oscillator which is allowed to exchange energy with its surroundings.

So we can set  $\mu = 0$ . The Hamiltonian of the system is

$$\hat{H} = \sum_{\mathbf{k}, \lambda} (\hbar ck) a_{\mathbf{k}\lambda}^{\dagger} a_{\mathbf{k}\lambda}.$$

According to the Bose-Einstein distribution the occupation of the energy state  $\epsilon(\omega)$  is

$$\bar{n}(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}.$$

The *total energy* is

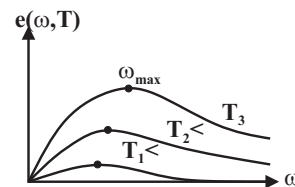
$$E = \int_0^{\infty} d\omega f(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}.$$

The *energy density* will be

$$\begin{aligned}\frac{E}{V} &= e(T) = \frac{\hbar}{\pi^2 c^3} \int_0^{\infty} d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \\ &= \int_0^{\infty} d\omega e(\omega, T),\end{aligned}$$

where the energy density at the given angular velocity obeys *Planck's law of radiation*

$$e(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\beta\hbar\omega} - 1)}.$$



We can see that the maximum of the intensity follows the *Wien displacement law*

$$\omega_{\max} = \text{constant} \times T.$$

At the long wave length limit,  $\lambda \gg \frac{hc}{k_B T}$  or  $\omega \ll \frac{k_B T}{\hbar}$ , the energy density obeys the *Rayleigh-Jeans law*

$$e(\omega, T) = \text{vakio} \times \omega^2 T.$$

At a given temperature the energy density will be

$$\begin{aligned} e(T) &= \int_0^\infty d\omega \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\beta\hbar\omega} - 1)} \\ &= \frac{\hbar}{\pi^2 c^3} \frac{1}{(\beta\hbar)^4} \int_0^\infty dx \frac{x^3}{e^x - 1} \\ &= \frac{k_B^4 T^4}{\pi^2 c^3 \hbar^3} \frac{\pi^4}{15}. \end{aligned}$$

Thus the energy density obeys the *Stefan-Boltzmann law*

$$e(T) = \frac{4}{c} \sigma T^4,$$

where  $\sigma$  is the *Stefan-Boltzmann constant*

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.67 \cdot 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}.$$

Now

$$\Omega = F - \mu N = F,$$

since  $\mu = 0$ . Thus the free energy is

$$\begin{aligned} F &= k_B T \int_0^\infty d\omega f(\omega) \ln [1 - e^{-\beta\hbar\omega}] \\ &= \frac{V}{\pi^2 c^3} k_B T \int_0^\infty d\omega \omega^2 \ln [1 - e^{-\beta\hbar\omega}] \\ &= \frac{V k_B T}{\pi^2 c^3 (\beta\hbar)^3} \int_0^\infty dx x^2 \ln [1 - e^{-x}] \\ &= -V \frac{k_B^4 T^4}{\pi^2 c^3 \hbar^3} \frac{\pi^4}{45}, \end{aligned}$$

or

$$F = -\frac{4}{3} \frac{\sigma}{c} V T^4 = -\frac{1}{3} E.$$

Here

$$E = e(T)V$$

is the total energy.

The *entropy* is

$$S = -\frac{\partial F}{\partial T}$$

or

$$S = \frac{16}{3} \frac{\sigma}{c} V T^3.$$

The *pressure* is

$$p = -\frac{\partial F}{\partial V}$$

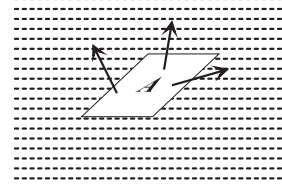
or

$$p = \frac{4}{3} \frac{\sigma}{c} T^4.$$

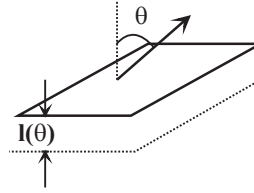
We see that the photon gas satisfies the relation

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

## Radiation of a black surface



We can think that the emitting surface is a hole on a hollow container filled with isotropic black body radiation. The radiation power can be determined by counting the number of photons escaping through the hole per time interval.



In the time interval  $\tau$  the photons escaping into the direction  $\theta$  originate from the region whose depth is

$$l(\theta) = c\tau \cos \theta.$$

The total energy of photons landing into the space angle element  $d\Omega$  at the direction  $\theta$  is

$$e(T) A c \tau \cos \theta \frac{d\Omega}{4\pi}.$$

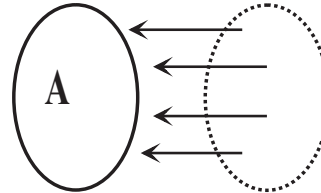
Thus the total energy of the radiation is

$$\begin{aligned} E_{\text{rad}} &= e(T) A c \tau \int_{\theta=0}^{\pi/2} \cos \theta \frac{d\Omega}{4\pi} \\ &= e(T) A c \tau \frac{1}{2} \int_0^{\pi/2} d\theta \sin \theta \cos \theta \\ &= \frac{1}{4} A e(T) c \tau. \end{aligned}$$

The radiation power per unit area is

$$\begin{aligned} P &= \frac{E_{\text{rad}}}{A\tau} = \frac{1}{4} c e(T) \\ &= \sigma T^4. \end{aligned}$$

## Absorption and intensity of radiation



When the radiation arrives from a given direction its intensity is

$$\begin{aligned} I &= \frac{E}{A\tau} = \frac{A c \tau e(T)}{A\tau} \\ &= c e(T) \end{aligned}$$

or

$$I = 4\sigma T^4.$$

The absorption power to a *perpendicular* surface is  $IA$ .

## Phonons

### Classical harmonic lattice

We let the ions of a crystal to oscillate in the vicinity of their equilibrium position. We suppose that

1. At the average equilibrium position the crystal is a Bravais lattice. With every point  $\mathbf{R}$  of the lattice we can thus associate an atom. The vector  $\mathbf{R}$ , however, represents only the average position of the ion.
2. Typical deviations from the equilibrium positions are small as compared with the interatomic distances.

According to the hypothesis 1 the atoms of the crystal can be identified with the Bravais lattice points  $\mathbf{R}$ ; e.g.  $\mathbf{r}(\mathbf{R})$  stands for the actual position of the ion associated with the lattice point  $\mathbf{R}$ . If  $\mathbf{u}(\mathbf{R})$  is the deviation of the ion  $\mathbf{R}$  from its equilibrium then

$$\mathbf{r}(\mathbf{R}) = \mathbf{R} + \mathbf{u}(\mathbf{R}).$$

Let  $\phi(\mathbf{r})$  be the potential energy of two ions separated by the distance  $\mathbf{r}$ . The energy of the whole lattice is then

$$\begin{aligned} U &= \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \phi(\mathbf{r}(\mathbf{R}) - \mathbf{r}(\mathbf{R}')) \\ &= \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \phi(\mathbf{R} - \mathbf{R}' + \mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}')). \end{aligned}$$

When we use the notation  $\mathbf{P}(\mathbf{R})$  for the momentum of the ion  $\mathbf{R}$  the total Hamiltonian is

$$H = \sum_{\mathbf{R}} \frac{\mathbf{P}^2(\mathbf{R})}{2m} + U.$$

### Harmonic approximation

Since the evaluation of the total potential  $U$  starting from the actual pair interactions is hopeless we approximate it resorting to the hypothesis 2 ( $\mathbf{u}(\mathbf{R})$  is small). The first terms in the Taylor series of the potential  $U$  are

$$\begin{aligned} U &= \frac{N}{2} \sum_{\mathbf{R}} \phi(\mathbf{R}) \\ &+ \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} (\mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}')) \cdot \nabla \phi(\mathbf{R} - \mathbf{R}') \\ &+ \frac{1}{4} \sum_{\mathbf{R}\mathbf{R}'} [(\mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}')) \cdot \nabla]^2 \phi(\mathbf{R} - \mathbf{R}') \\ &+ \mathcal{O}(u^3). \end{aligned}$$

In the equilibrium the total force due to other ions affecting the ion  $\mathbf{R}$  is

$$\mathbf{F} = - \sum_{\mathbf{R}'} \nabla \phi(\mathbf{R} - \mathbf{R}').$$

Since we are at an equilibrium this force must be zero. Thus the linear term in the series expansion of  $U$  vanishes. Up to the second order we are left with

$$U = U^{\text{eq}} + U^{\text{harm}},$$

where  $U^{\text{eq}}$  is the potential energy of the equilibrium and

$$\begin{aligned} U^{\text{harm}} &= \frac{1}{4} \sum_{\substack{\mathbf{R}\mathbf{R}' \\ \mu, \nu = x, y, z}} [u_\mu(\mathbf{R}) - u_\mu(\mathbf{R}')] \phi_{\mu\nu}(\mathbf{R} - \mathbf{R}') \\ &\quad \times [u_\nu(\mathbf{R}) - u_\nu(\mathbf{R}')] \\ \phi_{\mu\nu}(\mathbf{r}) &= \frac{\partial^2 \phi(\mathbf{r})}{\partial r_\mu \partial r_\nu}. \end{aligned}$$

If we are not interested in the quantities related to the equilibrium of the crystal (total energy, total volume, total compressibility, ...) we can forget the term  $U^{\text{eq}}$ . The harmonic potential is usually written more generally as

$$U^{\text{harm}} = \frac{1}{2} \sum_{\substack{\mathbf{R}\mathbf{R}' \\ \mu\nu}} u_\mu(\mathbf{R}) D_{\mu\nu}(\mathbf{R} - \mathbf{R}') u_\nu(\mathbf{R}').$$

The former expression can be obtained by setting

$$D_{\mu\nu}(\mathbf{R} - \mathbf{R}') = \delta_{\mathbf{R}\mathbf{R}'} \sum_{\mathbf{R}''} \phi_{\mu\nu}(\mathbf{R} - \mathbf{R}'') - \phi_{\mu\nu}(\mathbf{R} - \mathbf{R}').$$

### The heat capacity of classical lattice

The volume element of the the  $3N$  dimensional classical phase space formed by the  $N$  ions of the lattice is

$$d\Gamma = \prod_{\mathbf{R}} \frac{1}{h} d\mathbf{u}(\mathbf{R}) d\mathbf{P}(\mathbf{R}) = \prod_{\mathbf{R}, \mu} \frac{1}{h} du_\mu(\mathbf{R}) dP_\mu(\mathbf{R})$$

and the canonical partition sum

$$Z = \int d\Gamma e^{-\beta H}.$$

The total energy  $E$  is then

$$E = \frac{1}{Z} \int d\Gamma e^{-\beta H} H = - \frac{\partial}{\partial \beta} \ln Z.$$

When we change variables,

$$\begin{aligned} \mathbf{u}(\mathbf{R}) &= \beta^{-1/2} \bar{\mathbf{u}}(\mathbf{R}) \\ \mathbf{P}(\mathbf{R}) &= \beta^{-1/2} \bar{\mathbf{P}}(\mathbf{R}), \end{aligned}$$

the partition function can be written as

$$\begin{aligned} Z &= \int d\Gamma \exp \left[ -\beta \left( \sum_{\mathbf{R}} \frac{\mathbf{P}(\mathbf{R})^2}{2M} + U^{\text{eq}} + U^{\text{harm}} \right) \right] \\ &= e^{-\beta U^{\text{eq}}} \beta^{-3N} \int \prod_{\mathbf{R}} \frac{1}{h} d\bar{\mathbf{u}}(\mathbf{R}) d\bar{\mathbf{P}}(\mathbf{R}) \times \\ &\quad \exp \left[ - \sum_{\mathbf{R}} \frac{\bar{\mathbf{P}}(\mathbf{R})^2}{2M} - \frac{1}{2} \sum_{\mathbf{R}} \bar{u}_\mu(\mathbf{R}) D_{\mu\nu}(\mathbf{R} - \mathbf{R}') \bar{u}_\nu(\mathbf{R}') \right] \end{aligned}$$

Since all dependence on the temperature is outside of the integral the energy can be calculated easily

$$\begin{aligned} E &= -\frac{\partial}{\partial \beta} \ln(e^{-\beta U^{\text{eq}}} \beta^{-3N} \times \text{vakio}) \\ &= U^{\text{eq}} + 3Nk_B T. \end{aligned}$$

The heat capacity is

$$C_v = \frac{\partial E}{\partial T} = 3Nk_B.$$

This expression for heat capacity, due to the lattice vibrations, is known as *Dulong-Petit's law*.

Experimentally

- at low temperatures the heat capacity is smaller than the one obtained from the Dulong-Petit law. When we approach the temperature  $T = 0$  the heat capacity tends to zero.
- even at higher temperatures the measured heat capacities do not approach the Dulong-Petit limit.

