

Foundations of thermodynamics

Fundamental thermodynamical concepts

System is the macrophysical entity under consideration.

Surrounding is the world outside of the system.

Open system can exchange matter and heat with the surrounding.

Closed system can exchange heat with the surrounding while keeping the number of particles constant.

Isolated system can exchange neither matter nor heat with the surrounding.

Thermodynamical equilibrium

- No macroscopical changes.
- Uniquely described by external variables of state.
- System forgets its past; no hysteresis.
- In *global equilibrium* all parts of the system are in the same state.

Nonequilibrium

- For example, isolated systems each in an equilibrium state.
- In a *local thermodynamical equilibrium* semimicroscopical regions are in an equilibrium, neighbour regions in different equilibria \Rightarrow particles, heat ... will flow.
- From stronger nonequilibria the system usually *relaxes* to a local equilibrium.

Degree of freedom is the number of quantities needed for the exact description of the microscopic state (\propto number of particles).

State variables are parameters characterizing the macroscopic state.

Extensive variable is proportional to the quantity of the substance; e.g. volume V , particle number N , internal energy U , entropy S , magnetization $\mathbf{M} = \int d\mathbf{r} \mathbf{m}$, where \mathbf{m} is magnetic moment/volume.

Intensive variable is independent on the quantity of the substance and can be determined for every semimicroscopical volume element ΔV ; e.g. temperature T , pressure p , chemical potential μ , magnetic field \mathbf{H} , ratios of extensive variables like $\rho = N/V$, $s = S/N$, ...

Conjugated variables A and B appear in pairs in expressions for the differential of the energy, i.e. in forms $\pm A dB$ or $\pm B dA$; the one is always extensive and the other intensive.

Process is a change in the state.

Reversible process advances via states infinitesimally close to equilibrium, *quasistatically*. The direction of a reversible process can be reversed by infinitesimal changes of external variables.

Isothermic process : T constant.

Isobaric process : p constant.

Isochoric process : V constant.

Isentropic or adiabatic process: S constant.

Irreversible process is a sudden or spontaneous change during which the system is far from equilibria. In the intermediate steps global state variables (p , T , ...) are not usually defined.

Cyclic process consists of cycles which take the system every time to its initial state.

State variables and exact differentials

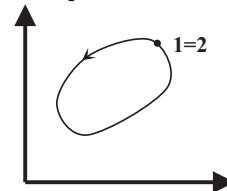
Let us suppose that, for example, T , V ja N tell uniquely the state of the system. State variables are then their unique functions:

$$\begin{aligned} p &= p(T, V, N) \\ U &= U(T, V, N) \\ S &= S(T, V, N). \end{aligned}$$

In an infinitesimal change state variables transform like

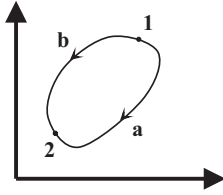
$$\begin{aligned} dp &= \left(\frac{\partial p}{\partial T} \right)_{V,N} dT + \left(\frac{\partial p}{\partial V} \right)_{T,N} dV + \left(\frac{\partial p}{\partial N} \right)_{T,V} dN \\ &\vdots \end{aligned}$$

The differentials of unique functions, dp , dT , dV , ..., are *exact differentials*: their total change evaluated over a closed path vanishes:



$$\oint_{1 \rightarrow 2} dp = \oint_{1 \rightarrow 2} dU = \dots = 0.$$

The total change of an exact differential is independent on the path of integration.



$$\int_a dU - \int_b dU = 0,$$

so

$$U(2) = U(1) + \int_1^2 dU.$$

Let us denote by $\mathbf{d}F$ a differential which is not necessarily exact. The differential

$$\mathbf{d}F = F_1(x, y) dx + F_2(x, y) dy$$

is exact if

$$\frac{\partial F_1}{\partial y} = \frac{\partial F_2}{\partial x}.$$

Then $\exists F(x, y)$ so that $F_1(x, y) = \frac{\partial F(x, y)}{\partial x}$ and $F_2(x, y) = \frac{\partial F(x, y)}{\partial y}$ and

$$\int_1^2 \mathbf{d}F = F(2) - F(1)$$

is independent on the path. We say that $\mathbf{d}F = dF$ is *integrable*.

If $\mathbf{d}F = F_1 dx + F_2 dy$ is not exact, there exists an *integrating factor* $\lambda(x, y)$ so that in the neighbourhood of the point (x, y)

$$\lambda \mathbf{d}F = \lambda F_1 dx + \lambda F_2 dy = \mathbf{d}f$$

is an exact differential.

Legendre transformations can be used to make changes in the set of the independent state variables. For example, let us look at the function $f(x, y)$ of two variables. We denote

$$z = f_y = \frac{\partial f(x, y)}{\partial y}$$

and define the function

$$g = f - y f_y = f - y z.$$

Now

$$\begin{aligned} dg &= df - y dz - z dy = f_x dx + f_y dy - y dz - z dy \\ &= f_x dx - y dz. \end{aligned}$$

Thus we can take x and z as independent variables of the function g , i.e. $g = g(x, z)$. Obviously

$$y = -\frac{\partial g(x, z)}{\partial z}.$$

Corresponding to the Legendre transformation $f \rightarrow g$ there is the inverse transformation $g \rightarrow f$

$$f = g - z g_z = g + y z.$$

Often needed identities

Let $F = F(x, y)$, $x = x(y, z)$, $y = y(x, z)$ and $z = z(x, y)$. Then

$$\begin{aligned} \left(\frac{\partial F}{\partial x} \right)_z &= \left(\frac{\partial F}{\partial x} \right)_y + \left(\frac{\partial F}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z \\ -1 &= \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y \\ \left(\frac{\partial x}{\partial y} \right)_z &= \frac{\left(\frac{\partial F}{\partial y} \right)_z}{\left(\frac{\partial F}{\partial x} \right)_z}. \end{aligned}$$

Equations of state

State variables of an *equilibrium* system are related by a state equation which, in most cases, is a relation between thermal variables (T or S) and mechanical variables.

Examples:

Classical ideal gas

$$\begin{aligned} pV &= N k_B T \\ N &= \text{number of molecules} \\ k_B &= 1.3807 \cdot 10^{-23} \text{ J/K} = \text{Boltzmann constant.} \end{aligned}$$

Chemists use often the form

$$\begin{aligned} pV &= nRT \\ n &= N/N_0 = \text{number of moles} \\ R &= k_B N_0 = 8.315 \text{ J/K mol} \\ &= \text{gas constant} \\ N_0 &= 6.0221 \cdot 10^{23} = \text{Avogadro's number.} \end{aligned}$$

If the gas is composed of m different species of molecules the equation of state is still

$$pV = N k_B T,$$

where now

$$N = \sum_{i=1}^m N_i$$

and

$$p = \sum_i p_i.$$

Here

$$p_i = N_i k_B T / V$$

is the *partial pressure* of the i :th gas.

Virial expansion of real gases

$$p = k_B T [\rho + \rho^2 B_2(T) + \rho^3 B_3(T) + \dots],$$

where

$$\rho = N/V = \text{particle density}$$

and B_n is the n :th *virial coefficient*.

Van der Waals equation

The molecules of real gases interact

- repulsively at short distances; every particle needs at least the volume $b \Rightarrow V \gtrsim Nb$.
- attractively at large distances due to the induced dipole momenta. The pressure decreases when two particles are separated by the attraction distance. The probability of this is $\propto (N/V)^2$.

We improve the ideal gas state equation

$$p'V' = Nk_B T$$

so that

$$\begin{aligned} V' &= V - Nb \\ p &= p' - ap^2 = \text{true pressure.} \end{aligned}$$

then

$$(p + ap^2)(V - Nb) = Nk_B T.$$

Solid substances

The thermal expansion coefficient

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N}$$

and the isothermal *compressibility*

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N}$$

of solid materials are very small, so the Taylor series

$$V = V_0(1 + \alpha_p T - \kappa_T p)$$

is a good approximation.

Typically

$$\begin{aligned} \kappa_T &\approx 10^{-10}/\text{Pa} \\ \alpha_p &\approx 10^{-4}/\text{K}. \end{aligned}$$

Stretched wire

Tension $[\text{N/m}^2]$

$$\sigma = E(t)(L - L_0)/L_0,$$

where L_0 is the length of the wire when $\sigma = 0$ and $E(t)$ is the temperature dependent elasticity coefficient.

Surface tension

$$\begin{aligned} \sigma &= \sigma_0 \left(1 - \frac{t}{t'} \right)^n \\ t &= \text{temperature } ^\circ\text{C} \\ t' \text{ and } n &= \text{experimental constants,} \\ &1 \lesssim n \lesssim 2 \\ \sigma_0 &= \text{surface tension when } t = 0^\circ\text{C}. \end{aligned}$$

Electric polarization

When a piece of material is in an external electric field \mathbf{E} , we define

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P},$$

where

$$\begin{aligned} \mathbf{P} &= \text{electric polarization} \\ &= \text{atomic total dipole moment/volume} \\ \mathbf{D} &= \text{electric flux density} \\ \epsilon_0 &= 8.8542 \cdot 10^{-12} \text{ As/Vm} \\ &= \text{vacuum permeability.} \end{aligned}$$

In homogenous dielectric material one has

$$\mathbf{P} = \left(a + \frac{b}{T} \right) \mathbf{E},$$

where a and b are almost constant and $a, b \geq 0$.

Curie's law

When a piece of paramagnetic material is in magnetic field \mathbf{H} we write

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{m}),$$

where

$$\begin{aligned} \mathbf{m} &= \text{magnetic polarization} \\ &= \text{atomic total magnetic moment/volume} \\ \mathbf{B} &= \text{magnetic flux density} \\ \mu_0 &= 4\pi \cdot 10^{-7} \text{ Vs/Am} = \text{vacuum permeability.} \end{aligned}$$

Polarization obeys roughly *Curie's law*

$$\mathbf{m} = \frac{\rho C}{T} \mathbf{H},$$

where ρ is the number density of paramagnetic atoms and C an experimental constant related to the individual atom.

Note Use as a thermometer: measure the quantity m/H .

0th law

If each of two bodies is separately in thermal equilibrium with a third body then they are also in thermal equilibrium with each other \Rightarrow there exists a property called *temperature* and *thermometer* which can be used to measure it.

Work

Work is exchange of such "noble" energy that can be completely transformed to some other noble form of energy; e.g. mechanical and electromagnetic energy. Sign convention: work ΔW is the work done by the system to its surrounding.

Example pVT system

$$\Delta W = p \Delta V.$$

Note dW is *not* an exact differential. Instead

$$\frac{1}{p}dW = dV$$

is exact, i.e. $1/p$ is the integrating factor for work.

Example

$$dW = p dV - \sigma A dL - \mathbf{E} \cdot d\mathbf{P} - \mathbf{H} \cdot d\mathbf{M}.$$

In general

$$dW = \sum_i f_i dX_i = \mathbf{f} \cdot d\mathbf{X},$$

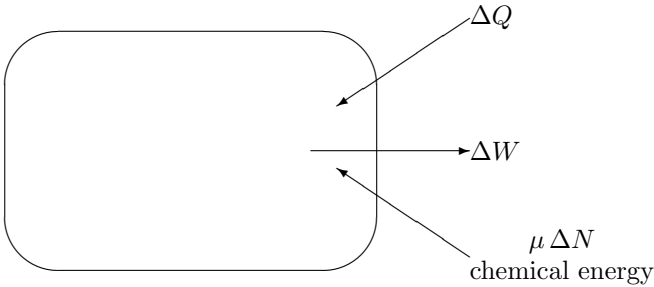
where f_i is a component of a *generalized force* and X_i a component of a *generalized displacement*.

1st law

In addition to work a system can exchange *thermal energy*, i.e. *heat* with its surroundings. Thermal energy is related to the energy of the thermal stochastic motion of microscopic particles.

The total energy of a body is called *internal energy*.