### Normal modes of the harmonic crystal

#### One dimensional Bravais lattice

If the separation of the lattice points in the one dimensional Bravais lattice is  $a$  the lattice points are  $na$ ,  $n$  an integer. Every lattice point  $na$  is associated with one atom.

We suppose that in this one dimensional lattice only the nearest neighbours interact. Using the notation

$$K = \phi''(x),$$

the harmonic potential of the lattice is

$$U^{\text{harm}} = \frac{1}{2} K \sum_n [u(na) - u((n+1)a)]^2.$$

The classical equations of motion are

$$\begin{aligned} M\ddot{u}(na) &= -\frac{\partial U^{\text{harm}}}{\partial u(na)} \\ &= -K[2u(na) - u((n-1)a) - u((n+1)a)]. \end{aligned}$$

We suppose that the  $N$  points of the lattice form a ring, i.e. the deviations satisfy the boundary conditions

$$u((N+1)a) = u(a); \quad u(0) = u(Na).$$

We seek solutions of the form

$$u(na, t) \propto e^{i(kna - \omega t)}$$

To satisfy the boundary conditions we must have

$$e^{ikNa} = 1.$$

We see that the allowed values for  $k$  are

$$k = \frac{2\pi}{a} \frac{n}{N}, \quad n \text{ integer.}$$

Substituting the exponential trial into the equation of motion we see that the angular velocity  $\omega$  must satisfy

$$\omega(k) = \sqrt{\frac{2K(1 - \cos ka)}{M}} = 2\sqrt{\frac{K}{M}} \left| \sin \frac{1}{2}ka \right|.$$

The solutions represent a wave advancing in the ring with the phase velocity  $c = \omega/k$  and with the group velocity  $v = \partial\omega/\partial k$ . If the wave length is large or the wave vector  $k$  small then the dispersion relation

$$\omega = \left( a\sqrt{\frac{K}{M}} \right) k$$

is linear and the phase and group velocities equal.

#### One dimensional lattice with base

We suppose that in the primitive cell there are two atoms. Let the equilibrium positions of the ions to be  $na$  and  $na + d$ , where  $d \leq a/2$ . We denote the deviations of the ions these equilibrium positions by  $u_1(na)$  and  $u_2(na)$ . For the simplicity we suppose that the masses of the atoms are equal. The harmonic interaction due to the nearest neighbours is

$$\begin{aligned} U^{\text{harm}} &= \frac{K}{2} \sum_n [u_1(na) - u_2(na)]^2 \\ &\quad + \frac{G}{2} \sum_n [u_2(na) - u_1((n+1)a)]^2, \end{aligned}$$

where  $K$  describes the interaction of the ions  $na$  and  $na + d$ , and  $G$  the interaction of  $na + d$  and  $(n+1)a$ . The classical equations of motion are

$$\begin{aligned} M\ddot{u}_1(na) &= -\frac{\partial U^{\text{harm}}}{\partial u_1(na)} \\ &= -K[u_1(na) - u_2(na)] \\ &\quad -G[u_1(na) - u_2((n-1)a)] \\ M\ddot{u}_2(na) &= -\frac{\partial U^{\text{harm}}}{\partial u_2(na)} \\ &= -K[u_2(na) - u_1(na)] \\ &\quad -G[u_2(na) - u_1((n+1)a)]. \end{aligned}$$

Again we look for a solution of the form

$$\begin{aligned} u_1(na) &= \epsilon_1 e^{i(kna - \omega t)} \\ u_2(na) &= \epsilon_2 e^{i(kna - \omega t)}. \end{aligned}$$

Substituting these into the equations of motion we end up with the linear homogenous simultaneous equations

$$\begin{aligned} [M\omega^2 - (K + G)]\epsilon_1 + (K + Ge^{-ika})\epsilon_2 &= 0 \\ (K + Ge^{ika})\epsilon_1 + [M\omega^2 - (K + G)]\epsilon_2 &= 0. \end{aligned}$$

This system has a non trivial solution only if the coefficient determinant vanishes. From this we obtain

$$\omega^2 = \frac{K + G}{M} \pm \frac{1}{M} \sqrt{K^2 + G^2 + 2KG \cos ka}.$$



The ration of the amplitudes is

$$\frac{\epsilon_1}{\epsilon_2} = \mp \frac{K + Ge^{ika}}{|K + Ge^{ika}|}.$$

For every allowed wave vector  $k$  (counting  $N$ ) we get *two* solutions. Altogether the number of the normal modes is now  $2N$ .

We consider couple of limiting cases.

*Case 1.*  $k \ll \pi/a$

The angular velocities of the modes are now

$$\begin{aligned}\omega &= \sqrt{\frac{2(K+G)}{M}} - \mathcal{O}((ka)^2) \\ \omega &= \sqrt{\frac{KG}{2M(K+G)}}(ka).\end{aligned}$$

Since the latter dispersion relation is linear the corresponding mode is called *acoustic*. In the former mode  $\omega = \sqrt{2(K+G)/M}$ , when  $k = 0$ . Since at the long wave length limit this mode can couple with electromagnetic radiation it is called the *optical branch*. At the long wave length limit, when  $k \approx 0$ , the amplitudes satisfy

$$\epsilon_1 = \mp \epsilon_2$$

the upper sign corresponding to the optical mode and the lower sing to the acoustic mode.

*Case 2.*  $k = \pi/a$

At the border of the Brillouin zone the modes are

$$\begin{aligned}\omega &= \sqrt{\frac{2K}{M}}, \text{ optical branch} \\ \omega &= \sqrt{\frac{2G}{M}}, \text{ acoustical branch.}\end{aligned}$$

Correspondingly for the amplitudes

$$\epsilon_1 = \mp \epsilon_2.$$

*Case 3.*  $K \gg G$

The dispersion relations are now

$$\begin{aligned}\omega &= \sqrt{\frac{2K}{M}} \left[ 1 + \mathcal{O}\left(\frac{G}{K}\right) \right] \\ \omega &= \sqrt{\frac{2G}{M}} \sin \frac{1}{2}ka \left[ 1 + \mathcal{O}\left(\frac{G}{K}\right) \right],\end{aligned}$$

and the amplitudes satisfy

$$\epsilon_1 \approx \mp \epsilon_2.$$

The frequency of the optical branch is now independent on the wave vector. Its magnitude corresponds to the vibration frequency of a molecule of two atoms with equal masses and coupled with the spring constant  $K$ .

On the other hand, the acoustical branch is the same as in the case of the linear chain.

*Case 4.*  $K = G$

Now we have a Bravais lattice formed by single atoms with the primitive cell length  $a/2$ .

**Three dimensional Bravais lattice of single atoms**

Using the matrix notation the harmonic potential can be written more compactly

$$U^{\text{harm}} = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}(\mathbf{R}) \mathbf{D}(\mathbf{R} - \mathbf{R}') \mathbf{u}(\mathbf{R}').$$

Independent on the interionic forces the matrix  $\mathbf{D}(\mathbf{R} - \mathbf{R}')$  obeys certain symmetries:

1.  $D_{\mu\nu}(\mathbf{R} - \mathbf{R}') = D_{\nu\mu}(\mathbf{R}' - \mathbf{R})$

This property can be verified by exchanging the order of differentiations in the definitions of the elements of  $\mathbf{D}$ :

$$D_{\mu\nu}(\mathbf{R} - \mathbf{R}') = \left. \frac{\partial^2 U}{\partial u_\mu(\mathbf{R}) \partial u_\nu(\mathbf{R}')} \right|_{\mathbf{u}=\mathbf{o}}.$$

2.  $\mathbf{D}(\mathbf{R}) = \mathbf{D}(-\mathbf{R})$

Let's consider a lattice where the displacements from the equilibrium are  $\mathbf{u}(\mathbf{R})$ . In the corresponding reversal lattice the displacements are  $-\mathbf{u}(-\mathbf{R})$ . Since every Bravais lattice has the inversion symmetry the energies of both lattices must be equal, no matter what the deviations  $\mathbf{u}(\mathbf{R})$  are, i.e.

$$\begin{aligned}U^{\text{harm}} &= \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}(\mathbf{R}) \mathbf{D}(\mathbf{R} - \mathbf{R}') \mathbf{u}(\mathbf{R}') \\ &= \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} (-\mathbf{u}(-\mathbf{R})) \mathbf{D}(\mathbf{R} - \mathbf{R}') (-\mathbf{u}(-\mathbf{R}')) \\ &= \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}(\mathbf{R}) \mathbf{D}(\mathbf{R}' - \mathbf{R}) \mathbf{u}(\mathbf{R}'),\end{aligned}$$

for an arbitrary  $\mathbf{u}(\mathbf{R})$ . This can be valid only if

$$\mathbf{D}(\mathbf{R} - \mathbf{R}') = \mathbf{D}(\mathbf{R}' - \mathbf{R}).$$

In addition, according to the symmetry 1, we have

$$D_{\mu\nu}(\mathbf{R} - \mathbf{R}') = D_{\nu\mu}(\mathbf{R} - \mathbf{R}'),$$

so the matrix  $\mathbf{D}$  is symmetric.

3.  $\sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) = \mathbf{o}$

We move every ion  $\mathbf{R}$  to  $\mathbf{R} + \mathbf{d}$ . This is equivalent with translating the whole lattice by the amount  $\mathbf{d}$ . The potential energies of the original and the translated lattices are equal; in particular at the equilibrium 0, i.e.

$$\begin{aligned}0 &= \sum_{\substack{\mathbf{R}\mathbf{R}' \\ \mu\nu}} d_\mu D_{\mu\nu}(\mathbf{R} - \mathbf{R}') d_\nu \\ &= \sum_{\mu\nu} N d_\mu d_\nu \left( \sum_{\mathbf{R}} D_{\mu\nu}(\mathbf{R}) \right).\end{aligned}$$

Since the vector  $\mathbf{d}$  is arbitrary we must have

$$\sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) = \mathbf{o}.$$

The classical equations of motion

$$M\ddot{u}_\mu(\mathbf{R}) = -\frac{\partial U^{\text{harm}}}{\partial u_\mu(\mathbf{R})} = -\sum_{\mathbf{R}'\nu} D_{\mu\nu}(\mathbf{R}-\mathbf{R}')u_\nu(\mathbf{R}'),$$

or in the matrix notation

$$M\ddot{\mathbf{u}}(\mathbf{R}) = -\sum_{\mathbf{R}'} \mathbf{D}(\mathbf{R}-\mathbf{R}')\mathbf{u}(\mathbf{R}')$$

form a system of  $3N$  equations. Again we seek solutions of the form

$$\mathbf{u}(\mathbf{R}, t) = \boldsymbol{\epsilon} e^{i(\mathbf{k}\cdot\mathbf{R}-\omega t)}.$$

Here the *polarisation vector*  $\boldsymbol{\epsilon}$  tells us the direction of the motion of the ions. Furthermore we require that for every primitive vector  $\mathbf{a}_i$  the solutions satisfy the Born-von Karman boundary conditions

$$\mathbf{u}(\mathbf{R} + N_i\mathbf{a}_i) = \mathbf{u}(\mathbf{R}),$$

when the total number of primitive cells is  $N = N_1N_2N_3$ . These conditions can be satisfied only if the wave vector  $\mathbf{k}$  is of form

$$\mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3.$$

Here  $\mathbf{b}_i$  are vectors in the reciprocal lattice and  $n_i$  integers.

We see that we get different solution only if  $\mathbf{k}$  is restricted into the 1st Brillouin zone, i.e. there are exactly  $N$  allowed values for the wave vector.

We substitute the trial into the equations of motion and end up with

$$M\omega^2\boldsymbol{\epsilon} = \mathbf{D}(\mathbf{k})\boldsymbol{\epsilon}, \quad (*)$$

where

$$\mathbf{D}(\mathbf{k}) = \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R})e^{-i\mathbf{k}\cdot\mathbf{R}}$$

is so called *dynamical matrix*. For every allowed  $\mathbf{k}$  we have as the solution of (\*) three eigen values and vectors. The number of normal modes is therefore  $3N$ .