Sign conventions:

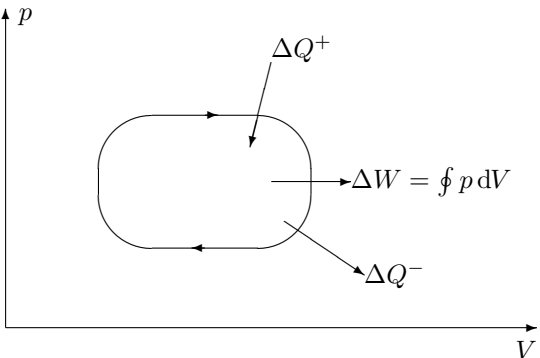


Due to the energy conservation law the change of the internal energy satisfies

$$dU = dQ - \mathbf{f} \cdot d\mathbf{X} + \sum_i \mu_i dN_i.$$

U is a state variable, i.e. dU is exact.

In a cyclic process $\oint dU = 0$, so $\Delta W = \Delta Q$ (no change in chemical energy). In a pVT -system



The total change of heat is

$$\Delta Q = \Delta Q^+ + \Delta Q^-,$$

where ΔQ^+ is the heat taken by the system and ΔQ^- the heat released by the system.

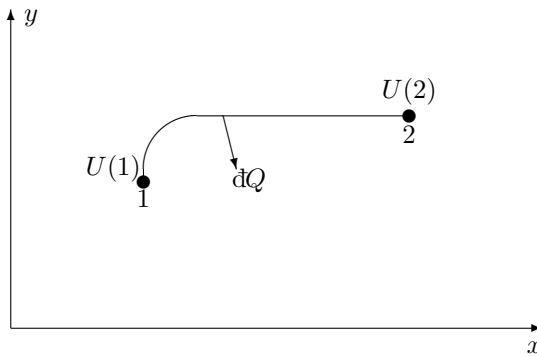
The *efficiency* η is

$$\eta = \frac{\Delta W}{\Delta Q^+} = \frac{\Delta Q^+ + \Delta Q^-}{\Delta Q^+} = 1 - \frac{|\Delta Q^-|}{|\Delta Q^+|}.$$

2nd law

- Heat cannot be transferred from a cooler heat reservoir to a warmer reservoir without any other consequences.
- In a cyclic process it is not possible to convert all heat taken from the hotter heat reservoir to work.
- It is not possible to reverse the evolution of a system towards thermodynamical equilibrium without converting work to heat.
- The change of the total entropy of the system and its surroundings is positive and can be zero only in reversible processes.
- Of all the engines working between the temperatures T_1 and T_2 the Carnot engine has the highest efficiency.

We consider the infinitesimal process



Now

$$dQ = dU + dW = dU + \mathbf{f} \cdot d\mathbf{X},$$

so there exists an integrating factor $1/T$ so that

$$\frac{1}{T}dQ = dS$$

is exact. The state variable S is *entropy* and T turns out to be the so called *absolute* temperature.

The second law (d) can now be written as

$$\frac{dS_{\text{tot}}}{dt} \geq 0.$$

For arbitrary processes we have

$$dS \geq \frac{1}{T}dQ,$$

where the equality holds only for reversible processes.
For reversible processes the first law can be rewritten as

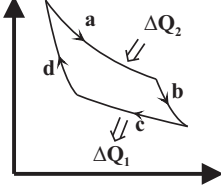
$$dU = dQ - dW + \mu dN = T dS - p dV + \mu dN.$$

Carnot's cycle

The Carnot cycle \mathcal{C} consists of reversible processes

- | | | | |
|----|------------|-----------------------|------------------|
| a) | isothermic | T_2 | $\Delta Q_2 > 0$ |
| b) | adiabatic | $T_2 \rightarrow T_1$ | $\Delta Q = 0$ |
| c) | isothermic | T_1 | $\Delta Q_1 > 0$ |
| d) | adiabatic | $T_1 \rightarrow T_2$ | $\Delta Q = 0$ |

Now $\Delta U = 0$, so $\Delta W = \Delta Q_2 - \Delta Q_1$.



We define the efficiency as

$$\eta = \frac{\Delta W}{\Delta Q_2} = 1 - \frac{\Delta Q_1}{\Delta Q_2}.$$

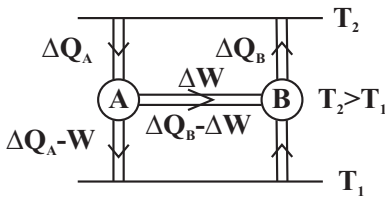
Because the processes are reversible the cycle \mathcal{C} can be reversed and \mathcal{C} works as a heat pump.

Let us consider two Carnot cycles \mathcal{A} and \mathcal{B} , for which

$$\Delta W_{\mathcal{A}} = \Delta W_{\mathcal{B}} = \Delta W.$$

\mathcal{A} is an engine and \mathcal{B} a heat pump. The efficiencies are correspondingly

$$\eta_{\mathcal{A}} = \frac{\Delta W}{\Delta Q_{\mathcal{A}}} \text{ and } \eta_{\mathcal{B}} = \frac{\Delta W}{\Delta Q_{\mathcal{B}}}.$$



Let us suppose that

$$\eta_{\mathcal{A}} > \eta_{\mathcal{B}},$$

so that $\Delta Q_{\mathcal{B}} > \Delta Q_{\mathcal{A}}$ or $\Delta Q_{\mathcal{B}} - \Delta Q_{\mathcal{A}} > 0$. The heat would transfer from the cooler reservoir to the warmer one without any other changes, which is in contradiction with the second law (form a). So we must have

$$\eta_{\mathcal{A}} \leq \eta_{\mathcal{B}}.$$

Similarly one can show that

$$\eta_{\mathcal{B}} \leq \eta_{\mathcal{A}},$$

so that $\eta_{\mathcal{A}} = \eta_{\mathcal{B}}$, i.e. all Carnot engines have the same efficiency.

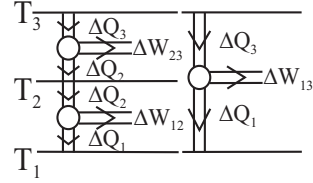
Note The efficiency does not depend on the realization of the cycle (e.g. the working substance) \Rightarrow The efficiency depends only on the temperatures of the heat reservoirs. Similarly, one can show that the Carnot engine has the highest efficiency among all engines (also irreversible) working between given temperatures.

Let us consider Carnot's cycle between temperatures T_3 and T_1 . Now

$$\eta = 1 - f(T_3, T_1),$$

where

$$f(T_3, T_1) = \frac{\Delta Q_1}{\Delta Q_3}.$$



Here

$$f(T_3, T_2) = \frac{\Delta Q_2}{\Delta Q_3}$$

$$f(T_2, T_1) = \frac{\Delta Q_1}{\Delta Q_2}$$

$$f(T_3, T_1) = \frac{\Delta Q_1}{\Delta Q_3}$$

so

$$f(T_3, T_1) = f(T_3, T_2)f(T_2, T_1).$$

The simplest solution is

$$f(T_2, T_1) = \frac{T_1}{T_2}.$$

We define the *absolute temperature* so that

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

The Carnot cycle satisfies

$$\oint \frac{dQ}{T} = 0,$$

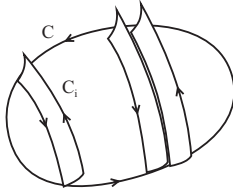
since

$$\int_a \frac{dQ}{T} = \frac{\Delta Q_2}{T_2}$$

and

$$\int_c \frac{dQ}{T} = -\frac{\Delta Q_1}{T_1} = -\frac{\Delta Q_2}{T_2}.$$

This is valid also for an arbitrary reversible cycle



3rd law

Nernst's law:

$$\lim_{T \rightarrow 0} S = 0.$$

A less strong form can be stated as:

When the maximum heat occurring in the process from a state a to a state b approaches zero then also the entropy change $\Delta S_{a \rightarrow b} \rightarrow 0$.

Note There are systems whose entropy at low temperatures is larger than true equilibria would allow.

because

$$\oint_C \frac{dQ}{T} = \sum_i \oint_{C_i} \frac{dQ}{T} = 0.$$

So

$$dS = \frac{dQ}{T}$$

is exact and the *entropy* S is a state variable.

Because the Carnot cycle has the highest efficiency a cycle containing irreversible processes satisfies

$$\eta_{\text{irr}} = 1 - \frac{\Delta Q_1}{\Delta Q_2} < \eta_{\text{Carnot}} = 1 - \frac{T_1}{T_2}$$

or

$$\frac{\Delta Q_2}{T_2} - \frac{\Delta Q_1}{T_1} < 0.$$

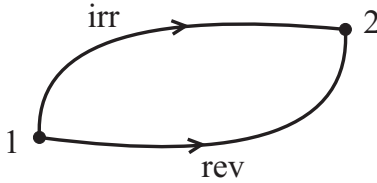
Thus for an arbitrary cycle we have

$$\oint \frac{dQ}{T} \leq 0, \quad (*)$$

where the equality holds only for reversible processes.

For an arbitrary process $1 \rightarrow 2$ the change of the entropy can be obtained from the formula

$$\Delta S = \int_{\text{rev}} dS = \int_{\text{rev}} \frac{dQ}{T}.$$



According to the formula (*) we have

$$\int_{\text{irr}} \frac{dQ}{T} - \int_{\text{rev}} \frac{dQ}{T} < 0,$$

or

$$\Delta S > \int_{\text{irr}} \frac{dQ}{T}.$$

This is usually written as

$$dS \geq \frac{dQ}{T}$$

and the equality is valid only for reversible processes.

In an isolated system we have

$$\Delta S \geq 0.$$

Thermodynamic potentials

Fundamental equation

According to the first law

$$dU = T dS - p dV + \mu dN \quad (*)$$

S , V and N are the natural variables of the internal energy U , i.e.

$$U = U(S, V, N).$$

Furthermore, from the law (*) one can read the relations

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_{V,N} &= T \\ \left(\frac{\partial U}{\partial V}\right)_{S,N} &= -p \\ \left(\frac{\partial U}{\partial N}\right)_{S,V} &= \mu. \end{aligned}$$

Now U , S , V and N are extensive so we have

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \quad \forall \lambda. \quad (***)$$

Let $S \rightarrow S + \epsilon S$, $V \rightarrow V + \epsilon V$ and $N \rightarrow N + \epsilon N$, when ϵ is infinitesimal. Then

$$U(S + \epsilon S, V + \epsilon V, N + \epsilon N) = U(S, V, N) + \left(\frac{\partial U}{\partial S}\right)_{V,N} \epsilon S + \left(\frac{\partial U}{\partial V}\right)_{S,N} \epsilon V + \left(\frac{\partial U}{\partial N}\right)_{S,V} \epsilon N.$$

On the other hand, according to the equation (***) we have

$$U(S + \epsilon S, V + \epsilon V, N + \epsilon N) = U(S, V, N) + \epsilon U(S, V, N).$$

We end up with the *Euler equation for homogenous functions*

$$U = S \left(\frac{\partial U}{\partial S}\right)_{V,N} + V \left(\frac{\partial U}{\partial V}\right)_{S,N} + N \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

Substituting the partial derivatives (**) this takes the form

$$U = TS - pV + \mu N$$

or

$$S = \frac{1}{T}(U + pV - \mu N).$$

This is called the *fundamental equation*.

Internal energy and Maxwell relations

Because

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

and

$$p = - \left(\frac{\partial U}{\partial V}\right)_{S,N},$$

so

$$\frac{\partial T}{\partial V} = \frac{\partial}{\partial V} \frac{\partial U}{\partial S} = \frac{\partial}{\partial S} \frac{\partial U}{\partial V} = - \frac{\partial p}{\partial S}.$$

Similar relations can be derived also for other partial derivatives of U and we get so called *Maxwell's relations*

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_{S,N} &= - \left(\frac{\partial p}{\partial S}\right)_{V,N} \\ \left(\frac{\partial T}{\partial N}\right)_{S,V} &= \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \\ \left(\frac{\partial p}{\partial N}\right)_{S,V} &= - \left(\frac{\partial \mu}{\partial V}\right)_{S,N}. \end{aligned}$$

In an irreversible process

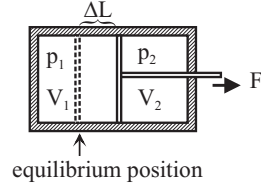
$$T \Delta S > \Delta Q = \Delta U + \Delta W,$$

so

$$\Delta U < T \Delta S - p \Delta V + \mu \Delta N.$$

If S , V and N stay constant in the process then the internal energy decreases. Thus we can deduce that *In an equilibrium with given S , V and N the internal energy is at the minimum.*

We consider a reversible process in an isolated system



We partition ΔW into the components

$$\begin{aligned} \int p dV &= \left[\begin{array}{l} \text{work due to the} \\ \text{change of the} \\ \text{volume} \end{array} \right] \\ \Delta W_{\text{free}} &= \left[\begin{array}{l} \text{work done by the} \\ \text{gas against the} \\ \text{force } \mathbf{F} \end{array} \right]. \end{aligned}$$

Now

$$\begin{aligned} \Delta W_{\text{free}} &= \Delta W_1 + \Delta W_2 = p_1 \Delta V_1 + p_2 \Delta V_2 \\ &= (p_1 - p_2) \Delta V_1 = (p_1 - p_2) A \Delta L \\ &= -F \Delta L. \end{aligned}$$

According to the first law we have

$$\begin{aligned} \Delta U &= \Delta Q - \Delta W = \Delta Q - \int p dV - \Delta W_{\text{free}} \\ &= \Delta Q - \Delta W_{\text{free}}. \end{aligned}$$

Because now $\Delta Q = 0$, we have

$$\Delta U = -\Delta W_{\text{free}} = F \Delta L,$$

i.e. when the variables S , V and N are kept constant the change of the internal energy is completely exchangeable with the work. ΔU is then called *free energy* and U *thermodynamic potential*.

Note If there are irreversible processes in an isolated system (V and N constants) then

$$\Delta W_{\text{free}} \leq -\Delta U.$$

Enthalpy

Using the Legendre transform

$$U \rightarrow H = U - V \left(\frac{\partial U}{\partial V} \right)_{S,N} = U + pV$$

We move from the variables (S, V, N) to the variables (S, p, N) . The quantity

$$H = U + pV$$

is called *enthalpy*.

Now

$$\begin{aligned} dH &= dU + p dV + V dp \\ &= T dS - p dV + \mu dN + p dV + V dp \end{aligned}$$

or

$$dH = T dS + V dp + \mu dN.$$

From this we can read the partial derivatives

$$\begin{aligned} T &= \left(\frac{\partial H}{\partial S} \right)_{p,N} \\ V &= \left(\frac{\partial H}{\partial p} \right)_{S,N} \\ \mu &= \left(\frac{\partial H}{\partial N} \right)_{S,V}. \end{aligned}$$

Corresponding Maxwell relations are

$$\begin{aligned} \left(\frac{\partial T}{\partial p} \right)_{S,N} &= \left(\frac{\partial V}{\partial S} \right)_{p,N} \\ \left(\frac{\partial T}{\partial N} \right)_{S,p} &= \left(\frac{\partial \mu}{\partial S} \right)_{p,N} \\ \left(\frac{\partial V}{\partial N} \right)_{S,p} &= \left(\frac{\partial \mu}{\partial p} \right)_{S,N}. \end{aligned}$$

In an irreversible process one has

$$\Delta Q = \Delta U + \Delta W - \mu \Delta N < T \Delta S.$$

Now $\Delta U = \Delta(H - pV)$, so that

$$\Delta H < T \Delta S + V \Delta p + \mu \Delta N.$$

We see that

In a process where S , p and N are constant spontaneous changes lead to the minimum of H , i.e. in an equilibrium of a (S, p, N) -system the enthalpy is at the minimum.

The enthalpy is a suitable potential for an isolated system in a *pressure bath* (p is constant).

Let us look at an isolated system in a pressure bath. Now

$$dH = dU + d(pV)$$

and

$$dU = dQ - dW + \mu dN.$$

Again we partition the work into two components:

$$dW = p dV + dW_{\text{free}}.$$

Now

$$dH = dQ + V dp - dW_{\text{free}} + \mu dN$$

and for a finite process

$$\Delta H \leq \int T dS + \int V dp - \Delta W_{\text{free}} + \int \mu dN.$$

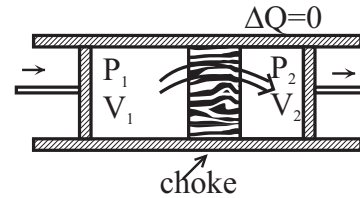
When (S, p, N) is constant one has

$$\Delta H \leq -\Delta W_{\text{free}}$$

i.e. ΔW_{free} is the minimum work required for the change ΔH .

Note Another name of enthalpy is *heat function* (in constant pressure).

Joule-Thomson phenomenon



p_1 and p_2 are temporal constants, $p_1 > p_2$ and the process is irreversible. When an infinitesimal amount of matter passes through the choke the work done by the system is

$$dW = p_2 dV_2 + p_1 dV_1.$$

	V_1	V_2
Initial state	V_{init}	0
Final state	0	V_{final}

The work done by the system is

$$\Delta W = \int dW = p_2 V_{\text{final}} - p_1 V_{\text{init}}.$$

According to the first law we have

$$\Delta U = U_{\text{final}} - U_{\text{init}} = \Delta Q - \Delta W = -\Delta W,$$

so that

$$U_{\text{init}} + p_1 V_{\text{init}} = U_{\text{final}} + p_2 V_{\text{final}}.$$

Thus in this process the enthalpy $H = U + pV$ is constant, i.e. the process is *isenthalpic*,

$$\Delta H = H_{\text{final}} - H_{\text{init}} = 0.$$

We consider now a *reversible* isenthalpic (and $dN = 0$) process init \rightarrow final. Here

$$dH = T dS + V dp = 0,$$

so

$$dS = -\frac{V}{T} dp. \quad (*) \text{ or}$$

Now $T = T(S, p)$, so that

$$dT = \left(\frac{\partial T}{\partial S}\right)_p dS + \left(\frac{\partial T}{\partial p}\right)_S dp.$$

On the other hand

$$\left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p},$$

where C_p is the isobaric heat capacity (see thermodynamical responses).

Using the Maxwell relation

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

and the partial derivative relation

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

we can write

$$dT = \frac{T}{C_p} dS + \frac{T}{C_p} \left(\frac{\partial V}{\partial T}\right)_p dp.$$

Substituting into this the differential dS in constant enthalpy (*) we get so called *Joule-Thomson coefficients*

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T}{C_p} \left[\left(\frac{\partial V}{\partial T}\right)_p - \frac{V}{T} \right].$$

Defining the *heat expansion coefficient* α_p so that

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p,$$

we can rewrite the Joule-Thomson coefficient as

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p} (T\alpha_p - 1).$$

We see that when the pressure decreases the gas

- cools down, if $T\alpha_p > 1$.
- warms up, if $T\alpha_p < 1$.

For ideal gases $\left(\frac{\partial T}{\partial p}\right)_H = 0$ holds. For real gases $\left(\frac{\partial T}{\partial p}\right)_H$ is below the *inversion temperature* positive, so the gas cools down.

Free energy

The Legendre transform

$$U \rightarrow F = U - S \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

$$F = U - TS$$

defines the (*Helmholtz*) *free energy*.

Now

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

so the natural variables of F are T , V and N . We can read the partial derivatives

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

From these we obtain the Maxwell relations

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{T,N} &= \left(\frac{\partial p}{\partial T}\right)_{V,N} \\ \left(\frac{\partial S}{\partial N}\right)_{T,V} &= -\left(\frac{\partial \mu}{\partial T}\right)_{V,N} \\ \left(\frac{\partial p}{\partial N}\right)_{T,V} &= -\left(\frac{\partial \mu}{\partial V}\right)_{T,N}. \end{aligned}$$

In an irreversible change we have

$$\Delta F < -S \Delta T - p \Delta V + \mu \Delta N,$$

i.e. when the variables T , V and N are constant the system drifts to the minimum of the free energy.

Correspondingly

$$\Delta W_{\text{free}} \leq -\Delta F,$$

when (T, V, N) is constant.

Free energy is suitable for systems where the exchange of heat is allowed.

Gibbs' function

The Legendre transformation

$$U \rightarrow G = U - S \left(\frac{\partial U}{\partial S}\right)_{V,N} - V \left(\frac{\partial U}{\partial V}\right)_{S,N}$$

defines the *Gibbs function* or the *Gibbs free energy*

$$G = U - TS + pV.$$

Its differential is

$$dG = -S dT + V dp + \mu dN,$$

so the natural variables are T , p and N . For the partial derivatives we can read the expressions

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{p,N} \\ V &= \left(\frac{\partial G}{\partial p}\right)_{T,N} \\ \mu &= \left(\frac{\partial G}{\partial N}\right)_{T,p}. \end{aligned}$$

From these we obtain the Maxwell relations

$$\begin{aligned} \left(\frac{\partial S}{\partial p}\right)_{T,N} &= -\left(\frac{\partial V}{\partial T}\right)_{p,N} \\ \left(\frac{\partial S}{\partial N}\right)_{T,p} &= -\left(\frac{\partial \mu}{\partial T}\right)_{p,N} \\ \left(\frac{\partial V}{\partial N}\right)_{T,p} &= \left(\frac{\partial \mu}{\partial p}\right)_{T,N}. \end{aligned}$$

In an irreversible process

$$\Delta G < -S \Delta T + V \Delta p + \mu \Delta N,$$

holds, i.e. when the variables T , p and N stay constant the system drifts to the minimum of G .

Correspondingly

$$\Delta W_{\text{free}} \leq -\Delta G,$$

when (T, p, N) is constant.

The Gibbs function is suitable for systems which are allowed to exchange mechanical energy and heat.

Grand potential

The Legendre transform

$$U \rightarrow \Omega = U - S \left(\frac{\partial U}{\partial S}\right)_{V,N} - N \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

defines the *grand potential*

$$\Omega = U - TS - \mu N.$$

Its differential is

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

so the natural variables are T , p and μ .

The partial derivatives are now

$$\begin{aligned} S &= -\left(\frac{\partial \Omega}{\partial T}\right)_{p,\mu} \\ p &= -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \\ N &= -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}. \end{aligned}$$

We get the Maxwell relations

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{T,\mu} &= \left(\frac{\partial p}{\partial T}\right)_{V,\mu} \\ \left(\frac{\partial S}{\partial \mu}\right)_{T,V} &= \left(\frac{\partial N}{\partial T}\right)_{V,\mu} \\ \left(\frac{\partial p}{\partial \mu}\right)_{T,V} &= \left(\frac{\partial N}{\partial V}\right)_{T,\mu}. \end{aligned}$$

In an irreversible process

$$\Delta \Omega < -S \Delta T - p \Delta V - N \Delta \mu,$$

holds, i.e. when the variables T , V and μ are kept constant the system moves to the minimum of Ω .

Correspondingly

$$\Delta W_{\text{free}} \leq -\Delta \Omega,$$

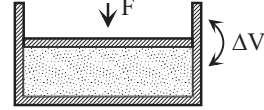
when (T, V, μ) is constant.

The grand potential is suitable for systems that are allowed to exchange heat and particles.

Bath

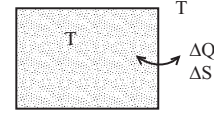
A *bath* is an equilibrium system, much larger than the system under consideration, which can exchange given extensive property with our system.

Pressure bath

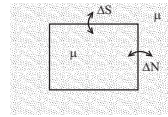


The exchanged property is the volume or a corresponding generalized displacement; for example magnetization in a magnetic field.