Employing symmetry properties of  $\mathbf{D}(\mathbf{R})$  we can rewrite the dynamical matrix as

$$\begin{aligned} \mathbf{D}(\mathbf{k}) &= \frac{1}{2} \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R})[e^{-i\mathbf{k}\cdot\mathbf{R}} + e^{i\mathbf{k}\cdot\mathbf{R}} - 2] \\ &= \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R})[\cos(\mathbf{k}\cdot\mathbf{R}) - 1]. \end{aligned}$$

Thus the dynamical matrix is

$$\mathbf{D}(\mathbf{k}) = -2 \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) \sin^2\left(\frac{1}{2}\mathbf{k}\cdot\mathbf{R}\right).$$

We see that  $\mathbf{D}(\mathbf{k})$  is a real and symmetric function of  $\mathbf{k}$ . Since  $\mathbf{D}(\mathbf{R})$  is symmetric  $\mathbf{D}(\mathbf{k})$  is also symmetric. We rewrite the equation (\*) as

$$\mathbf{D}(\mathbf{k})\boldsymbol{\epsilon}_s(\mathbf{k}) = \lambda_s(\mathbf{k})\boldsymbol{\epsilon}_s(\mathbf{k}).$$

As the eigen values of a real and symmetric matrix  $\lambda_s(\mathbf{k})$  are real and the eigenvectors  $\boldsymbol{\epsilon}_s(\mathbf{k})$  can be orthonormalized, i.e.

$$\boldsymbol{\epsilon}_s(\mathbf{k}) \cdot \boldsymbol{\epsilon}_{s'}(\mathbf{k}) = \delta_{ss'}, \quad s, s' = 1, 2, 3.$$

The polarizations of three normal modes are  $\boldsymbol{\epsilon}_s(\mathbf{k})$  and the angular velocities correspondingly

$$\omega_s(\mathbf{k}) = \sqrt{\frac{\lambda_s(\mathbf{k})}{M}}.$$

Let us suppose now that the mutual interaction of the ions decreases rapidly with the increasing separation. Strictly speaking we suppose that

$$\lim_{\mathbf{R}\rightarrow\infty} \mathbf{D}(\mathbf{R}) = \mathcal{O}(R^{-5}).$$

Then, at long wave length, i.e. when  $\mathbf{k} \approx \mathbf{0}$ , we have

$$\sin^2\left(\frac{1}{2}\mathbf{k}\cdot\mathbf{R}\right) \approx \left(\frac{1}{2}\mathbf{k}\cdot\mathbf{R}\right)^2$$

and

$$\mathbf{D}(\mathbf{k}) \approx -\frac{k^2}{2} \sum_{\mathbf{R}} (\hat{\mathbf{k}}\cdot\mathbf{R})^2 \mathbf{D}(\mathbf{R}).$$

Let  $c_s(\hat{\mathbf{k}})^2$  be the eigenvalues of the matrix

$$-\frac{1}{2M} \sum_{\mathbf{R}} (\hat{\mathbf{k}}\cdot\mathbf{R})^2 \mathbf{D}(\mathbf{R}).$$

We see that at small wave vectors the frequency is

$$\omega_s(\mathbf{k}) = c_s(\hat{\mathbf{k}})k.$$

Thus the dispersion of all three modes is a linear function of  $k$  so all three modes are acoustical. In general  $c_s(\hat{\mathbf{k}})$ , together with  $\omega_s(\mathbf{k})$ , depend also on the direction  $\hat{\mathbf{k}}$  of the propagation in addition to the mode  $s$ .

### Three dimensional lattice with base

We proceed exactly like in the case the one dimensional lattice with base. We suppose that there are  $p$  ions in the primitive cell. Every ion in the primitive cell adds one degree of freedom so the total number of modes at a given wave vector  $\mathbf{k}$  is  $3p$ . The corresponding frequencies are  $\omega_s^i(\mathbf{k})$ , where now  $s = 1, 2, 3$  and  $i = 1, 2, \dots, p$ . The corresponding displacements are

$$\mathbf{u}_s^i(\mathbf{R}, t) = \boldsymbol{\epsilon}_s^i(\mathbf{k}) e^{i(\mathbf{k}\cdot\mathbf{R} - \omega_s^i(\mathbf{k})t)}.$$

The polarizations are no more orthogonal but satisfy

$$\sum_{i=1}^p \boldsymbol{\epsilon}_s^{i*}(\mathbf{k}) \cdot \boldsymbol{\epsilon}_{s'}^i(\mathbf{k}) = \delta_{ss'}.$$

Analogically with one dimensional lattice 3 of the modes are now acoustical and the rest  $3(p-1)$  modes optical.

### Quantum mechanical treatment

Let us consider the harmonic Hamiltonian

$$H^{\text{harm}} = \sum_{\mathbf{R}} \frac{1}{2M} P(\mathbf{R})^2 + \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}(\mathbf{R}) D(\mathbf{R} - \mathbf{R}') \mathbf{u}(\mathbf{R}')$$

describing the lattice. Let  $\omega_s(\mathbf{k})$  and  $\epsilon_s(\mathbf{k})$  be the frequencies and polarizations in the corresponding classical lattice. We define the operator  $a_{\mathbf{k}s}$  so that

$$a_{\mathbf{k}s} = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \epsilon_s(\mathbf{k}) \cdot \left[ \sqrt{\frac{M\omega_s(\mathbf{k})}{2\hbar}} \mathbf{u}(\mathbf{R}) + i \sqrt{\frac{1}{2\hbar M\omega_s(\mathbf{k})}} P(\mathbf{R}) \right].$$

The Hermitean conjugate  $a_{\mathbf{k}s}^\dagger$  of the operator  $a_{\mathbf{k}s}$  is

$$a_{\mathbf{k}s}^\dagger = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \epsilon_s(\mathbf{k}) \cdot \left[ \sqrt{\frac{M\omega_s(\mathbf{k})}{2\hbar}} \mathbf{u}(\mathbf{R}) - i \sqrt{\frac{1}{2\hbar M\omega_s(\mathbf{k})}} P(\mathbf{R}) \right].$$

The operator  $a_{\mathbf{k}s}^\dagger$  is called the phonon creation operator and  $a_{\mathbf{k}s}$  the phonon destruction operator.

We employ the canonical commutation relations for the position and momentum

$$\begin{aligned} [u_\mu(\mathbf{R}), P_\nu(\mathbf{R}')] &= i\hbar \delta_{\mu\nu} \delta_{\mathbf{R}\mathbf{R}'} \\ [u_\mu(\mathbf{R}), u_\nu(\mathbf{R}')] &= [P_\mu(\mathbf{R}), P_\nu(\mathbf{R}')] = 0, \end{aligned}$$

the identities

$$\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = \begin{cases} 0, & \mathbf{k} \text{ is not a reciprocal vector} \\ N, & \mathbf{k} \text{ is a reciprocal vector} \end{cases}$$

and

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}} = 0, \quad \mathbf{R} \neq 0$$

together with the property of an orthogonal vector set

$$\sum_{s=1}^3 [\epsilon_s(\mathbf{k})]_\mu [\epsilon_s(\mathbf{k})]_\nu = \delta_{\mu\nu}.$$

One can straightforwardly show that the creation and annihilation operators obey the commutation relations

$$\begin{aligned} [a_{\mathbf{k}s}, a_{\mathbf{k}'s'}^\dagger] &= \delta_{\mathbf{k}\mathbf{k}'} \delta_{ss'} \\ [a_{\mathbf{k}s}, a_{\mathbf{k}'s'}] &= [a_{\mathbf{k}s}^\dagger, a_{\mathbf{k}'s'}^\dagger] = 0. \end{aligned}$$

With the help of the creation and destruction operators the operators  $\mathbf{u}(\mathbf{R})$  and  $P(\mathbf{R})$  can be written as

$$\mathbf{u}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}s} \sqrt{\frac{\hbar}{2M\omega_s(\mathbf{k})}} (a_{\mathbf{k}s} + a_{-\mathbf{k}s}^\dagger) \times$$

$$P(\mathbf{R}) = \frac{-i}{\sqrt{N}} \sum_{\mathbf{k}s} \sqrt{\frac{\hbar M\omega_s(\mathbf{k})}{2}} (a_{\mathbf{k}s} - a_{-\mathbf{k}s}^\dagger) \times \epsilon_s(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}}.$$

The Hamiltonian is now

$$H = \sum_{\mathbf{k}s} \hbar\omega_s(\mathbf{k}) (a_{\mathbf{k}s}^\dagger a_{\mathbf{k}s} + \frac{1}{2}).$$

This is simply the Hamiltonian of the system of  $3N$  independent harmonic oscillators whose energies are correspondingly

$$E = \sum_{\mathbf{k}s} (n_{\mathbf{k}s} + \frac{1}{2}) \hbar\omega_s(\mathbf{k}).$$

Here  $n_{\mathbf{k}s}$  the eigenvalues of the occupation number operator  $\hat{n}_{\mathbf{k}s} = a_{\mathbf{k}s}^\dagger a_{\mathbf{k}s}$ , i.e.  $n_{\mathbf{k}s} = 0, 1, 2, \dots$

### Einstein's model

Let us suppose that every ion of the crystal moves in a similar potential well. Then

$$H = \sum_{\mathbf{k}s} \hbar\omega_E (a_{\mathbf{k}s}^\dagger a_{\mathbf{k}s} + \frac{1}{2}),$$

where the parameter

$$\omega_E \equiv \frac{k_B T_E}{\hbar}$$

is the *Einstein frequency* common for all  $3N$  oscillators and  $T_E$  the corresponding *Einstein temperature*.

The partition function of one single harmonic oscillator is

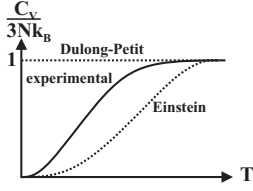
$$\begin{aligned} Z_{\text{harm}}(\omega) &= \text{Tr} e^{-\beta\hbar\omega(a^\dagger a + \frac{1}{2})} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n + \frac{1}{2})} \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \sum_n (e^{-\beta\hbar\omega})^n = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \\ &= \frac{1}{2 \sinh(\frac{1}{2}\beta\hbar\omega)}. \end{aligned}$$

Since the number of modes is  $3N$  the canonical partition function is

$$\begin{aligned} Z &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \sum_{n_{3N}=1}^{\infty} e^{-\beta\hbar\omega_E \sum_{j=1}^{3N} (n_j + \frac{1}{2})} \\ &= \prod_{j=1}^{3N} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_E (n + \frac{1}{2})} = Z_{\text{harm}}^{3N}(\omega_E) \\ &= \left[ 2 \sinh\left(\frac{T_E}{2T}\right) \right]^{-3N}. \end{aligned}$$

The heat capacity is

$$\begin{aligned} C_V &= \frac{\partial E}{\partial T} = -\frac{\partial}{\partial T} \frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial T} \left( k_B T^2 \frac{\partial \ln Z}{\partial T} \right) \\ &= k_B T \frac{\partial^2}{\partial T^2} T \ln Z = 3N k_B \frac{(T_E/2T)^2}{\sinh^2(T_E/2T)}. \end{aligned}$$



### Debye's model

To get the exact solution we should evaluate the partition function

$$\begin{aligned} Z &= \text{Tr} e^{-\beta \sum_{\mathbf{k}_s} \hbar \omega_s(\mathbf{k}) (a_{\mathbf{k}_s}^\dagger a_{\mathbf{k}_s} + \frac{1}{2})} \\ &= \sum_{\{n_{\mathbf{k}_s}=0\}} e^{-\beta \sum_{\mathbf{k}_s} \hbar \omega_s(\mathbf{k}) (n_{\mathbf{k}_s} + \frac{1}{2})}, \end{aligned}$$

which in turn would require the knowledge of of the dispersions  $\omega_s(\mathbf{k})$ . In practice we have to be satisfied with, normally quite realistic, *Debye's model*:

- At low temperatures only the contribution of the low energetic phonons is prominent, so
  - we take into account only the acoustic modes: 2 transversal and 1 longitudinal.
  - we take only the phonons associated with small  $k$ , so we can employ the linear dispersions

$$\begin{aligned} \omega_l(k) &= c_l k \\ \omega_t(k) &= c_t k. \end{aligned}$$

- We cut the spectra at the *Debye frequency*

$$\omega_D \equiv \frac{k_B T_D}{\hbar},$$

where  $T_D$  is the corresponding *Debye temperature*.

In each mode  $j$  the density of states is

$$dN_j(\omega) = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 dk = \frac{V}{2\pi^2 c_j^3} \omega^2 d\omega.$$

Thus the total density of states is

$$dN(\omega) = \frac{V}{2\pi^2} \left(\frac{2}{c_t^3} + \frac{1}{c_l^3}\right) \omega^2 d\omega.$$

Since the total number of states is

$$3N = \int_{\omega=0}^{\omega_D} dN(\omega) = \frac{V}{6\pi^2} \left(\frac{2}{c_t^3} + \frac{1}{c_l^3}\right) \omega_D^3,$$

where  $N$  is the number of primitive cells, we get as the Debye temperature

$$\omega_D^3 = \frac{N}{V} 18\pi^2 \left(\frac{2}{c_t^3} + \frac{1}{c_l^3}\right)^{-1}.$$

Correspondingly the state density is

$$dN(\omega) = \frac{9N}{\omega_D^3} \omega^2 d\omega \quad (\omega < \omega_D).$$

The canonical partition function is

$$\begin{aligned} Z &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \sum_{n_{3N}=0}^{\infty} e^{-\beta \sum_{\mathbf{k}_s} \hbar \omega_s(\mathbf{k}) (n_{\mathbf{k}_s} + \frac{1}{2})} \\ &= \prod_{\mathbf{k}_s} \frac{e^{-\frac{1}{2} \beta \hbar \omega_s(\mathbf{k})}}{1 - e^{-\beta \hbar \omega_s(\mathbf{k})}}, \end{aligned}$$

from which we can derive as the free energy

$$F = \underbrace{\sum_{\mathbf{k}_s} \frac{1}{2} \hbar \omega_s(\mathbf{k})}_{\text{0-point energy}} + k_B T \sum_{\mathbf{k}_s} \ln \left[ 1 - e^{-\beta \hbar \omega_s(\mathbf{k})} \right]$$

or

$$F = F_0 + k_B T \frac{9N}{\omega_D^3} \int_0^{\omega_D} d\omega \omega^2 \ln(1 - e^{-\beta \hbar \omega}).$$

Since  $S = -\frac{\partial F}{\partial T}$  and  $C_V = T \frac{\partial S}{\partial T}$ , is  $C_V = -T \frac{\partial^2 F}{\partial T^2}$ , so we have

$$C_V = 3Nk_B f_D \left( \frac{T_D}{T} \right).$$

Here

$$f_D(x) = \frac{3}{x^3} \int_0^x dy \frac{y^4 e^y}{(e^y - 1)^2}$$

is the so called *Debye function*.

Typical Debye temperatures

	$T_D$
Au	170
Cu	315
Fe	420
Cr	460
B	1250
C (diamond)	1860

**Note** The higher  $T_D$  the stiffer, harder crystal. Behaviour of  $C_V$ :

$T \rightarrow \infty$

Since

$$f_D(x) \xrightarrow{x \rightarrow 0} \frac{3}{x^3} \int_0^x dy y^2 = 1,$$

we have

$$C_V \rightarrow 3Nk_B,$$

or we end up with the Dulong-Petit heat capacity.

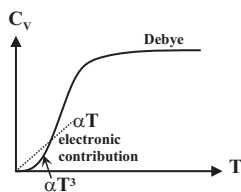
$T \rightarrow 0$

Since

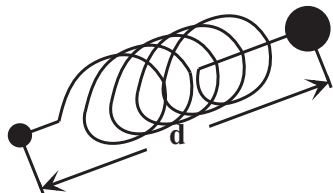
$$f_D(x) \xrightarrow{x \rightarrow \infty} \frac{3}{x^3} \int_0^{\infty} dy \frac{y^4 e^y}{(e^y - 1)^2} = \frac{\text{constant}}{x^3},$$

we get

$$C_V(T) \rightarrow \text{vakio} \times T^3 = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{T_D} \right)^3.$$



## Diatomic ideal gas



We classify molecules of two atoms as

- homopolar molecules (identical atoms), e.g.  $H_2$ ,  $N_2$ ,  $O_2$ , ..., and
- heteropolar molecules (different atoms), e.g.  $CO$ ,  $NO$ ,  $HCl$ , ...

When the density of the gas is low the intermolecular interactions are minimal and the ideal gas equation of state holds. The internal degrees of freedom, however, change the thermal properties (like  $C_V$ ).

When we suppose that the modes corresponding to the internal degrees of freedom are independent on each other, we can write the total Hamiltonian of the molecule as the sum

$$H \approx H^{tr} + H^{rot} + H^{vibr} + H^{el} + H^{nucl}.$$

Here

$$H^{tr} = \frac{\mathbf{p}^2}{2m} = \text{kinetic energy}$$

$m$  = mass of molecule

$$H^{rot} = \frac{\mathbf{L}^2}{2I} = \text{rotational energy}$$

$\mathbf{L}$  = angular momentum

$I$  = moment of inertia

$$I = \sum_i m_i x_i^2 = \frac{m_1 m_2}{m_1 + m_2} d^2$$

*Example*  $H_2$ -molecule

$$d = 0.75 \text{ \AA}$$

$$L = \hbar \sqrt{l(l+1)}, \quad l = 0, 1, 2, \dots$$

$$\frac{\hbar^2}{2Ik_B} = 85.41 \text{ K}$$

eigenvalues

$$\frac{\hbar^2}{2I} l(l+1)$$

are  $(2l+1)$ -fold degenerated

$$H^{vibr} = \hbar \omega_v \left( \hat{n} + \frac{1}{2} \right) = \text{vibration energy}$$

The vibrational degrees of freedom of the separation  $d$  of nuclei correspond at small amplitudes to a linear harmonic oscillator.

$$\hat{n} = a^\dagger a = 0, 1, 2, \dots$$

Each energy level is non degenerate

$H^{el}$  = electronic energies

- jumping of electrons from an orbital to another
- ionization
- energies  $\gtrsim 1 \text{ eV} \approx k_B 10^4 \text{ K}$
- in normal circumstances these degrees of freedom are frozen and can be neglected.

$H^{nucl}$  = energies corresponding to nucleonic degrees of freedom

In normal circumstances only the nuclear spins are interesting. The spin degeneracy is

$$g_y = (2I_1 + 1)(2I_2 + 1),$$

where  $I_1$  and  $I_2$  are the spins of the nuclei

Energy terms do not couple appreciably, i.e. the energy  $E_i$  of the state  $i$  is

$$E_i \approx E_{tr} + E_{rot} + E_{vibr},$$

so the partition sum of one molecule is

$$\begin{aligned} Z_1 &= \sum_{\mathbf{p}} \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} g_y (2l+1) \times \\ &\quad e^{-\beta \frac{p^2}{2m} - \beta \frac{\hbar^2}{2I} l(l+1) - \beta \hbar \omega_v (n + \frac{1}{2})} \\ &= Z^{tr} Z^{rot} Z^{vibr} Z^{nucl}, \end{aligned}$$

i.e. the state sum can be factorized.

Above

$$Z^{tr} = \sum_{\mathbf{p}} e^{-\beta \frac{p^2}{2m}} = \frac{V}{\lambda_T^3}$$

$$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

$$Z^{rot} = \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)}$$

$$T_r = \frac{\hbar^2}{2Ik_B}$$

$$\begin{aligned}
Z^{\text{vibr}} &= \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_v (n + \frac{1}{2})} \\
&= \left[ 2 \sinh \frac{T_v}{2T} \right]^{-1} \\
T_v &= \frac{\hbar \omega_v}{k_B} \\
Z^{\text{nucl}} &= g_y = (2I_1 + 1)(2I_2 + 1).
\end{aligned}$$

Approximatively (neglecting the multiple occupation of states) the state sum of  $N$  molecules is

$$Z_N = \frac{1}{N!} Z_1^N,$$

where  $1/N!$  takes care of the identity of molecules. We associate this factor with the translational sum.

The free energy

$$F = -k_B T \ln Z_N$$

can be divided into terms

$$\begin{aligned}
F^{\text{tr}} &= -k_B T \ln \left[ \frac{1}{N!} (Z^{\text{tr}})^N \right] \\
&= -k_B T \ln \left[ \frac{1}{N!} V \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2} N} \right] \\
&= -k_B T N \left[ \ln \frac{V}{N} + 1 + \frac{3}{2} \ln k_B T + \frac{3}{2} \ln \frac{2\pi m}{h^2} \right] \\
F^{\text{rot}} &= -N k_B T \ln \left\{ \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \right\} \\
F^{\text{vibr}} &= N k_B T \ln \left[ 2 \sinh \frac{T_v}{2T} \right] \\
F^{\text{nucl}} &= -N k_B T \ln g_y.
\end{aligned}$$

The internal energy is

$$\begin{aligned}
U &= F + TS = F - T \frac{\partial F}{\partial T} \\
&= -T^2 \frac{\partial}{\partial T} \left( \frac{F}{T} \right),
\end{aligned}$$

so the internal energy corresponding to translational degrees of freedom is

$$U^{\text{tr}} = -T^2 \frac{\partial}{\partial T} \left( \frac{F^{\text{tr}}}{T} \right) = N \frac{3}{2} k_B T$$

and

$$C_V^{\text{tr}} = \frac{3}{2} N k_B$$

so we end up with the ideal gas result.

Since only  $F^{\text{tr}}$  depends on volume  $V$  the pressure is

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial F^{\text{tr}}}{\partial V} = \frac{N k_B T}{V},$$

i.e. we end up with the ideal gas equation of state

$$pV = N k_B T.$$

## Rotation

Typical rotational temperatures

Gas	$T_r$
H <sub>2</sub>	85.4
N <sub>2</sub>	2.9
NO	2.4
HCl	15.2
Cl <sub>2</sub>	0.36

We see that  $T_r \ll$  the room temperature.

$T \ll T_r$

Now

$$Z^{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \approx 1 + 3e^{-2\frac{T_r}{T}},$$

so the corresponding free energy is

$$F^{\text{rot}} \approx -3N k_B T e^{-2\frac{T_r}{T}}$$

and the internal energy

$$U^{\text{rot}} = -T^2 \frac{\partial}{\partial T} \left( \frac{F^{\text{rot}}}{T} \right) \approx 6N k_B T_r e^{-2\frac{T_r}{T}}.$$

Rotations contribute to the heat capacity like

$$C_V^{\text{rot}} \approx 12N k_B \left( \frac{T_r}{T} \right)^2 e^{-2\frac{T_r}{T}} \xrightarrow{T \rightarrow 0} 0.$$

$T \gg T_r$

Now

$$\begin{aligned}
Z^{\text{rot}} &\approx \int_0^{\infty} dl (2l+1) e^{-\frac{T_r}{T} l(l+1)} \\
&= -\frac{T}{T_r} \int_0^{\infty} e^{-\frac{T_r}{T} l(l+1)} = \frac{T}{T_r},
\end{aligned}$$

so the free energy is

$$F^{\text{rot}} \approx -N k_B T \ln \frac{T}{T_r}$$

and the internal energy

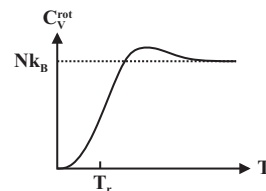
$$U^{\text{rot}} \approx N k_B T.$$

The contribution to the heat capacity is

$$C_V^{\text{rot}} \approx N k_B = f^{\text{rot}} \frac{1}{2} N k_B,$$

or in the limit  $T \gg T_r$  there are  $f^{\text{rot}} = 2$  rotational degrees of freedom.

Precisely:



## Vibration

Typical vibrational temperatures:

Gas	$T_v$
H <sub>2</sub>	6100
N <sub>2</sub>	3340
NO	2690
O <sub>2</sub>	2230
HCl	4140

We see that  $T_v \gg$  the room temperature.

$T \ll T_v$

The free energy is

$$F^{\text{vibr}} = Nk_B T \ln \left[ e^{\frac{T_v}{2T}} (1 - e^{-\frac{T_v}{T}}) \right]$$

$$\approx \frac{1}{2} Nk_B T_v - Nk_B T e^{-\frac{T_v}{T}},$$

so

$$C_V^{\text{vibr}} \approx Nk_B \left( \frac{T_v}{T} \right)^2 e^{-\frac{T_v}{T}}.$$

$T \gg T_v$

Now the free energy is

$$F^{\text{vibr}} \approx Nk_B T \ln \frac{T_v}{T}$$

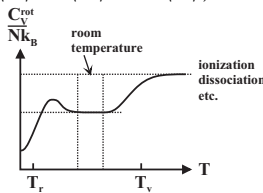
and the internal energy correspondingly

$$U^{\text{vibr}} \approx Nk_B T,$$

so the heat capacity is

$$C_V^{\text{vibr}} \approx Nk_B.$$

We see that in the limit  $T \gg T_v$  two degrees of freedom are associated with vibrations like always with harmonic oscillators ( $E = \langle T \rangle + \langle V \rangle = 2 \langle T \rangle$ ).



## Rotation of homopolar molecules

The symmetries due to the identity of nuclei must be taken into account.