Heat bath



Particle bath



Baths can also be combined; for example a suitable potential for a pressure and heat bath is the Gibbs function G .

Thermodynamic responses

1) Volume heat expansion coefficient

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

or

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_{p,N},$$

where $\rho = N/V$.

2) Isothermic compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{T,N}$$

3) Adiabatic compressibility

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{S,N} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{S,N}.$$

The velocity of sound depends on the adiabatic compressibility like

$$c_S = \sqrt{\frac{1}{m\rho\kappa_S}},$$

where m the particle mass.

One can show that

$$\kappa_T = \kappa_S + VT \frac{\alpha_p^2}{C_p}.$$

4) Isochoric heat capacity

In a reversible process we have

$$\Delta Q = T \Delta S.$$

The heat capacity C is defined so that

$$C = \frac{\Delta Q}{\Delta T} = T \frac{\Delta S}{\Delta T}.$$

In constant volume we define

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

In constant volume and the number particles being fixed, according to the first law

$$dU = T dS - p dV + \mu dN = T dS,$$

we can write

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

5) Isobaric heat capacity

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{p,N}$$

Because

$$dH = T dS + V dp + \mu dN,$$

one can write

$$C_p = \left(\frac{\partial H}{\partial T} \right)_{p,N}.$$

Now

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

and (a Maxwell relation)

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

so

$$C_p = C_V + T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p.$$

Since

$$\left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T = -1$$

or

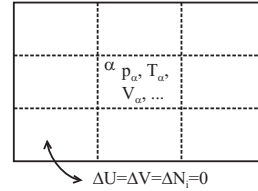
$$\left(\frac{\partial p}{\partial T} \right)_V = - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} = \frac{\alpha_p}{\kappa_T},$$

so

$$C_p = C_V + VT \frac{\alpha_p^2}{\kappa_T}.$$

Thermodynamic equilibrium conditions

We divide the system into fictitious semimicroscopic parts:



Extensive variables satisfy

$$\begin{aligned} S &= \sum_{\alpha} S_{\alpha} \\ V &= \sum_{\alpha} V_{\alpha} \\ U &= \sum_{\alpha} U_{\alpha} \\ N_j &= \sum_{\alpha} N_{j\alpha}. \end{aligned}$$

Since each element is in equilibrium the state variables are defined in each element, e.g.

$$S_{\alpha} = S_{\alpha}(U_{\alpha}, V_{\alpha}, \{N_{j\alpha}\})$$

and

$$\Delta S_{\alpha} = \frac{1}{T_{\alpha}} \Delta U_{\alpha} + \frac{p_{\alpha}}{T_{\alpha}} \Delta V_{\alpha} - \frac{\mu_{j\alpha}}{T_{\alpha}} \Delta N_{j\alpha}.$$

We suppose that the system is composed of two parts: $\alpha \in \{A, B\}$. Then

$$\Delta U_B = -\Delta U_A, \quad \Delta V_B = -\Delta V_A \quad \text{and} \quad \Delta N_{jB} = -\Delta N_{jA}$$

so

$$\begin{aligned}\Delta S &= \sum_{\alpha} \Delta S_{\alpha} \\ &= \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A + \left(\frac{p_A}{T_A} - \frac{p_B}{T_B} \right) \Delta V_A \\ &\quad - \sum_j \left(\frac{\mu_{jA}}{T_A} - \frac{\mu_{jB}}{T_B} \right) \Delta N_{jA}.\end{aligned}$$

In an equilibrium S is at its maximum, so $\Delta S = 0$ and

$$\begin{aligned}T_A &= T_B \\ p_A &= p_B \\ \mu_{jA} &= \mu_{jB}.\end{aligned}$$

This is valid also when the system consists of several phases.

Stability conditions of matter

In a steady equilibrium the entropy has the true maximum so that small variations can only reduce the entropy.

We denote the equilibrium values common for all fictitious parts by the symbols T , p and $\{\mu_j\}$ and the equilibrium values of other variables by the superscript 0 .

We write the entropy S_{α} of the fictitious partial system α close to an equilibrium as the Taylor series

$$\begin{aligned}S_{\alpha}(U_{\alpha}, V_{\alpha}, \{N_{j\alpha}\}) &= \\ &S_{\alpha}^0(U_{\alpha}^0, V_{\alpha}^0, \{N_{j\alpha}^0\}) \\ &+ \left(\frac{\partial S}{\partial U_{\alpha}} \right)_{V,N}^0 \Delta U_{\alpha} + \left(\frac{\partial S}{\partial V_{\alpha}} \right)_{U,N}^0 \Delta V_{\alpha} \\ &+ \sum_j \left(\frac{\partial S}{\partial N_{j\alpha}} \right)_{U,V}^0 \Delta N_{j\alpha} \\ &+ \frac{1}{2} \left\{ \Delta \left(\frac{\partial S}{\partial U_{\alpha}} \right)_{V,N}^0 \Delta U_{\alpha} + \Delta \left(\frac{\partial S}{\partial V_{\alpha}} \right)_{U,N}^0 \Delta V_{\alpha} \right. \\ &\quad \left. + \sum_j \Delta \left(\frac{\partial S}{\partial N_{j\alpha}} \right)_{U,V}^0 \Delta N_{j\alpha} \right\} \\ &+ \dots\end{aligned}$$

Here $\Delta U_{\alpha} = U_{\alpha} - U_{\alpha}^0$ and correspondingly for other quantities. The variations of partial derivatives stand for

$$\begin{aligned}\Delta \left(\frac{\partial S}{\partial U_{\alpha}} \right)_{V,N}^0 &= \\ &\left(\frac{\partial^2 S}{\partial U^2} \right)_{V,N}^0 \Delta U_{\alpha} + \left[\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial U} \right)_{V,N} \right]_{U,N}^0 \Delta V_{\alpha} \\ &+ \sum_j \left[\frac{\partial}{\partial N_j} \left(\frac{\partial S}{\partial U} \right)_{V,N} \right]_{U,V}^0 \Delta N_{j\alpha}\end{aligned}$$

and similarly for other partial derivatives.

In an equilibrium

$$\left(\frac{\partial S}{\partial U} \right)^0 = \left(\frac{\partial S}{\partial V} \right)^0 = \left(\frac{\partial S}{\partial N_j} \right)^0 = 0,$$

so

$$\begin{aligned}\Delta S_{\alpha} &= \\ &\frac{1}{2} \left\{ \Delta \left(\frac{\partial S}{\partial U_{\alpha}} \right)_{V,N}^0 \Delta U_{\alpha} + \Delta \left(\frac{\partial S}{\partial V_{\alpha}} \right)_{U,N}^0 \Delta V_{\alpha} \right. \\ &\quad \left. + \sum_j \Delta \left(\frac{\partial S}{\partial N_{j\alpha}} \right)_{U,V}^0 \Delta N_{j\alpha} \right\}.\end{aligned}$$

This can be rewritten as

$$\begin{aligned}\Delta S_{\alpha} &= \\ &\frac{1}{2} \left\{ \Delta \left(\frac{1}{T_{\alpha}} \right) \Delta U_{\alpha} + \Delta \left(\frac{p_{\alpha}}{T_{\alpha}} \right) \Delta V_{\alpha} \right. \\ &\quad \left. - \sum_j \Delta \left(\frac{\mu_{j\alpha}}{T_{\alpha}} \right) \Delta N_{j\alpha} \right\}.\end{aligned}$$

Using the first law we get

$$\begin{aligned}\Delta S &= \frac{1}{2T} \sum_{\alpha} \left\{ \begin{aligned} &-\Delta T_{\alpha} \Delta S_{\alpha} + \Delta p_{\alpha} \Delta V_{\alpha} \\ &- \sum_j \Delta \mu_{j\alpha} \Delta N_{j\alpha} \end{aligned} \right\}.\end{aligned}$$

This can be further written as

$$\begin{aligned}\Delta S &= -\frac{1}{2T} \sum_{\alpha} \left\{ \begin{aligned} &\frac{C_V}{T} (\Delta T_{\alpha})^2 + \frac{1}{\kappa_T V} [(\Delta V_{\alpha})_{N_{\alpha}}^2] \\ &+ \left(\frac{\partial \mu}{\partial N} \right)_{p,T}^0 (\Delta N_{\alpha})^2 \end{aligned} \right\},\end{aligned}$$

where

$$(\Delta V_{\alpha})_{N_{\alpha}} = \left(\frac{\partial V}{\partial T} \right)_{N,p}^0 \Delta T_{\alpha} + \left(\frac{\partial V}{\partial p} \right)_{N,T}^0 \Delta p_{\alpha}.$$

Since $\Delta S \leq 0$, we must have

$$C_V \geq 0, \quad \kappa_T \geq 0, \quad \frac{\partial \mu}{\partial N} \geq 0.$$

Application of thermodynamics

Classical ideal gas

From the equation of state

$$pV = Nk_B T$$

we obtain the mechanical response functions

$$\begin{aligned}\alpha_p &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N} = \frac{Nk_B}{Vp} = \frac{1}{T} \\ \kappa_T &= -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = \frac{Nk_B T}{Vp^2} = \frac{1}{p}.\end{aligned}$$

Thermal response functions cannot be derived from the equation of state. Empirically we have

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

Here $\frac{1}{2} f k_B$ is the specific heat capacity/molecule and f is the number of degrees of freedom of the molecule.

Atoms/molecule	f	translations	rotations
1	3	3	0
2	5	3	2
poly	6	3	3

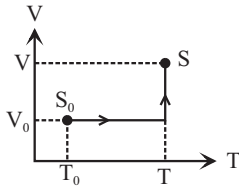
For real gases $f = f(T, p)$.

Entropy

$$\begin{aligned}dS &= \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \\ &= \frac{1}{T} C_V dT + \left(\frac{\partial p}{\partial T} \right)_V dV,\end{aligned}$$

since according to Maxwell relations

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



Integrating we get

$$\begin{aligned}S &= S_0 + \int_{T_0}^T dT \frac{C_V}{T} + \int_{V_0}^V dV \frac{Nk_B}{V} \\ &= S_0 + C_V \ln \frac{T}{T_0} + Nk_B \ln \frac{V}{V_0}\end{aligned}$$

or

$$S = S_0 + Nk_B \ln \left[\left(\frac{T}{T_0} \right)^{f/2} \frac{V}{V_0} \right].$$

Note A contradiction with the third law: $S \rightarrow -\infty$, when $T \rightarrow 0$.

Internal energy

We substitute into the first law

$$dU = T dS - p dV$$

the differential

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV,$$

and get

$$dU = C_V dT + \left[T \left(\frac{\partial S}{\partial V} \right)_T - p \right] dV.$$

According to a Maxwell relations and to the equation of state we have

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

so

$$dU = C_V dT$$

and

$$U = U_0 + C_V (T - T_0) = U_0 + \frac{1}{2} f k_B N (T - T_0).$$

If we choose $U_0 = C_V T_0$, we get for the internal energy

$$U = \frac{1}{2} f k_B N T.$$

Now

$$C_p = C_V + VT \frac{\alpha_p^2}{\kappa_T}$$

or

$$C_p = Nk_B \left(\frac{1}{2} f + 1 \right)$$

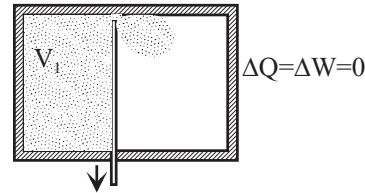
or

$$C_p = \gamma C_V,$$

where γ is the *adiabatic constant*

$$\gamma = C_p / C_V = (f + 2) / f.$$

Free expansion of gas



In the process $V_1 \rightarrow V_2$ and $\Delta Q = \Delta W = 0$, so $\Delta U = 0$. Process is irreversible.

a) Ideal gas

Now

$$U = \frac{1}{2} f k_B N T,$$

so $T_1 = T_2$, because $U_1 = U_2$. The change in the entropy is thus

$$\Delta S = Nk_B \ln \frac{V_2}{V_1}.$$

b) Other material

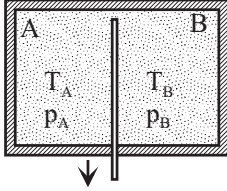
The internal energy (and the number of particle) being constant ($dU = 0$) we obtain from the expression

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

for the *Joule coefficient* $\left(\frac{\partial T}{\partial V} \right)_{U,N}$ the form

$$\begin{aligned} \left(\frac{\partial T}{\partial V} \right)_{U,N} &= - \frac{\left(\frac{\partial U}{\partial V} \right)_T}{\left(\frac{\partial U}{\partial T} \right)_V} \\ &= \frac{1}{C_V} \left(p - T \frac{\alpha_p}{\kappa_T} \right). \end{aligned}$$

Mixing entropy



Suppose that initially $p_A = p_B = p$ and $T_A = T_B = T$. The process is adiabatic so $\Delta Q = 0$.