Example H<sub>2</sub>-gas:

The nuclear spins are

$$I_1 = I_2 = \frac{1}{2},$$

so the total spin of the molecule is

$$I = 0, 1.$$

We consider these two cases:

$I = 1$	$I = 0$
$I_z = -1, 0, 1$	$I_z = 0$
triplet	singlet
orthohydrogen	parahydrogen
spin wavefunctions	spin wave function
symmetric:	antisymmetric:
$ 11\rangle =  \uparrow\uparrow\rangle$	$ 00\rangle = \frac{1}{\sqrt{2}} ( \uparrow\downarrow\rangle -  \downarrow\uparrow\rangle)$
$ 10\rangle = \frac{1}{\sqrt{2}} ( \uparrow\downarrow\rangle +  \downarrow\uparrow\rangle)$	
$ 1-1\rangle =  \downarrow\downarrow\rangle$	
Space wave function	Space wave function
antisymmetric:	symmetric:
$(-1)^l = -1$	$(-1)^l = 1$

The corresponding partition functions are

$$Z_{\text{ortho}} = \sum_{l=1,3,5,\dots} (2l+1) e^{-\frac{T_r}{T} l(l+1)}$$

$$Z_{\text{para}} = \sum_{l=0,2,4,\dots} (2l+1) e^{-\frac{T_r}{T} l(l+1)}$$

and the partition function associated with rotation is

$$Z^{\text{rot}} = 3Z_{\text{ortho}} + Z_{\text{para}}.$$

When  $T \gg T_r$  collisions cause conversions between ortho and para states so the system is in an equilibrium. In addition  $Z_{\text{ortho}} \approx Z_{\text{para}}$ , so all 4 spin states are equally probable.

When  $T \lesssim T_r$  the gas may remain as a *metastable mixture* of ortho and para hydrogens. In the mixture the ratio of the spin populations is 3 : 1. Then we must use the partition sum

$$Z_N^{\text{rot}} = Z_{\text{ortho}}^{\frac{3N}{4}} Z_{\text{para}}^{\frac{N}{4}}.$$

The internal energy is now

$$U^{\text{rot}} = \frac{3}{4} U^{\text{ortho}} + \frac{1}{4} U^{\text{para}}$$

and the heat capacity correspondingly

$$C^{\text{rot}} = \frac{3}{4} C^{\text{ortho}} + \frac{1}{4} C^{\text{para}}.$$



## Fermionic systems

### Electron gas

The ideal Fermi gas is a good approximation for example for the conducting electrons in a metal.

When the single particle energies are  $\epsilon_k = \frac{\hbar^2 k^2}{2m}$  the density of states is

$$\begin{aligned}\omega_1(\epsilon) &= V \frac{g_s}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon} \\ &= V 2\pi g_s \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon}.\end{aligned}$$

As the density we get

$$\rho = \frac{\bar{N}}{V} = \frac{g_s}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\epsilon \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)} + 1}.$$

The energy per particle will be

$$\bar{\epsilon} = \frac{E}{\bar{N}} = \frac{\int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} + 1}}{\int_0^\infty d\epsilon \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} + 1}}.$$

### Degenerated Fermi gas

Suppose that  $k_B T \ll \mu$ .

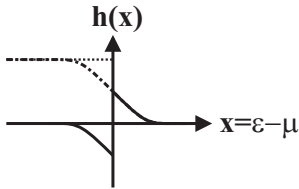
Let's write

$$\frac{1}{e^{\beta(\epsilon-\mu)} + 1} = \theta(\mu - \epsilon) + h(\epsilon - \mu),$$

where

$$h(x) = \text{sign}(x) \frac{1}{e^{\beta|x|} + 1}.$$

The function  $h(x)$  deviates from zero only at the narrow domain  $|x| \lesssim k_B T \ll \mu$ .



Let's evaluate the integral

$$\begin{aligned}\int_0^\infty d\epsilon \frac{\phi(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1} &= \int_0^\infty d\epsilon \phi(\epsilon) [\theta(\mu - \epsilon) + h(\epsilon - \mu)] \\ &= \int_0^\mu d\epsilon \phi(\epsilon) + \int_0^\infty d\epsilon h(\epsilon) [\phi(\mu + \epsilon) - \phi(\mu - \epsilon)] \\ &\quad + \int_\mu^\infty d\epsilon h(\epsilon) \phi(\mu - \epsilon).\end{aligned}$$

The last term is of the order

$$h(\mu) = \frac{1}{e^{\mu/k_B T} + 1} \approx e^{-\mu/k_B T}$$

and can be discarded.

If  $\phi(\epsilon)$  regular enough in the vicinity of  $\epsilon \approx \mu$  we can expand

$$\phi(\mu + \epsilon) - \phi(\mu - \epsilon) \approx 2\phi'(\mu)\epsilon + 2\frac{1}{3!}\phi'''(\mu)\epsilon^3 + \dots$$

Now

$$\begin{aligned}\int_0^\infty d\epsilon \frac{\phi(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1} &\approx \int_0^\mu d\epsilon \phi(\epsilon) \\ &\quad + 2\phi'(\mu)(k_B T)^2 \int_0^\infty dz \frac{z}{e^z + 1} \\ &\quad + 2\phi'''(\mu) \frac{1}{3!} (k_B T)^4 \int_0^\infty dz \frac{z^3}{e^z + 1} \\ &\quad + \dots\end{aligned}$$

and we end up with *Sommerfeld's expansion*

$$\begin{aligned}\int_0^\infty d\epsilon \frac{\phi(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1} &\approx \int_0^\mu d\epsilon \phi(\epsilon) + \frac{\pi^2}{6} (k_B T)^2 \phi'(\mu) \\ &\quad + \frac{7\pi^4}{360} (k_B T)^4 \phi'''(\mu) + \dots\end{aligned}$$

### Temperature $T = 0$

Now

$$\bar{n}(\epsilon) = \theta(\mu - \epsilon)$$

and  $h(x) = 0$ .

The *Fermi energy* is

$$\epsilon_F = \mu = \frac{\hbar^2 k_F^2}{2m}.$$

The *Fermi momentum* is

$$p_F = \hbar k_F.$$

The density is

$$\begin{aligned}\rho &= \frac{g_s}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\mu d\epsilon \sqrt{\epsilon} \\ &= \frac{g_s}{6\pi^2} \left(\frac{2m\epsilon_F}{\hbar^2}\right)^{3/2}\end{aligned}$$

or

$$\rho = \frac{g_s}{6\pi^2} k_F^3.$$

The spin degeneracy factor of electrons is

$g_s = 2 \cdot \frac{1}{2} + 1 = 2$ , so

$$\rho = \frac{k_F^3}{3\pi^2}.$$

For the energy per particle we get

$$\begin{aligned}\bar{\epsilon} &= \epsilon_F \frac{\int_0^1 dx x^{3/2}}{\int_0^1 dx x^{1/2}} = \epsilon_F \frac{2/5}{2/3} \\ &= \frac{3}{5} \epsilon_F.\end{aligned}$$

The total energy is

$$E = \frac{3}{5} \epsilon_F N = \frac{3}{5} N \frac{\hbar^2}{2m} \left( \frac{6\pi^2 \rho}{g_s} \right)^{2/3}.$$

Since

$$E = \text{constant} \times N^{5/3} V^{-2/3},$$

we have

$$-p = \left( \frac{\partial E}{\partial V} \right)_N = -\frac{2}{3} \frac{E}{V}$$

or

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

### Metallic electron gas

When we write the density as

$$\rho = \frac{\bar{N}}{V} = \frac{1}{\frac{4}{3} \pi r_i^3}$$

and define the dimensionless number

$$r_s = \frac{r_i}{a_0},$$

where  $a_0$  is the Bohr radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529\text{\AA},$$

we can see that

$$\rho = \frac{1.613 \cdot 10^{30}}{r_s^3} \frac{1}{\text{m}^3}.$$

For metals we have

$$1.9 \lesssim r_s \lesssim 5.6.$$

The Fermi wave vector will become

$$k_F = \frac{1}{a_0 r_s} \sqrt[3]{\frac{9\pi}{4}} = \frac{1.92}{a_0 r_s}.$$

The Fermi velocity is

$$\begin{aligned} v_F &= \frac{p_F}{m} = \frac{\hbar k_F}{m} = \frac{1.92\hbar}{ma_0 r_s} \\ &= \frac{4.2 \cdot 10^6 \text{ m}}{r_s} \frac{1}{\text{s}}. \end{aligned}$$

For example in aluminium

$$v_F = 2029 \frac{\text{km}}{\text{s}} = \frac{c}{148}.$$

The Fermi temperature or the degeneracy temperature  $T_F$  is defined so that

$$k_B T_F = \epsilon_F.$$

Now

$$\epsilon_F = \underbrace{\frac{\hbar^2}{2ma_0^2}}_{\text{binding energy of hydrogen}} \left( \frac{1.92}{r_s} \right)^2 = \frac{3.69}{r_s^2} 13.6\text{eV}.$$

binding  
energy of  
hydrogen

Since

$$1\text{eV} = 11604 k_B \text{K},$$

we have

$$T_F = \left( \frac{1.92}{r_s} \right)^2 13.6 \cdot 11604 \text{K}.$$

For aluminium the Fermi temperature is  $T_F = 136\,000\text{K}$ . In general, the metals satisfy

$$T \ll T_F,$$

so the metallic electron gas is strongly degenerated.

*Specific heat* Let now  $T > 0$ , but  $T \ll T_F$ .

We need  $\mu = \mu(T)$ , when  $\frac{\bar{N}}{V} = \rho$  is known.

With the help of the Sommerfeld expansion we get

$$\begin{aligned} \frac{2}{3} \epsilon_F^{3/2} &= \frac{4\pi^2}{g_s} \left( \frac{\hbar^2}{2m} \right)^{3/2} \rho = \int_0^\infty d\epsilon \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} + 1} \\ &\approx \frac{2}{3} \mu^{3/2} + \frac{\pi^2}{12} (k_B T)^2 \frac{1}{\sqrt{\mu}} + \dots \end{aligned}$$

so we can write

$$\frac{2}{3} \mu^{3/2} \left[ 1 + \frac{\pi^2}{8} (k_B T)^2 \frac{1}{\epsilon_F^2} + \dots \right] = \frac{2}{3} \epsilon_F^{3/2}.$$

From this we get for the chemical potential the expression

$$\mu(T) = \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\epsilon_F} \right)^2 + \dots \right].$$

Employing again the Sommerfeld expansion we get

$$\begin{aligned} \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} + 1} \\ &\approx \frac{2}{5} \mu^{5/2} + \frac{\pi^2}{4} (k_B T)^2 \sqrt{\mu} + \dots \\ &= \frac{2}{5} \epsilon_F^{5/2} \left[ 1 + \frac{5}{12} \pi^2 \left( \frac{k_B T}{\epsilon_F} \right)^2 \right] + \dots \end{aligned}$$

Now the energy/particle is

$$\begin{aligned} \bar{\epsilon}(T) &= \frac{\int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} + 1}}{\int_0^\infty d\epsilon \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} + 1}} \\ &= \frac{3}{5} \epsilon_F \left[ 1 + \frac{5}{12} \pi^2 \left( \frac{k_B T}{\epsilon_F} \right)^2 \right] \\ &= \frac{3}{5} \epsilon_F + \frac{\pi^2}{4} \frac{k_B^2 T^2}{\epsilon_F}. \end{aligned}$$

The heat capacity which can be written as

$$\begin{aligned} C_V &= \frac{\partial N\bar{\epsilon}}{\partial T} = N \frac{\pi^2}{2} \frac{k_B^2}{\epsilon_F} T \\ &= Nk_B \frac{\pi^2}{2} \frac{T}{T_F}, \end{aligned}$$

is small when compared e.g. with the specific heat of the Maxwell-Boltzmann gas ( $C_V = Nk_B \frac{3}{2}$ ). This is understandable since the number of those particles that can be excited with the thermal energy  $\sim k_B T$  in Fermi gas is much less than in MB or BE gases due to the Pauli exclusion principle.

### Pauli's paramagnetism

The magnetic moment of the electron is

$$\boldsymbol{\mu} = -\frac{e}{m} \mathbf{s}$$

or

$$\mu_z = -\mu_B \sigma_z,$$

where

$$\mu_B = \frac{e\hbar}{2m} = 5.66 \cdot 10^{-5} \frac{\text{eV}}{\text{T}}$$

and

$$\sigma_z = \frac{2}{\hbar} s_z = \pm 1.$$

In an external magnetic field the energy of an electron is

$$\epsilon_{\mathbf{p}\sigma_z} = \epsilon_{p\pm} = \frac{\mathbf{p}^2}{2m} - \mu_z B = \epsilon_{\mathbf{p}} + \mu_B B \sigma_z$$

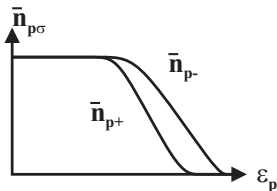
when the kinetic energy is

$$\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m}.$$

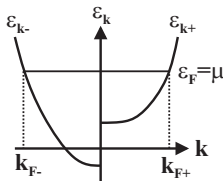
We still treat electrons as non interacting so the grand canonical partition function is as before, provided that we replace  $\epsilon_{\mathbf{p}} \rightarrow \epsilon_{\mathbf{p}} + \mu_B B \sigma_z$ .

The occupation numbers of the states are now

$$\bar{n}_{\mathbf{p}\sigma_z} = \bar{n}_{p\pm} = \frac{1}{e^{\beta(\epsilon_{\mathbf{p}} + \mu_B B \sigma_z - \mu)} + 1}.$$



Since the metallic electron gas is strongly degenerated ( $T \ll T_F$ ), we can restrict to the temperature  $T = 0$ .



The Fermi wave vectors can be determined from the conditions

$$\begin{aligned} \frac{\hbar^2 k_{F+}^2}{2m} + \mu_B B &= \mu \\ \frac{\hbar^2 k_{F-}^2}{2m} - \mu_B B &= \mu. \end{aligned}$$

Since the number density is

$$\rho = \frac{g_s}{6\pi^2} k_F^3,$$

the spin population densities are

$$\begin{aligned} \rho_+ &= \frac{k_{F+}^3}{6\pi^2} \\ \rho_- &= \frac{k_{F-}^3}{6\pi^2}. \end{aligned}$$

If the strength of the magnetic field is

$$B_0 = \frac{\epsilon_F}{\mu_B},$$

the magnetic energy is of the same order as the Fermi energy. For metals  $\epsilon_F \approx 5\text{eV}$ , so  $B_0 \approx 10^5\text{T}$ . So the realistic magnetic fields are  $\ll B_0$  and we can work at the small  $B$  limit. Let us denote

$$k_{F\pm} = k_F \pm \delta k_F,$$

so

$$\begin{aligned} \frac{\hbar^2 k_{F\pm}^2}{2m} \pm \mu_B B &= \frac{\hbar^2 k_F^2}{2m} \pm \frac{\hbar^2 k_F}{m} \delta k_F \pm \mu_B B \\ &= \mu = \frac{\hbar^2 k_F^2}{2m}. \end{aligned}$$

From this we get

$$\delta k_F = -\frac{m\mu_B}{\hbar^2 k_F} B$$

and

$$\begin{aligned} \rho_{\pm} &= \frac{k_F^3}{6\pi^2} \pm \frac{k_F^2}{2\pi^2} \delta k_F \\ &= \frac{k_F^3}{6\pi^2} \mp \frac{k_F m \mu_B}{2\pi^2 \hbar^2} B. \end{aligned}$$

The relative polarization is

$$\begin{aligned} r &\equiv \frac{\rho_+ - \rho_-}{\rho_+ + \rho_-} = -\frac{3m\mu_B}{\hbar^2 k_F^2} B \\ &= -\frac{3\mu_B}{2\epsilon_F} B. \end{aligned}$$

The magnetization per volume element is

$$M = \frac{N}{V} \langle \mu_z \rangle = -\rho \mu_B \langle \sigma_z \rangle = -\rho \mu_B r$$

or

$$M = \frac{3}{2} \rho \frac{\mu_B^2}{\epsilon_F} B.$$

The susceptibility is, according to its definition,

$$\chi = \frac{\partial M}{\partial H} = \mu_0 \frac{\partial M}{\partial B}.$$

*Pauli's paramagnetic susceptibility* is then

$$\chi = \frac{3}{2} \mu_0 \rho \frac{\mu_B^2}{\epsilon_F}$$

provided that  $T \ll T_F$  and  $\mu_B B \ll \epsilon_F$ .

In aluminium the electron density is

$$\rho = 1.82 \cdot 10^{29} \text{m}^{-3}$$

and the Fermi energy

$$\epsilon_F = \left( \frac{1.92}{2.07} \right)^2 13.6 \text{eV} = 11.7 \text{eV}.$$

The susceptibility

$$\begin{aligned} \chi &= \frac{3}{2} \cdot 4\pi \cdot 10^{-7} \cdot 1.82 \cdot 10^{29} \cdot \frac{(5.66 \cdot 10^{-5})^2}{11.7} \\ &= \frac{\text{Vs}}{\text{Am}} \frac{1}{\text{m}^3} \frac{(\text{eV})^2}{\text{T}^2 \text{eV}} \\ &= 9.4 \cdot 10^{13} \frac{\text{eV Vs}}{\text{Am}^4} \left( \frac{\text{m}^2}{\text{Vs}} \right)^2 \\ &= 9.4 \cdot 10^{13} \cdot 1.6 \cdot 10^{-19} \\ &= 1.5 \cdot 10^{-5} \end{aligned}$$

is now small since only the electrons very close to the Fermi surface can be polarized magnetically.

## Two dimensional electron gas

The Hamiltonian for a free electron in the magnetic field

$$\mathbf{B} = \nabla \times \mathbf{A}$$

is given by

$$\mathcal{H}_0 = \frac{1}{2m^*} \left( -i\hbar\nabla + \frac{e}{c} \mathbf{A} \right)^2.$$

Convenient unit of

- the energy for non-interacting electrons is  $\hbar\omega_c$ , where  $\omega_c = eB/m^*c$  is the cyclotron frequency.
- the energy for interacting electrons is  $e^2/\epsilon\ell_0$ , where
- the length is  $\ell_0 = (\hbar c/eB)^{\frac{1}{2}}$ , the magnetic length.

Consider electrons

- confined to  $xy$ -plane.
- subjected to a perpendicular magnetic field  $\mathbf{B} \parallel \hat{z}$ .

The eigenenergies are the discrete *Landau levels*

$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega_c, \quad n = 0, 1, 2, \dots$$

Choosing the Landau gauge

$$\mathbf{A} = (0, Bx, 0)$$

the single particle Hamiltonian is

$$\mathcal{H}_0 = \frac{1}{2m^*} \left[ p_x^2 + \left( p_y + \frac{eB}{c} x \right)^2 \right].$$

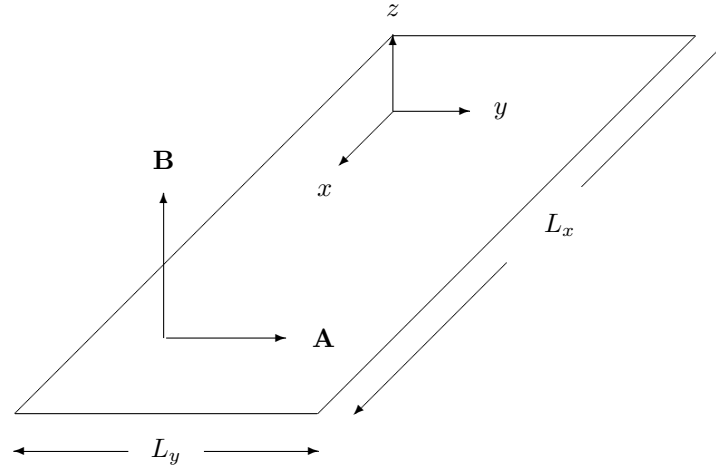
The eigenfunctions are

$$\phi_{nX} = e^{ik_y y} e^{-(x-X)^2/2\ell_0^2} H_n \left( \frac{x-X}{\ell_0} \right),$$

where the center of the oscillatory motion is given by

$$X = -k_y \ell_0^2.$$

Confine the system in a rectangular cell



Using periodic boundary conditions we have

$$k_y = \frac{2\pi n_y}{L_y}, \quad n_y = 0, \pm 1, \pm 2, \dots$$

and

$$X = -\frac{2\pi n_y}{L_y} \ell_0^2, \quad 0 \leq X < L_x.$$

The number of allowed values of  $n_y$ , i.e. the degeneracy of each Landau level, is

$$N_s = \frac{L_x L_y}{2\pi \ell_0^2} = \frac{e}{hc} \Phi = \frac{\Phi}{\Phi_0},$$

where  $\Phi_0 = hc/e$  is the flux quantum.

Thus, *on each Landau level there is exactly one state for each flux quantum and for each spin polarization.*

# Quantum Hall states

Consider an experiment like

When  $N_e$  is the number of electrons in an area and  $N_s$  the number of flux quanta we define *the filling fraction* as

$$\nu = \frac{N_e}{N_s} \left( = 4.136 \frac{n_0}{10^{15} \text{m}^{-2}} \frac{\text{T}}{B} \right).$$

To treat the spin we note that

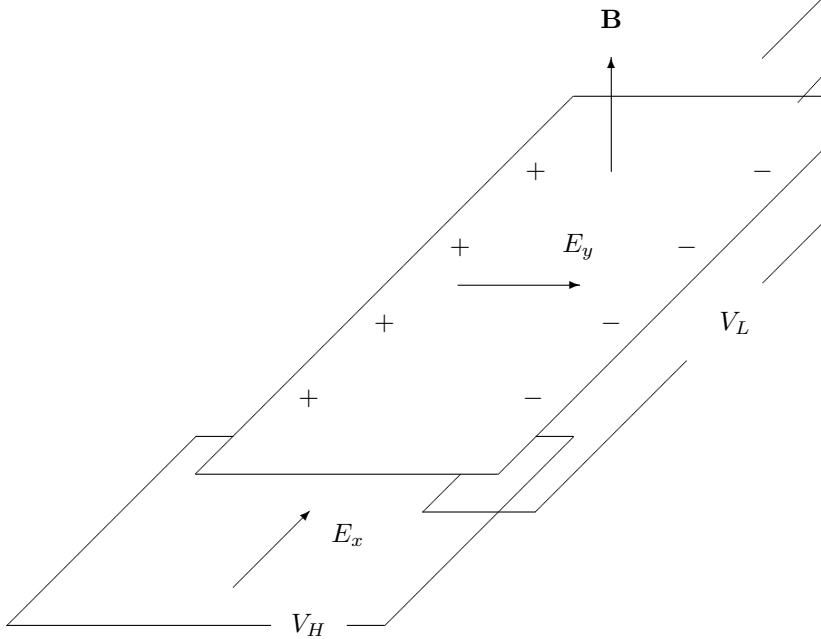
- there should be the Zeeman coupling term

$$\mathcal{H}_{\text{Zeeman}} = \boldsymbol{\mu} \cdot \mathbf{B} = -g\mu_B B s_z$$

in the Hamiltonian. Here  $g$  is the Lande factor and  $\mu_B$  the Bohr magneton.

- in addition to the Zeeman term there are no spin dependent terms in the Hamiltonian, not even in the interacting many body system.
- the problem can be solved disregarding the spin. At later stages we can add the total Zeeman energy

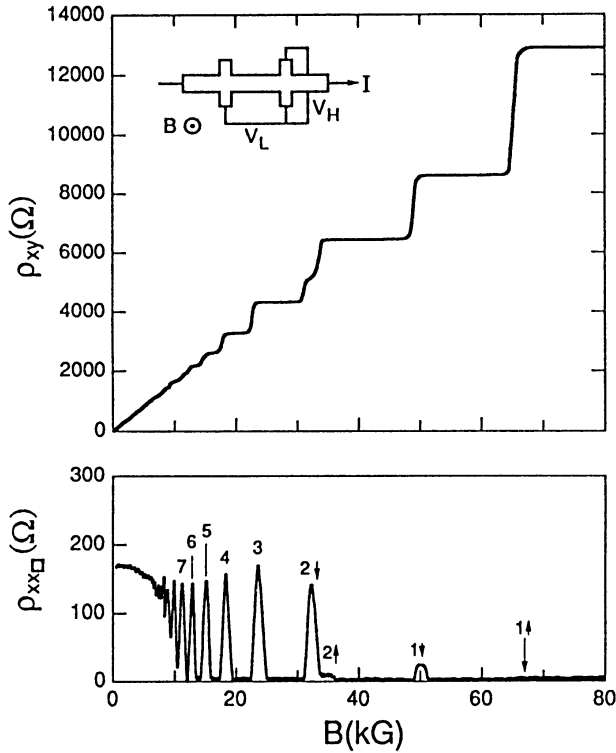
$$E_{\text{Zeeman}} = g\mu_B B S_z.$$



The conductivity  $\sigma$  and the resistivity  $\rho$  are defined by  $\mathbf{j} = \sigma \mathbf{E}$ ,  $\mathbf{E} = \rho \mathbf{j}$ . Classically the diagonal and Hall conductivities are

$$\begin{aligned} \sigma_{xx} &= \frac{n_0 e^2 \tau}{m} \frac{1}{1 + (\omega_c \tau)^2} \\ \sigma_{xy} &= -\frac{n_0 e c}{B} + \frac{\sigma_{xx}}{\omega_c \tau}, \end{aligned}$$

where  $\tau$  is the relaxation time. In particular  $\rho_{xy} = -B/n_0 e c$ . Experimentally the resistivities behave like



The Hall conductivity can be written in the form

$$\sigma_{xy} = -\frac{n_0 ec}{B} + \Delta\sigma_{xy},$$

where, according to the Kubo formula, the contribution from a localized state  $|\alpha\rangle$  to  $\Delta\sigma_{xy}$  is

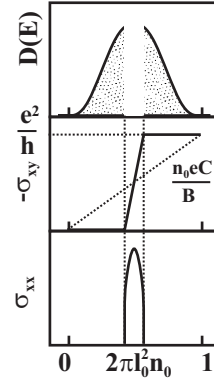
$$\Delta\sigma_{xy}^\alpha = \frac{f(E_\alpha)ec}{B}.$$

Here  $f(E)$  is the Fermi distribution function.