In a mixture of ideal gases every component satisfies the state equation

$$p_j V = N_j k_B T.$$

The concentration of the component j is

$$x_j = \frac{N_j}{N} = \frac{p_j}{p},$$

where the total pressure p is

$$p = \sum_j p_j.$$

Way 1

Each constituent gas expands in turn into the volume V . Since $p_A = p_B$ and $T_A = T_B$, we have $V_j = V x_j$. The change in the entropy is (see the free expansion of a gas)

$$\Delta S = \sum_j N_j k_B \ln \frac{V}{V_j}$$

or

$$\Delta S_{\text{mix}} = -Nk_B \sum_j x_j \ln x_j.$$

Now $\Delta S_{\text{mix}} \geq 0$, since $0 \leq x_j \leq 1$.

Way 2

For a process taking place in constant pressure and temperature the Gibbs function is the suitable potential:

$$\begin{aligned} G &= U - TS + pV \\ &= \frac{1}{2} f k_B T N - TS + pV = \dots \\ &= Nk_B T [\phi(T) + \ln p] = N\mu(p, T), \end{aligned}$$

where

$$\phi(T) = \frac{\mu^0}{k_B T} - \xi - \left(\frac{f}{2} + 1 \right) \ln T.$$

Before mixing

$$G_{(b)} = \sum_j N_j k_B T [\phi_j(T) + \ln p]$$

and after mixing

$$G_{(a)} = \sum_j N_j k_B T [\phi_j(T) + \ln p_j],$$

so the change in the Gibbs function is

$$\begin{aligned} \Delta G_{(\text{mix})} &= G_{(a)} - G_{(b)} = \sum_j N_j k_B T \ln \frac{p_j}{p} \\ &= \sum_j N_j k_B T \ln x_j. \end{aligned}$$

Because

$$S = - \left(\frac{\partial G}{\partial T} \right)_{P, \{N_j\}},$$

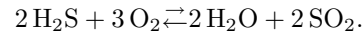
we get for the mixing entropy

$$\Delta S_{\text{mix}} = S_{(a)} - S_{(b)} = - \sum_j N_j k_B \ln x_j.$$

Gibbs' paradox: If $A \equiv B$, i.e. the gases are identical no changes take place in the process. However, according to the former discussion, $\Delta S > 0$. The contradiction can be removed by employing quantum statistics of identical particles.

Chemical reaction

Consider for example the chemical reaction



In general the *chemical reaction formula* is written as

$$0 = \sum_j \nu_j M_j.$$

Here $\nu_j \in \mathcal{I}$ are the *stoichiometric coefficients* and M_j stand for the molecular species.

Example

j	A	B	C	D
M_j	H ₂ S	O ₂	H ₂ O	SO ₂
ν_j	-2	-3	2	2

We define the *degree of reaction* ξ so that

$$dN_j = \nu_j d\xi.$$

When ξ increments by one, one reaction of the reaction formula from left to right takes place.

Convention: When $\xi = 0$ the reaction is as far left as it can be. Then we always have

$$\xi \geq 0.$$

We suppose that p and T are constant in the reaction. Then a suitable potential is the Gibbs function

$$G = U - TS + pV = \sum_j \mu_j N_j.$$

Its differential is

$$dG = \sum_j \mu_j dN_j = d\xi \sum_j \nu_j \mu_j.$$

We define

$$\Delta_r G \equiv \Delta_r \equiv \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_j \nu_j \mu_j.$$

Δ_r is thus the change in the Gibbs function per one reaction.

Since (p, T) is constant G has a minimum at an equilibrium. The equilibrium condition is thus

$$\Delta_r G^{\text{eq}} = \sum_j \nu_j \mu_j^{\text{eq}} = 0.$$

In a nonequilibrium $dG/dt < 0$, so if $\Delta_r > 0$ we must have $d\xi/dt < 0$, i.e. the reaction proceeds to left and vice versa. We assume that the components obey the ideal gas equation of state. Then

$$\mu_j = k_B T [\phi_j(T) + \ln p + \ln x_j],$$

where

$$\phi_j(T) = \frac{\mu_j^0}{k_B T} - \eta_j - (1 + \frac{1}{2} f_j) \ln T.$$

So

$$\Delta_r G = k_B T \sum_j \nu_j \phi_j(T) + k_B T \ln \left(p^{\sum_j \nu_j} \prod x_j^{\nu_j} \right).$$

The equilibrium condition can now be written as

$$\prod x_j^{\nu_j} = p^{-\sum_j \nu_j} K(T),$$

where

$$K(T) = e^{-\sum_j \nu_j \phi_j(T)}$$

is the *equilibrium constant* of the reaction. The equilibrium condition is called the *law of mass action*. The *reaction heat* is the change of heat $\Delta_r Q$ per one reaction to right. A reaction is

- *Endothermic*, if $\Delta_r Q > 0$ i.e. the reaction takes heat.
- *Exothermic*, if $\Delta_r Q < 0$ i.e. the reaction releases heat.

We write $\Delta_r G$ as

$$\Delta_r G = -k_B T \ln K(T) + k_B T \sum_j \nu_j \ln p x_j.$$

Now

$$\begin{aligned} \Delta_r Q &= \Delta U + \Delta W = \Delta U + p \Delta V = \Delta(U + pV) \\ &= \Delta H, \end{aligned}$$

since $\Delta p = 0$.

When the total amount matter is constant

$$dG = -S dT + V dp$$

holds in a reversible process and

$$\begin{aligned} d\left(\frac{G}{T}\right) &= \frac{1}{T} dG - \frac{G}{T^2} dT = -\left(\frac{G}{T^2} + \frac{S}{T}\right) dT + \frac{V}{T} dp \\ &= -\frac{H}{T^2} dT + \frac{V}{T} dp, \end{aligned}$$

because $G = H - TS$. We see that

$$H = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{G}{T} \right) \right]_{p,N}.$$

Now

$$\frac{\partial}{\partial T} \left(\frac{\Delta_r G}{T} \right) = -k_B \frac{d}{dT} \ln K(T),$$

so that

$$\Delta_r H = k_B T^2 \frac{d}{dT} \ln K(T).$$

This expression is known as the *reaction heat*.

Phase equilibrium

In a system consisting of several phases the equilibrium conditions for each pair (A and B) of phases are

$$\begin{aligned} T_A &= T_B = T \\ p_A &= p_B = p \\ \mu_{jA} &= \mu_{jB}, \quad j = 1, \dots, H, \quad (*) \end{aligned}$$

where H is the number of particle species in the system. Let us assume that the number of phases is F , so for each species there are $F - 1$ independent conditions (*). Now $\mu_{i\alpha} = \mu_{i\alpha}(p, T, \{N_{j\alpha}\})$. Because the chemical potential is an intensive quantity it depends only on relative fractions, so

$$\mu_{j\alpha} = \mu_{j\alpha}(p, T, x_{1\alpha}, \dots, x_{H-1,\alpha}),$$

and the conditions (*) take the form

$$\begin{aligned} \mu_{1A}(p, T, x_{1A}, \dots, x_{H-1,A}) &= \\ \mu_{1B}(p, T, x_{1B}, \dots, x_{H-1,B}) &= \\ \vdots &= \\ \mu_{HA}(p, T, x_{1A}, \dots, x_{H-1,A}) &= \\ \mu_{HB}(p, T, x_{1B}, \dots, x_{H-1,B}). & \end{aligned}$$

There are

- $M = (H - 1)F + 2$ variables,
- $Y = H(F - 1)$ equations.

The simultaneous equations can have a solution only if $M \geq Y$ or

$$F \leq H + 2.$$

This condition is known as the *Gibbs phase rule*. For *pure matter* the equilibrium condition

$$\mu_A(p, T) = \mu_B(p, T)$$

defines in the (p, T) -plane a *coexistence curve*. If the phase B is in equilibrium with the phase C we get another curve

$$\mu_B(p, T) = \mu_C(p, T).$$

The phases A , B can C can be simultaneously in equilibrium in a crossing point, so called *triple point*, of these curves.

Phase transitions

In a phase transition the chemical potential

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{p, T}$$

is continuous. Instead

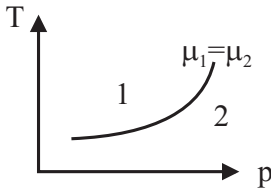
$$S = - \left(\frac{\partial G}{\partial T} \right)_p$$

and

$$V = \left(\frac{\partial G}{\partial p} \right)_T$$

are not necessarily continuous.

A transition is of *first order*, if the first order derivatives (S, V) of G are discontinuous and of *second order*, if the second order derivatives are discontinuous. Otherwise the transition is *continuous*



In a first order transition from a phase 1 to a phase 2

$$\begin{aligned} \Delta S &= - \left(\frac{\partial G}{\partial T} \right)_p^{(2)} + \left(\frac{\partial G}{\partial T} \right)_p^{(1)} \\ \Delta V &= \left(\frac{\partial G}{\partial p} \right)_T^{(2)} - \left(\frac{\partial G}{\partial p} \right)_T^{(1)}. \end{aligned}$$

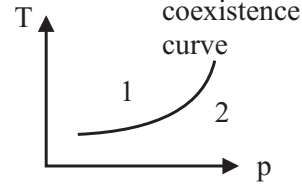
When we cross a coexistence curve p and T stay constant, so

$$\begin{aligned} \Delta Q &= T \Delta S = \Delta U + p \Delta V = \Delta(U + pV) \\ &= \Delta H. \end{aligned}$$

ΔQ is called the *phase transition heat* or the *latent heat*.

Note First order transitions are associated with the heat of phase transitions but not the higher order transitions.

Coexistence



On the coexistence curve

$$G_1(p, T, N) = G_2(p, T, N)$$

and

$$dG = -S dT + V dp$$

when the number of particles N is constant. Along the curve

$$G_1(p + dp, T + dT, N) = G_2(p + dp, T + dT, N),$$

so that

$$-S_1 dT + V_1 dp = -S_2 dT + V_2 dp$$

or on the curve

$$\frac{dp}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V} = \frac{T^{-1} \Delta H}{\Delta V}$$

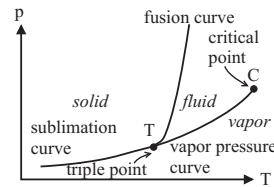
and we end up with the *Clausius-Clapeyron equation*

$$\left(\frac{dp}{dT} \right)_{\text{coex}} = \frac{1}{T} \frac{\Delta H}{\Delta V}.$$

Here $\Delta H = H_2 - H_1$ and $\Delta V = V_2 - V_1$.

Examples

a) Vapor pressure curve



We consider the transition

liquid \rightarrow vapor.

Supposing that we are dealing with ideal gas we have

$$\Delta V = V_v = \frac{N k_B T}{p},$$

since

$$V_{\text{l(liquid)}} \ll V_{\text{v(vapor)}}.$$

Because the vaporization heat (the phase transition heat) ΔH_{lv} is roughly constant on the vapor pressure curve we have

$$\frac{dp}{dT} = \frac{\Delta H_{lv} p}{N k_B T^2}.$$

Integration gives us

$$p = p_0 e^{-\Delta H_{lv}/N k_B T}.$$

b) Fusion curve

Now

$$\Delta V_{ls} = V_{l(\text{liquid})} - V_{s(\text{solid})}$$

can be positive or negative (for example H_2O).