When the number of electrons changes we observe (at  $T = 0$ ) that

- as long as the Fermi level lies within the localized states,  $\sigma_{xy}$  remains constant.
- if all states below the Fermi level are localized, the terms in  $\sigma_{xy}$  cancel exactly and  $\sigma_{xy} = 0$ .
- for QHE to exist there must be extended states in Landau levels.

As a function of the density the conductivities behave like



Noting that

$$\nu = \frac{N_e}{N_s} = 2\pi\ell_0^2 n_0 \propto \frac{n_0}{B},$$

decreasing magnetic field corresponds to increasing filling factor, i.e. decreasing the magnetic field is equivalent to increasing the number of electrons.

Increasing the magnetic field (i.e. reducing the electron density) furthermore one finds resistivities to behave like

We observe that

- the Hall resistivity develops plateaus with

$$\rho_{xy} = \frac{h}{ne^2}, \quad n = 1, 2, 3, \dots$$

This quantization condition is obeyed with extreme accuracy. In fact, the current ISO standard for resistivity defines

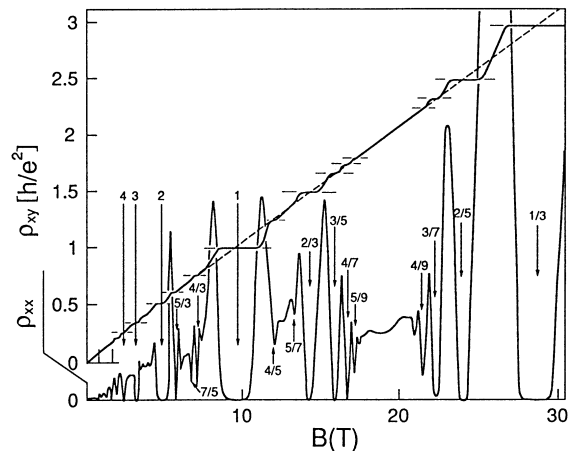
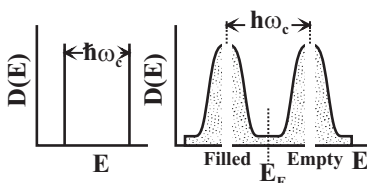
$$\rho_{xy} = \frac{25812.807}{n} \Omega.$$

- at the same time the diagonal resistivity practically vanishes.

For the moment we suppose that the electrons are polarized. If the current carrying electrons fill up exactly  $n$  Landau levels, it can be shown that  $\rho_{xy} = h/ne^2$  and  $\rho_{xx} = 0$ .

The plateaus can be explained by noting that

- in an ideal pure 2DEG the density of states is a series of  $\delta$ -peaks separated by  $\hbar\omega_c$ .
- In a real impure system the  $\delta$ -peaks are spread and between the Landau levels there are localized states.



The plateaus in the Hall resistivity and the minima in the longitudinal resistivity correspond to filling fractions

$$\nu = \frac{p}{q},$$

where

- $p$  and  $q$  are small integers ( $\lesssim 11$ ).
- $q$  is an *odd* integer.

This behaviour is called as the *Fractional Quantum Hall Effect* (FQHE) as opposed to the previous *Integer Quantum Hall Effect* (IQHE).

Regarding the IQHE we note that

- the plateaus correspond to full Landau levels,
- the Landau levels are energetically far from each other as compared to typical electron-electron interaction energies (at least when  $\nu \lesssim 5$ ).
- the mutual electronic interactions play practically no role.

While this single particle picture is sufficient in the IQHE it cannot explain the FQHE where

- the Landau levels are only partially filled, so that
- there is room for the Coulomb intra level interaction.

It turns out that the correlations due to the electron interaction are essential in the FQHE.

### Laughlin's theory

For a while we work in the symmetric gauge

$$\mathbf{B} = \frac{1}{2}(-y, x, 0)$$

and in the cylindrical coordinate system. The single particle Hamiltonian is now

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m^*} + \frac{1}{2} \omega_c p_\phi + \frac{1}{8} m^* \omega_c^2 r^2.$$

The Schrödinger equation takes the form

$$-\frac{\hbar^2}{2m^*} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{1}{2} i \hbar \omega_c \frac{\partial \psi}{\partial \phi} + \left( \frac{1}{8} m^* \omega_c^2 r^2 - E \right) \psi = 0.$$

Its solutions can be written as

$$\psi_{n,m}(r, \phi) = \left[ \frac{n!}{2\pi \ell_0^2 2^m m!} \right]^{\frac{1}{2}} e^{-im\phi - r^2/4\ell_0^2} \times \left( \frac{r}{\ell_0} \right)^{|m|} L_n^{|m|} \left( \frac{r^2}{2\ell_0^2} \right).$$

The corresponding energies are

$$E_{n,m} = \frac{1}{2} (2n + |m| + 1 - m) \hbar \omega_c.$$

In particular, in the lowest Landau level ( $n = 0, m \geq 0$ ), the wave functions are

$$\psi_m(z) = \left[ \frac{1}{2\pi \ell_0^2 2^m m!} \right]^{\frac{1}{2}} \left( \frac{z}{\ell_0} \right)^m e^{-|z|^2/4\ell_0^2},$$

where we have written

$$z = r e^{-i\phi} = x - iy.$$

It is easy to show, that the quantum number  $m$  can take the values

$$m = 0, 1, \dots, N_s - 1,$$

where

$$N_s = \frac{A}{2\pi \ell_0^2}$$

is the degeneracy of a Landau level. In the lowest Landau level the wave functions are therefore of the form

$$1, z, z^2, \dots, z^{N_s-1} \text{ times Gaussian.}$$

The great idea of Laughlin was to propose the Jastrow type function

$$\psi_m = \prod_{j < k}^{N_e} (z_j - z_k)^m \prod_{j=1}^{N_e} e^{-|z_j|^2/4\ell_0^2}$$

as the many body ground state wave function. To get the Fermi statistics  $m$  must be odd.

Laughlin's wave function has some remarkable properties:

- in the thermodynamical limit the parameter  $m$  is related to the filling fraction  $\nu$  as

$$m = \frac{1}{\nu}.$$

- it can be mapped to a charge neutral two dimensional classical plasma, which makes it possible to use classical statistical mechanics to evaluate e.g. the energy.
- small systems ( $\lesssim 12$  particles) can be solved exactly. Comparisons with Laughlin's wave function show that it is practically the exact solution of the many body problem

## Spin polarization

We consider the filling fraction  $\nu = 1$ , i.e. the lowest Landau level is fully occupied. We turn on the electron-electron interaction and note that

- typically the Landau level separation  $\hbar\omega_c$  is (much) larger than the characteristic Coulomb interaction energy  $e^2/\epsilon\ell_0$ .
- if the electrons remain polarized the interaction cannot do much: all energetically favorable states are already occupied.

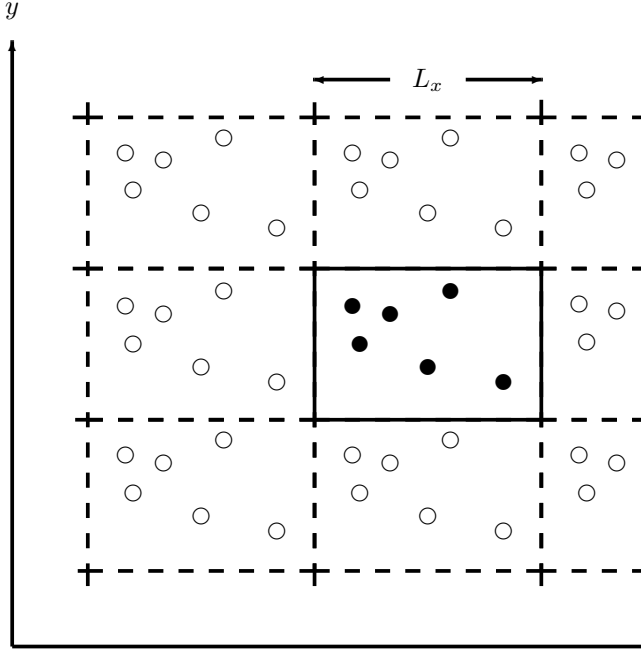
So, we let electrons to flip their spins. However,

- according to Hund's rule the repulsive interaction is the smaller the larger the total spin  $S$ .
- In the absence of the Zeeman coupling all possible  $S_z$  states are degenerate.
- the Zeeman coupling  $g\mu_B B S_z$  tends to polarize the system, although the Lande  $g$ -factor is rather small (in GaAs  $g \approx 0.5$ ).

We conclude that the ground state at  $\nu = 1$  is polarized.

### The diagonalization method

We will work in rectangular geometry with periodical boundary conditions.



Our Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{e-e} + \mathcal{H}_{e-im} + \mathcal{H}_{e-b} + \mathcal{H}_{b-b},$$

where

- we suppose a homogenous positive background,

- $\mathcal{H}_0$  is the single particle Hamiltonian,
- $\mathcal{H}_{e-e}$  is the Coulomb interaction between an electron and all other electrons and their images summed over all electrons,
- $\mathcal{H}_{e-im}$  is the interaction between an electron and its images,
- $\mathcal{H}_{e-b}$  is the electron-background interaction,
- $\mathcal{H}_{b-b}$  is the background-background interaction.

The Zeeman coupling is treated afterwards.

We

1. restrict to the lowest Landau level.
2. work in occupation representation. There

$$\mathcal{H} = \sum_{j\sigma} w_j a_{j\sigma}^\dagger a_{j\sigma} + \sum_{\substack{j_1\sigma_1 \quad j_2\sigma_2 \\ j_3\sigma_3 \quad j_4\sigma_4}} A_{j_1 j_2 j_3 j_4} a_{j_1\sigma_1}^\dagger a_{j_2\sigma_2}^\dagger a_{j_3\sigma_3} a_{j_4\sigma_4},$$

where operators  $a_{j\sigma}^\dagger$  ( $a_{j\sigma}$ ) create (destroy) an electron with spin  $\sigma$  in a single particle state  $j$ .

3. fix  $N_s$ , the number of flux quanta ( $\approx 10$ ). This is also the number of allowed single particle states.
4. fix  $N_e$ , the number of electrons. At full Landau level ( $\nu = 1$ )  $N_e = N_s$ .
5. fix the polarization  $S_z$  and the total momentum since they are preserved by Coulomb interaction.
6. form the basis by constructing all possible non-interacting states satisfying the above conditions.
7. represent the Hamiltonian as a matrix in the basis constructed above.
8. diagonalize the matrix. As a result we have the energy spectrum and corresponding eigenvectors.
9. for each eigenstate find its total spin  $S$ . Since  $[\mathcal{H}, S] = 0$ , we know that these eigenstates are eigenstates of spin, too.

$\langle S_z \rangle$

We now have the spectrum  $E_0, E_1, E_2, \dots$  for the interacting many particle system. To calculate the polarization we note that

- the energies  $E_i$  are associated with other quantum numbers like the total spin  $S_i$  and its  $z$ -component  $S_{zi}$ .