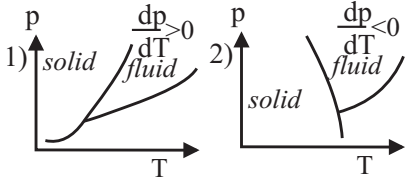
According to the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{ls}}{T \Delta V_{ls}}$$

we have

$$\frac{dp}{dT} > 0, \quad \text{if } \Delta V_{ls} > 0 \quad 1)$$

$$\frac{dp}{dT} < 0, \quad \text{if } \Delta V_{ls} < 0 \quad 2) \quad .$$



We see that when the pressure is increased in constant temperature the system

1) drifts "deeper" into the solid phase,

2) can go from the solid phase to the liquid phase.

c) Sublimation curve

Now

$$dH = T dS + V dp = C_p dT + V(1 - T\alpha_p) dp,$$

since $S = S(p, T)$ and using Maxwell relations and definitions of thermodynamic response functions

$$dS = \left(\frac{\partial S}{\partial p} \right)_T dp + \left(\frac{\partial S}{\partial T} \right)_p dT = - \left(\frac{\partial V}{\partial T} \right)_p dp + \frac{C_p}{T} dT.$$

The vapor pressure is small so $dp \approx 0$, and

$$H_s = H_s^0 + \int_0^T C_p^s dT \quad \text{solid phase}$$

$$H_v = H_v^0 + \int_0^T C_p^v dT \quad \text{vapor (gas)}.$$

Let us suppose that the vapor satisfies the ideal gas state equation. Then

$$\Delta V_{vs} = \frac{N k_B T}{p} - V_s \approx \frac{N k_B T}{p},$$

so

$$\frac{dp}{dT} = \frac{\Delta H_{vs}}{T \Delta V_{vs}} \approx \frac{p \Delta H_{vs}}{N k_B T^2},$$

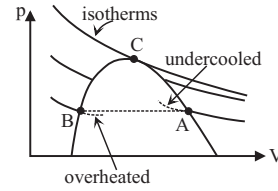
where $\Delta H_{vs} = H_s - H_v$.

For a mono atomic ideal gas $C_p = \frac{5}{2} k_B N$, so that

$$\ln p = -\frac{\Delta H_{vs}^0}{N k_B T} + \frac{5}{2} \ln T - \frac{1}{k_B N} \int \frac{\int_0^T C_p^s dT'}{T^2} dT + \text{constant}.$$

Here ΔH_{vs}^0 is the sublimation heat at 0 temperature and pressure.

Coexistence range



Matter is mechanically stable only if $\frac{dV}{dp} < 0$. Thus the range of stability lies outside of the points A and B.

Overheated liquid and undercooled vapor are metastable.

According to the Gibbs-Duhem relation

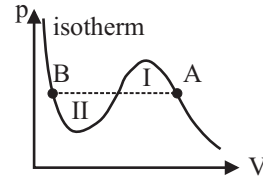
$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dp$$

we have on an isotherm

$$d\mu = \frac{V}{N} dp.$$

Thus, when the phases A and B are in equilibrium,

$$\mu_A - \mu_B = \int_A^B \frac{V}{N} dp = 0.$$



Maxwell's construction: The points A and B have to be chosen so that the area I = area II.

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

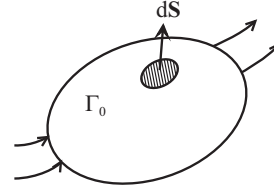
$$\langle f \rangle = \int d\Gamma f(P) \rho(P).$$

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 Γ_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* Γ_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 Γ_{Ei} . 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 Γ_E .

Ergodic flow: Almost all points of the surface Γ_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 ρ_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 ρ 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

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

ρ 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

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

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

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

where

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

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 ± 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:

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

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:

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

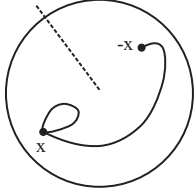
Since the particles are identical we identify the points

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

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° .



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.

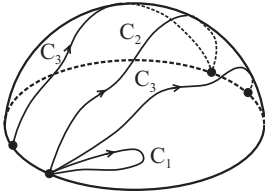
The space of the relative motion can be represented as the product

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

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 ψ 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 ξ is independent on the point \mathbf{x} ; ξ 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 ξ to 0 (bosons) or π (fermions).
- In three dimensional space the extra condition $P_{\mathbf{x}}^2 = 1$ forces the condition $\xi = 0$ or π .

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* ρ 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 ψ^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 ρ is hermitean there exists an orthonormal basis $\{|\alpha\rangle\}$ for \mathcal{H} , where ρ 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_{α} 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 ρ 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

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

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 Γ_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 smoothened 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 ΔE 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 λ and λ' 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 ψ 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 ϵ_ν 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

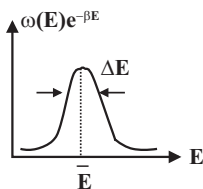
$$\rho = e^{\beta(F-H)}.$$

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

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

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

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

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 μ , 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

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

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.

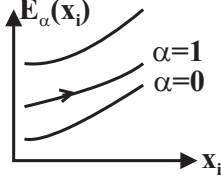
Connection with thermodynamics

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 δx_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

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

where

$$dx = dx_1 \dots dx_n$$

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 :

$$g = \frac{1}{V} \begin{pmatrix} T & V \\ \frac{C_V}{k_B T^2} & 0 \\ 0 & \frac{1}{V k_B T \kappa_T} \end{pmatrix}.$$

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 ΔR is the minimum reversible work required for the fluctuation ΔX . 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 γ is the gyromagnetic ratio. For electrons we have

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

where γ_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 σ_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

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

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

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

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

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

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

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

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

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

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

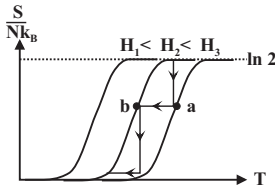
$$\begin{aligned} \tanh x &= \frac{e^x (1 - e^{-2x})}{e^x (1 + e^{-2x})} \\ &= 1 - 2e^{-2x} + \dots \end{aligned}$$

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

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

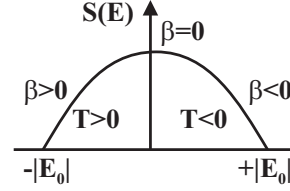
Negative temperature

The entropy of the spin system is

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

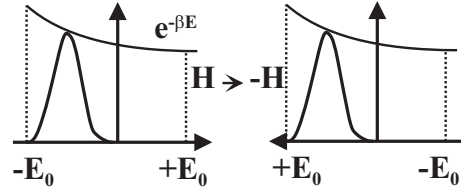
where

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



Now

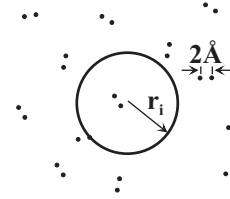
$$\beta(E) = \frac{1}{k_B} \frac{\partial S}{\partial E} = -\frac{N}{2E_0} \ln \frac{E + E_0}{E - E_0}.$$



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

$$\frac{d}{2} \ll \frac{r_i}{20} \ll \frac{l}{600} \quad \text{\AA}$$

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*

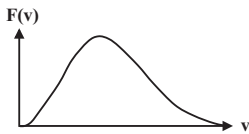
$$f(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m v^2}{2k_B T}}.$$

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*

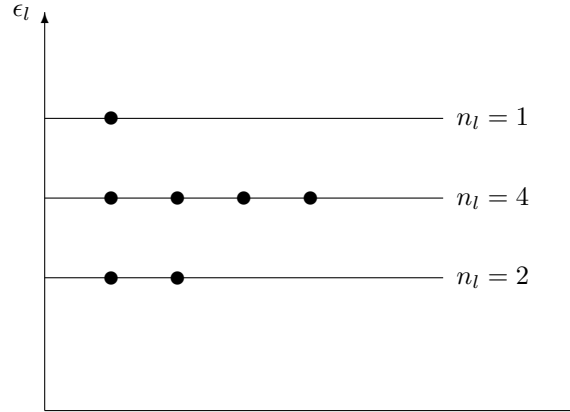
$$pV = \bar{N} k_B T.$$

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 $N!$ permutatations 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

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

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 ϵ_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

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

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

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

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 ϕ_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

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

The grand potential is

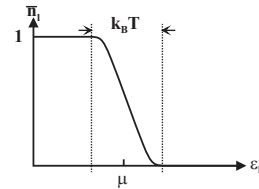
$$\Omega_{\text{FD}} = -k_B T \sum_l \ln \left[1 + e^{-\beta(\epsilon_l - \mu)} \right].$$

The average occupation number of the state l is

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

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

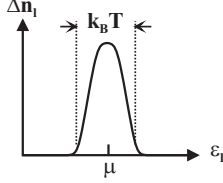
$$\begin{aligned} \langle n_l^2 \rangle &= \frac{1}{Z_{\text{G,FD}}} \text{Tr} \hat{n}_l^2 e^{-\beta(\hat{H} - \mu \hat{N})} \\ &= \frac{1}{Z_{\text{G,FD}}} \sum_{n_1=0}^1 \sum_{n_2=0}^1 \cdots n_l^2 e^{-\beta \sum_{l'} n_{l'} (\epsilon_{l'} - \mu)} \\ &= \frac{1}{\beta^2} \frac{1}{Z_{\text{G,FD}}} \frac{\partial^2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

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

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 μ .

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

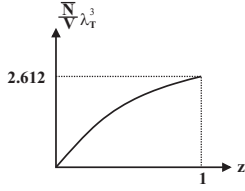
$$\bar{N} = \bar{n}_0 + \frac{V}{\lambda_T^3} g_{3/2}(z).$$

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*

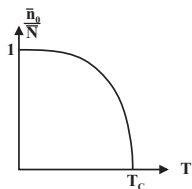
$$T_c = \left(\frac{2\pi\hbar^2}{mk_B} \right) \left(\frac{\rho}{2.612} \right)^{2/3}$$

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

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



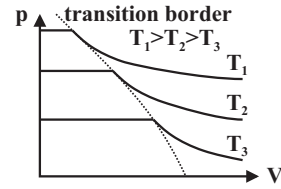
Pressure

With the help of the grand potential the pressure is

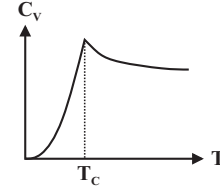
$$\begin{aligned} p &= - \left(\frac{\partial \Omega}{\partial V} \right)_{T,N} = - \frac{\Omega_{BE}}{V} \\ &= \frac{k_B T}{\lambda_T^3} g_{5/2}(z), \end{aligned}$$

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.

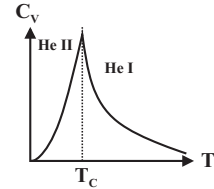


⁴He liquid

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 λ -transition.

Two liquid modell

When $T < T_c$, we suppose that ⁴He 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 ⁴He is *not* an ideal liquid: between ⁴He 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 ω the energy is

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

Since the wave length λ 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 ω . The total energy of this system is

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

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

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

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

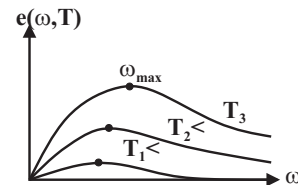
$$E = \int_0^\infty d\omega f(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}.$$

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 σ 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

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

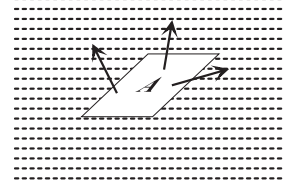
or

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

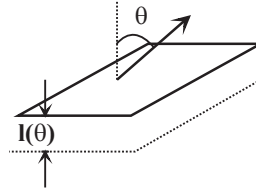
We see that the photon gas satisfies the relation

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

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 τ the photons escaping into the direction θ originate from the region whose depth is

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

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

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

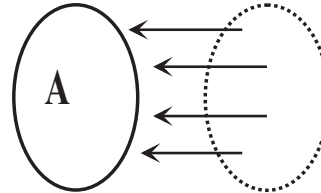
Thus the total energy of the radiation is

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

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 a 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^{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^{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 partion 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 ω 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

$$M\ddot{u}_\mu(\mathbf{R}) = -\frac{\partial U^{\text{harm}}}{\partial u_\mu(\mathbf{R})} = -\sum_{\mathbf{R}'} D_{\mu\nu}(\mathbf{R} - \mathbf{R}') u_\nu(\mathbf{R}'),$$

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 $N = N_1 N_2 N_3$. 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

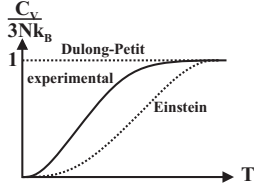
$$\begin{aligned} Z_{\text{harm}}(\omega) &= \text{Tr} e^{-\beta\hbar\omega(a^\dagger a + \frac{1}{2})} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n + \frac{1}{2})} \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \sum_n (e^{-\beta\hbar\omega})^n = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \\ &= \frac{1}{2 \sinh(\frac{1}{2}\beta\hbar\omega)}. \end{aligned}$$

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 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

$$\begin{aligned} Z &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} e^{-\beta \sum_{\mathbf{k}s} \hbar \omega_s(\mathbf{k}) (n_{\mathbf{k}s} + \frac{1}{2})} \\ &= \prod_{\mathbf{k}s} \frac{e^{-\frac{1}{2} \beta \hbar \omega_s(\mathbf{k})}}{1 - e^{-\beta \hbar \omega_s(\mathbf{k})}}, \end{aligned}$$

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.

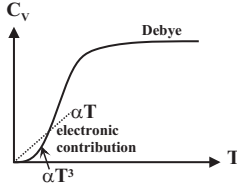
$T \rightarrow 0$

Since

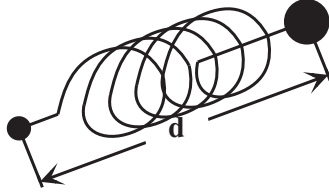
$$f_D(x) \xrightarrow{x \rightarrow \infty} \frac{3}{x^3} \int_0^{\infty} dy \frac{y^4 e^y}{(e^y - 1)^2} = \frac{\text{constant}}{x^3},$$

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

$$H \approx H^{\text{tr}} + H^{\text{rot}} + H^{\text{vibr}} + H^{\text{el}} + H^{\text{nucl}}.$$

Here

$$H^{\text{tr}} = \frac{\mathbf{p}^2}{2m} = \text{kinetic energy}$$

m = mass of molecule

$$H^{\text{rot}} = \frac{\mathbf{L}^2}{2I} = \text{rotational energy}$$

\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

$$H^{\text{vibr}} = \hbar \omega_v \left(\hat{n} + \frac{1}{2} \right) = \text{vibration energy}$$

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

$$H^{\text{el}} = \text{electronic energies}$$

- 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.

$$H^{\text{nucl}} = \text{energies corresponding to nucleonic degrees of freedom}$$

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

$$E_i \approx E_{\text{tr}} + E_{\text{rot}} + E_{\text{vibr}},$$

so the partition sum of one molecule is

$$\begin{aligned} Z_1 &= \sum_{\mathbf{p}} \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} g_y (2l+1) \times \\ &\quad e^{-\beta \frac{\mathbf{p}^2}{2m} - \beta \frac{\hbar^2}{2I} l(l+1) - \beta \hbar \omega_v (n + \frac{1}{2})} \\ &= Z^{\text{tr}} Z^{\text{rot}} Z^{\text{vibr}} Z^{\text{nucl}}, \end{aligned}$$

i.e. the state sum can be factorized.

Above

$$Z^{\text{tr}} = \sum_{\mathbf{p}} e^{-\beta \frac{\mathbf{p}^2}{2m}} = \frac{V}{\lambda_T^3}$$

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

$$Z^{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)}$$

$$T_r = \frac{\hbar^2}{2Ik_B}$$

$$\begin{aligned}
Z^{\text{vibr}} &= \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_v (n + \frac{1}{2})} \\
&= \left[2 \sinh \frac{T_v}{2T} \right]^{-1} \\
T_v &= \frac{\hbar \omega_v}{k_B} \\
Z^{\text{nucl}} &= g_y = (2I_1 + 1)(2I_2 + 1).
\end{aligned}$$

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^{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 ₂	85.4
N ₂	2.9
NO	2.4
HCl	15.2
Cl ₂	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

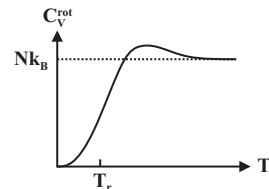
$$U^{\text{rot}} \approx N k_B T.$$

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 ₂	6100
N ₂	3340
NO	2690
O ₂	2230
HCl	4140

We see that $T_v \gg$ the room temperature.

$T \ll T_v$

The free energy is

$$\begin{aligned} F^{\text{vibr}} &= Nk_B T \ln \left[e^{\frac{T_v}{2T}} (1 - e^{-\frac{T_v}{T}}) \right] \\ &\approx \frac{1}{2} Nk_B T_v - Nk_B T e^{-\frac{T_v}{T}}, \end{aligned}$$

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

$$F^{\text{vibr}} \approx Nk_B T \ln \frac{T_v}{T}$$

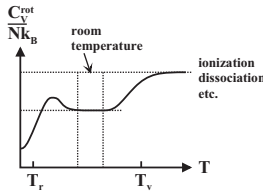
and the internal energy correspondingly

$$U^{\text{vibr}} \approx Nk_B T,$$

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 H₂-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

$$\begin{aligned} Z_{\text{ortho}} &= \sum_{l=1,3,5,\dots} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \\ Z_{\text{para}} &= \sum_{l=0,2,4,\dots} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \end{aligned}$$

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 $k_B T \ll \mu$.

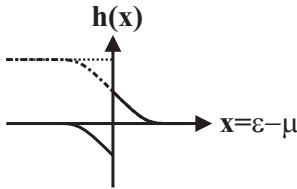
Let's write

$$\frac{1}{e^{\beta(\epsilon-\mu)} + 1} = \theta(\mu - \epsilon) + h(\epsilon - \mu),$$

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

$$\epsilon_F = \underbrace{\frac{\hbar^2}{2ma_0^2}}_{\text{binding energy of hydrogen}} \left(\frac{1.92}{r_s} \right)^2 = \frac{3.69}{r_s^2} 13.6 \text{ eV}.$$

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

$$\begin{aligned} C_V &= \frac{\partial N\bar{\epsilon}}{\partial T} = N \frac{\pi^2}{2} \frac{k_B^2}{\epsilon_F} T \\ &= N k_B \frac{\pi^2}{2} \frac{T}{T_F}, \end{aligned}$$

is small when compared e.g. with the specific heat of the Maxwell-Boltzmann gas ($C_V = N k_B \frac{3}{2}$). 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

$$\mu_B = \frac{e\hbar}{2m} = 5.66 \cdot 10^{-5} \text{ eV/T}$$

and

$$\sigma_z = \frac{2}{\hbar} s_z = \pm 1.$$

In an external magnetic field the energy of an electron is

$$\epsilon_{\mathbf{p}\sigma_z} = \epsilon_{p\pm} = \frac{p^2}{2m} - \mu_z B = \epsilon_{\mathbf{p}} + \mu_B B \sigma_z$$

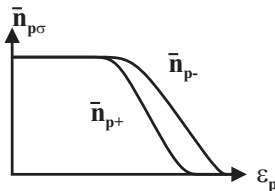
when the kinetic energy is

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

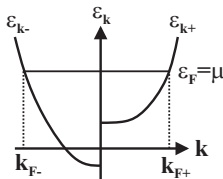
We still treat electrons as non interacting so the grand canonical partition function is as before, provided that we replace $\epsilon_{\mathbf{p}} \rightarrow \epsilon_{\mathbf{p}} + \mu_B B \sigma_z$.

The occupation numbers of the states are now

$$\bar{n}_{\mathbf{p}\sigma_z} = \bar{n}_{p\pm} = \frac{1}{e^{\beta(\epsilon_p + \mu_B B \sigma_z - \mu)} + 1}.$$



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

$$\begin{aligned} \chi &= \frac{3}{2} \cdot 4\pi \cdot 10^{-7} \cdot 1.82 \cdot 10^{29} \cdot \frac{(5.66 \cdot 10^{-5})^2}{11.7} \\ &\quad \frac{\text{Vs}}{\text{Am}} \frac{1}{\text{m}^3} \frac{(\text{eV})^2}{\text{T}^2 \text{eV}} \\ &= 9.4 \cdot 10^{13} \frac{\text{eV Vs}}{\text{Am}^4} \left(\frac{\text{m}^2}{\text{Vs}} \right)^2 \\ &= 9.4 \cdot 10^{13} \cdot 1.6 \cdot 10^{-19} \\ &= 1.5 \cdot 10^{-5} \end{aligned}$$

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

$$\mathcal{H}_0 = \frac{1}{2m^*} \left[p_x^2 + \left(p_y + \frac{eB}{c} x \right)^2 \right].$$

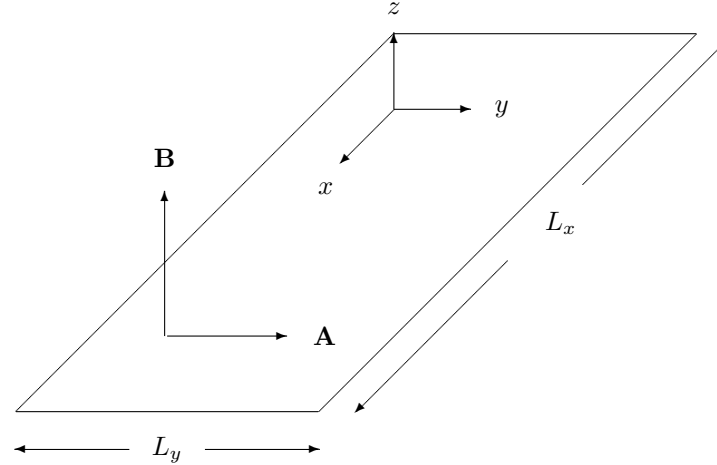
The eigenfunctions are

$$\phi_{nX} = e^{ik_y y} e^{-(x-X)^2/2\ell_0^2} H_n \left(\frac{x-X}{\ell_0} \right),$$

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

$$\nu = \frac{N_e}{N_s} \quad \left(= 4.136 \frac{n_0}{10^{15} \text{m}^{-2}} \frac{\text{T}}{B} \right).$$

To treat the spin we note that

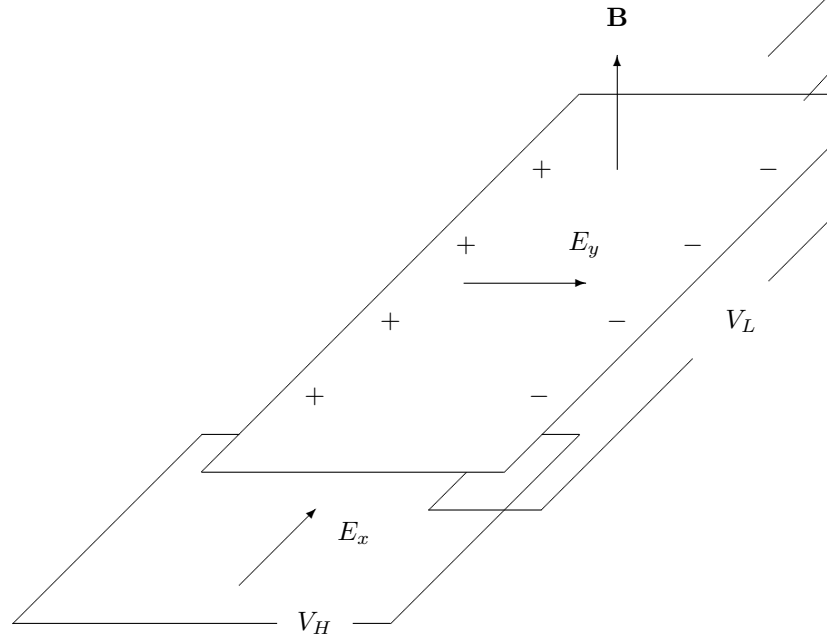
- there should be the Zeeman coupling term

$$\mathcal{H}_{\text{Zeeman}} = \boldsymbol{\mu} \cdot \mathbf{B} = -g\mu_B B s_z$$

in the Hamiltonian. Here g is the Lande factor and μ_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