- since there are no spin dependent term in the Hamiltonian all states with quantum numbers  $(E_i, S_i, S_{zi} = -S_i)$ ,  $(E_i, S_i, S_{zi} = -S_i + 1)$ ,  $\dots$ ,  $(E_i, S_i, S_{zi} = +S_i)$  are degenerate. So, the expectation value of  $S_z$  would be 0.
- the Zeeman interaction must be turned on. The energies will shift like

$$\epsilon_i = E_i - g\mu_B B S_{zi}.$$

It turns out that, as expected, the total spin in the ground state is  $S_0 = N_e/2$  (supposing  $N_e$  to be even). Due to the Zeeman coupling the ground state is polarized at  $T = 0$ . The spins of the excited states, however, have all the possible values  $0, 1, \dots, N_e/2$ . So, we expect the polarization to decrease with increasing temperature. The dependence on temperature is evaluated in the canonical ensemble as

$$\langle S_z \rangle = \frac{1}{Z} \sum_i S_{zi} e^{-(E_i - g\mu_B B S_{zi})/k_B T},$$

where  $Z$  is the canonical partition sum

$$Z = \sum_i e^{-(E_i - g\mu_B B S_{zi})/k_B T}.$$

## Relativistic electron gas

The rest energy of an electron is

$$mc^2 = 0.511 \text{keV}$$

and the relativistic total energy

$$\begin{aligned} \epsilon_p &= \sqrt{(mc^2)^2 + (cp)^2} \\ &= mc^2 + \frac{p^2}{2m} + \dots \end{aligned}$$

Denote by

$$k_c = \frac{mc}{\hbar} = 2.59 \cdot 10^{12} \text{m}^{-1}$$

the Compton wave vector of an electron and by

$$\lambda_c = \frac{2\pi}{k_c} = 2.43 \cdot 10^{-12} \text{m}$$

its Compton wave length.

Since  $p = \hbar k$ , we have

$$\epsilon_k = c\hbar\sqrt{k^2 + k_c^2}.$$

Periodic boundary conditions are the same as in the non relativistic case i.e.

$$\mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z),$$

so we have

$$\rho = \frac{k_F^3}{3\pi^2}.$$

When  $k_F = (3\pi^2\rho)^{1/3}$  is of the order  $k_c$ , the relativistic corrections must be taken into account. The corresponding density is

$$\begin{aligned} \rho_c &= \frac{k_c^3}{3\pi^2} = 5.87 \cdot 10^{35} \frac{1}{\text{m}^3} \\ &\approx 10^6 \times \text{density of metallic electron gas} \end{aligned}$$

We have an *ultrarelativistic electron gas* when  $k_F \gg k_c$  or correspondingly  $\rho \gg \rho_c$ .

Let us consider *cold* relativistic material, i.e. let us suppose  $T \ll T_F$ .

The total energy is

$$E = N\bar{\epsilon} = N \frac{\int_0^{k_F} dk k^2 c\hbar\sqrt{k^2 + k_c^2}}{\int_0^{k_F} dk k^2},$$

where

$$\begin{aligned} \bar{\epsilon} &= mc^2 \frac{\int_0^{k_F/k_c} dx x^2 \sqrt{1+x^2}}{\int_0^{k_F/k_c} dx x^2} \\ &= mc^2 + mc^2 \frac{\int_0^{k_F/k_c} dx x^2 [\sqrt{1+x^2} - 1]}{\int_0^{k_F/k_c} dx x^2} \end{aligned}$$

is the average electronic energy.

At the non relativistic limit we have

$$\begin{aligned} \bar{\epsilon} &\approx mc^2 \left[ 1 + \frac{\int_0^{k_F/k_c} dx x^2 [\frac{1}{2}x^2 + \dots]}{\int_0^{k_F/k_c} dx x^2} \right] \\ &= mc^2 \left[ 1 + \frac{3}{10} \left( \frac{k_F}{k_c} \right)^2 + \dots \right], \end{aligned}$$

from which our earlier results can be derived, provided that the rest energy of electrons is taken into account.

At the ultrarelativistic limit  $k_F \gg k_c$  we get

$$\bar{\epsilon} \approx mc^2 \frac{\int_0^{k_F/k_c} dx x^3}{\int_0^{k_F/k_c} dx x^2} = \frac{3}{4} c\hbar k_F.$$

Thus the energy density is

$$\frac{E}{V} = \frac{3}{4} (3\pi^2)^{1/3} c\hbar\rho^{4/3}$$

and the pressure

$$p = - \left( \frac{\partial E}{\partial V} \right)_N$$

at the *ultrarelativistic limit*

$$p = \frac{1}{3} \frac{E}{V} = \frac{1}{4} (3\pi^2)^{1/3} c\hbar\rho^{4/3}.$$

## White dwarf

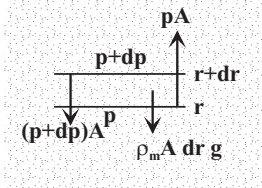
In a properly functioning star the energy released in nuclear reactions (mainly  $2\text{H} \rightarrow \text{He}$ ) and the collapsing gravitational force are in balance. When the nuclear fuel is consumed the star collapses. If the mass of the star is large enough all material will become ionized. Depending on the mass of the star the final state can be for example

- *white dwarf*, if the pressure of the degenerated electronic plasma prohibits further compression.
- *neutron star* if the electronic pressure is not enough to compensate the gravitational force. The matter compresses further to neutrons and their degeneracy pressure prohibits further collapse.

Typical properties of a white dwarf:

- the diameter of the star  $2R \approx 10^4 \text{ km}$ .
- the total number of nuclei  $N_N \approx 10^{57}$ .
- the mass  $M \approx 10^{30} \text{ kg} \approx M_\odot$ , where  $M_\odot = 1.989 \cdot 10^{30} \text{ kg}$  is the mass of the sun.
- the mass density  $\rho_m \approx 10^{10} \text{ kg m}^{-3}$  is about  $10^6 \times$  the density of the sun or of the earth.
- the number density of electrons  $\rho \approx 10^{36} \text{ m}^{-3}$ . Then  $k_F \approx k_c$ , so the electron gas is only moderately relativistic. In inner parts the gas can be much denser and thus ultrarelativistic.
- the pressure  $p \approx 10^{22} \text{ Pa} \approx 10^{17} \text{ atm}$ .
- the temperature in inner parts  $T \approx 10^7 \text{ K} \approx T_\odot$ . Since the Fermi temperature is  $T_F \approx 10^{10} \text{ K} \gg T$  we, however, have a cold electron gas.

Let  $p(r)$  be the pressure at the distance  $r$  from the center of the star,  $g(r)$  the corresponding gravitational acceleration and  $\rho_m(r)$  the density.



The condition for the balance of hydrostatic mechanical forces is

$$\frac{dp}{dr} = -g(r)\rho_m(r).$$

Now

$$g(r) = \frac{GM(r)}{r^2},$$

where  $M(r)$  is the mass inside of the radius  $r$  and

$$G = 6.673 \cdot 10^{-11} \frac{\text{Nm}^2}{\text{kg}^2}$$

is the gravitational constant. We get the pair of equations

$$\begin{aligned} \frac{dp(r)}{dr} &= -G \frac{M(r)\rho_m(r)}{r^2} \\ \frac{dM(r)}{dr} &= 4\pi r^2 \rho_m(r). \end{aligned}$$

Because in nuclei there are roughly as many neutrons as protons, and, on the other hand, there are as many protons as electrons, we have

$$\rho_m(r) \approx 2m_p \rho(r).$$

Here

$$m_p = 1.673 \cdot 10^{-27} \text{ kg}$$

is the proton mass and  $\rho(r)$  the number density of the electrons.

As a good approximation the electron density of a star can be taken as a constant,  $\rho$  say. Then

$$M(r) = \frac{8}{3} \pi m_p \rho r^3$$

and thus the total mass

$$M = \frac{8}{3} \pi m_p \rho R^3,$$

when  $R$  is the radius of the star. The pressure must now satisfy the differential equation

$$\frac{dp}{dr} = -\frac{16}{3} \pi m_p^2 \rho^2 G r$$

with the boundary condition that the pressure vanishes at the surface, i.e.

$$p(R) = 0.$$

Integrating the differential equation we get for the pressure at the center

$$p = \frac{8\pi}{3} G m_p^2 \rho^2 R^2.$$

Since the electron gas is not quite ultrarelativistic we calculate more accurately than before. The average electronic energy is

$$\begin{aligned} \bar{\epsilon} &= mc^2 \frac{\int_0^{k_F/k_c} dx x^2 \sqrt{x^2 + 1}}{\int_0^{k_F/k_c} dx x^2} \\ &= mc^2 \frac{\int_0^{k_F/k_c} dx x^3 \left[1 + \frac{1}{2} \frac{1}{x^2} + \dots\right]}{\int_0^{k_F/k_c} dx x^2} \\ &= mc^2 \left[ \frac{3}{4} \frac{k_F}{k_c} + \frac{3}{4} \frac{k_c}{k_F} + \dots \right]. \end{aligned}$$

From this we can get for the pressure

$$\begin{aligned} p &= \frac{\hbar c}{12\pi^2} (k_F^4 - k_c^2 k_F^2 + \dots) \\ &= \frac{1}{4} (3\pi^2)^{1/3} \hbar c \rho^{4/3} \left[ 1 - \frac{m^2 c^2}{\hbar^2 (3\pi^2 \rho)^{2/3}} + \dots \right]. \end{aligned}$$

This is the equation of state of the relativistic electron gas.

We require that the pressures obtained from the equation of state and from the hydrodynamic balance conditions are equal in the center, i.e.

$$\frac{8\pi}{3} G m_p \rho^2 R^2 = \frac{1}{4} (3\pi^2)^{1/3} \hbar c \rho^{4/3} \left[ 1 - \frac{m^2 c^2}{\hbar^2 (3\pi^2 \rho)^{2/3}} + \dots \right].$$

When we substitute the electron density (as a function of the mass and radius)

$$\rho = \frac{3M}{8\pi m_p R^3}$$

we get the condition

$$\left( \frac{M}{M_c} \right)^{2/3} = 1 - \left( \frac{R}{R_c} \right)^2 \left( \frac{M_c}{M} \right)^{2/3},$$

where

$$M_c = m_p \left( \frac{9\pi}{512} \right)^{1/2} \left( \frac{\hbar c}{G m_p^2} \right)^{3/2} \approx 0.52 \cdot 10^{57} m_p$$

$$R_c = \frac{\hbar}{m c} \left( \frac{9\pi}{8} \right)^{1/3} \left( \frac{M_c}{m_p} \right)^{1/3} \approx 4700 \text{ km}.$$

For the radius of the star we get

$$R = R_c \left( \frac{M}{M_c} \right)^{1/3} \left[ 1 - \left( \frac{M}{M_c} \right)^{1/3} \right].$$

We see that the white dwarf has the maximum mass  $M = M_c$ . A more careful calculation shows that the mass of a white dwarf cannot exceed *Chandrasekhar's limit*, about  $1.4 M_\odot$ , without collapsing to a neutron star or a black hole.

## Other Fermionic systems

### Nuclear matter

The mass density of heavy nuclei is

$$\rho_m \approx 2.8 \cdot 10^{17} \text{ kg m}^{-3}.$$

When we assume that the proton and neutron densities are equal the Fermi wave vectors of both gases are

$$k_F \approx 1.36 \cdot 10^{15} \text{ m}^{-1}$$

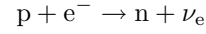
and the Fermi energies

$$\epsilon_F \approx 38 \text{ MeV}.$$

Since  $m_n c^2 = 938 \text{ MeV}$ , the nuclear matter is non relativistic. The attractive nucleon interactions cancel the pressure due to the kinetic energy.

### Neutron star

When the mass of a star exceeds the Chandrasekar limit the Fermi pressure of the electrons is not enough to cancel the gravitational force. The star continues its collapse. The star forms a giant nucleus where most electrons and protons have transformed via the reaction



to neutrons. The radius of the star is

$$R \approx 10 \text{ km},$$

the nucleon count

$$N_N \approx 10^{57}$$

and the mass density

$$\rho_m \approx 10^{18} \text{ kg m}^{-3}.$$

The pressure acting against the gravitation is mostly due to the pressure of the Fermi gas and to the strong, at short distances very repulsive nuclear forces.

### Quark matter

When nuclear matter is compressed 2–10 times denser than in atomic nuclei the nucleons start to "overlap" and their constituent quarks form a quark plasma.

### Liquid $^3\text{He}$

The nucleus is p+p+n and the nuclear spin  $\frac{1}{2}$ . At low temperatures the nuclear spin determines the statistics, i.e.  $^3\text{He}$  atoms are Fermions. The Fermi temperature corresponding to the normal density is

$$T_F = \frac{\epsilon_F}{k_B} \approx 5 \text{ K}.$$

Since the mutual interactions between  $^3\text{He}$  atoms are considerable the  $^3\text{He}$  matter forms an interacting *Fermi liquid*. The  $^3\text{He}$  liquid has two super phases (A and B). These are in balance with the normal phase at the critical point

$$T_c \approx 2.7 \text{ mK} < \frac{T_F}{1000}.$$