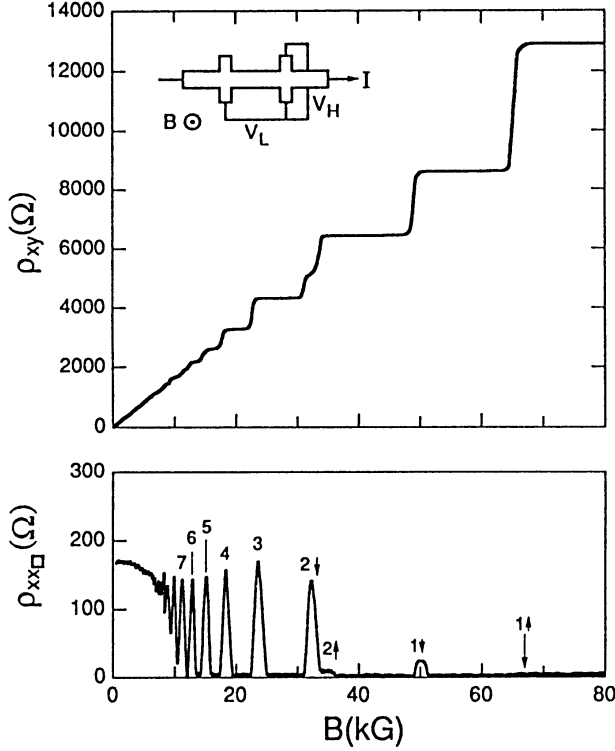
$$E_{\text{Zeeman}} = g\mu_B B S_z.$$



The conductivity σ and the resistivity ρ 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 τ is the relaxation time. In particular $\rho_{xy} = -B/n_0 e c$. Experimentally the resistivities 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

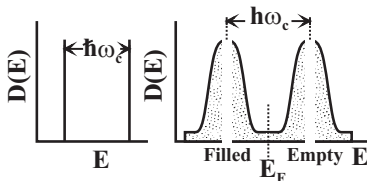
$$\rho_{xy} = \frac{25812.807}{n} \Omega.$$

- 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 δ -peaks separated by $\hbar\omega_c$.
- In a real impure system the δ -peaks are spread and between the Landau levels there are localized states.



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

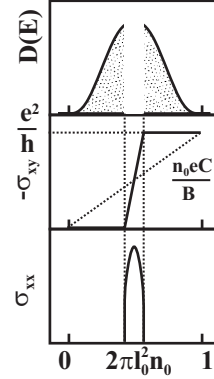
$$\Delta\sigma_{xy}^\alpha = \frac{f(E_\alpha)ec}{B}.$$

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, σ_{xy} remains constant.
- if all states below the Fermi level are localized, the terms in σ_{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

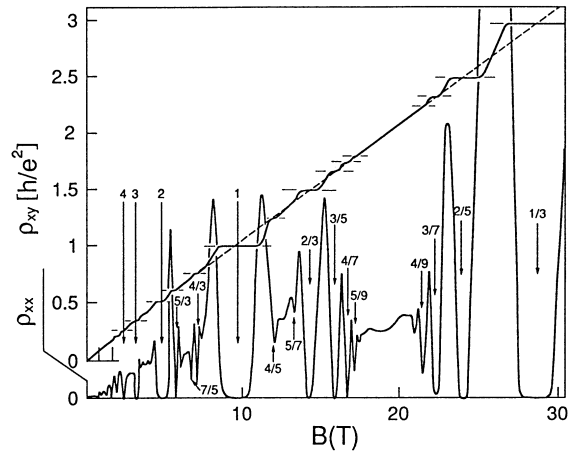


Noting that

$$\nu = \frac{N_e}{N_s} = 2\pi\ell_0^2 n_0 \propto \frac{n_0}{B},$$

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



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 ν 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.

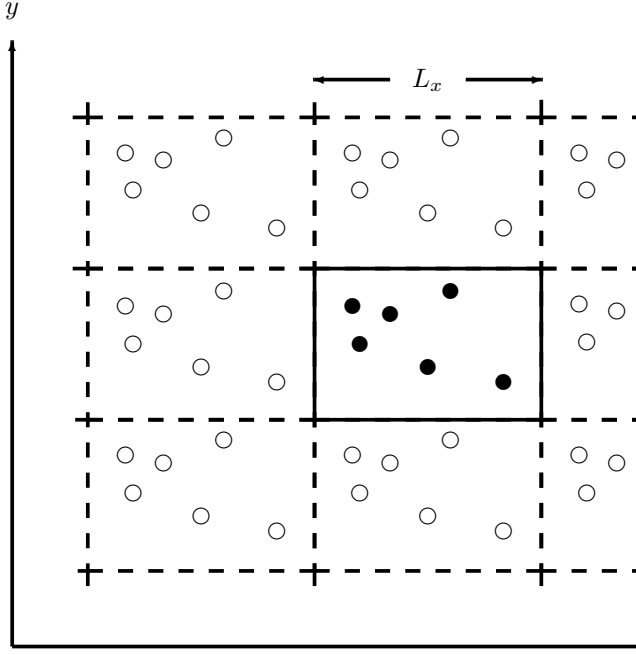
So, we let electrons to flip their spins. However,

- 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

$$\begin{aligned} \mathcal{H} = & \sum_{j\sigma} w_j a_{j\sigma}^\dagger a_{j\sigma} \\ & + \sum_{\substack{j_1\sigma_1 \quad j_2\sigma_2 \\ j_3\sigma_3 \quad j_4\sigma_4}} A_{j_1 j_2 j_3 j_4} a_{j_1\sigma_1}^\dagger a_{j_2\sigma_2}^\dagger a_{j_3\sigma_3} a_{j_4\sigma_4}, \end{aligned}$$

where operators $a_{j\sigma}^\dagger$ ($a_{j\sigma}$) create (destroy) an electron with spin σ in a single particle state j .

3. fix N_s , the number of flux quanta (≈ 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

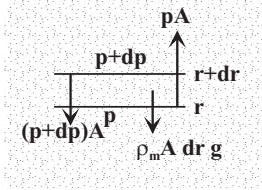
In a properly functioning star the energy released in nuclear reactions (mainly $2\text{H} \rightarrow \text{He}$) and the collapsing gravitational force are in balance. When the nuclear fuel is consumed the star collapses. If the mass of the star is large enough all material will become ionized. Depending 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, ρ 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

$$k_F \approx 1.36 \cdot 10^{15} \text{ m}^{-1}$$

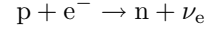
and the Fermi energies

$$\epsilon_F \approx 38 \text{ MeV}.$$

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 ^3He

The nucleus is p+p+n and the nuclear spin $\frac{1}{2}$.

At low temperatures the nuclear spin determines the statistics, i.e. ^3He 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 ^3He atoms are considerable the ^3He matter forms an interacting *Fermi liquid*. The ^3He liquid has two super phases (A and B). These are in balance with the normal phase at the critical point

$$T_c \approx 2.7 \text{ mK} < \frac{T_F}{1000}.$$

Interacting matter

Classical real gas

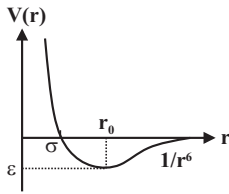
We take into account the mutual interactions of atoms (molecules)

The Hamiltonian operator is

$$H^{(N)} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} v(r_{ij}), \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|.$$

For example, for noble gases an excellent interaction potential is the *Lennard-Jones 6-12-potential*

$$v(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right].$$



We evaluate the partition sums in the classical phase space. The canonical partition function is

$$Z_N(T, V) = Z(T, V, N) = \text{Tr}_N e^{-\beta H^{(N)}} \xrightarrow{\text{classical limit, Maxwell-Boltzmann}} \frac{1}{N!} \int d\Gamma e^{-\beta H}.$$

Since the momentum variables appear only as quadratic in the kinetic energy terms they can be integrated and we get

$$\begin{aligned} Z_N &= \frac{1}{N!} \frac{1}{h^{3N}} \int \cdots \int d\mathbf{p}_1 \cdots d\mathbf{p}_N d\mathbf{r}_1 \cdots d\mathbf{r}_N \times \\ &\quad \exp \left[-\beta \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} v(r_{ij}) \right] \\ &= \frac{1}{N!} \frac{1}{\lambda_T^{3N}} Q_N(T, V), \end{aligned}$$

where

$$\lambda_T = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2}$$

is the thermal wave length and

$$Q_N(T, V) = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta \sum_{i<j} v(r_{ij})}.$$

The grand canonical partition function is

$$\begin{aligned} Z(T, V, \mu) &= \sum_N e^{\beta \mu N} Z_N(T, V) \\ &= \sum_N \frac{1}{N!} \left(\frac{z}{\lambda_T^3} \right)^N Q_N(T, V), \end{aligned}$$

when $z = e^{\beta \mu}$ is the fugacity.

We define an intensive function

$$\omega(z, T) = \frac{1}{V} \ln Z(T, V, \mu).$$

The grand potential is now

$$\Omega = -k_B T V \omega(z, T)$$

and

$$\begin{aligned} \frac{p}{k_B T} &= \omega(z, T) \\ \rho &= \frac{N}{V} = z \frac{\partial \omega(z, T)}{\partial z}. \end{aligned}$$

Eliminating z we can write the equation of state as

$$p = k_B T \varphi(\rho, T).$$

Expanding φ as the power series of ρ we end up with the virial expansion.

Ursell-Mayer graphs

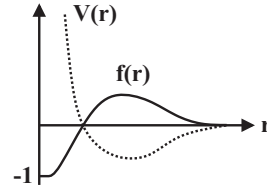
Let's write

$$\begin{aligned} Q_N &= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{i<j} e^{-\beta v(r_{ij})} \\ &= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{i<j} (1 + f_{ij}), \end{aligned}$$

where

$$f_{ij} = f(r_{ij}) = e^{-\beta v(r_{ij})} - 1$$

is *Mayer's function*.



The function f is bounded everywhere and it has the same range as the potential v . In general f is a small correction as compared with the term 1. If $v(r) \equiv 0$, then $f \equiv 0$ and $Q_N = Q_N^0 = V^N$ i.e. we end up with the Maxwell-Boltzmann ideal gas.

We write Q_N as the power series of Mayer functions f_{ij} :

$$\begin{aligned} Q_N &= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \left[1 + \sum_{(ij)} f_{ij} + \sum_{(ij)<(kl)} f_{ij} f_{kl} \right. \\ &\quad \left. + \sum_{(ij)<(kl)<(mn)} f_{ij} f_{kl} f_{mn} + \cdots \right]. \end{aligned}$$

Here

$$\begin{aligned} (ij) &\Leftrightarrow \text{pair } 1 \leq i < j \leq N, \frac{1}{2} N(N-1) \text{ terms} \\ (ij) < (kl) &\Leftrightarrow (ij) \neq (kl) \text{ and only one} \\ &\quad \text{of terms } (ij)(kl), (kl)(ij) \text{ selected,} \\ &\quad \frac{1}{2} \left[\frac{1}{2} N(N-1) \right] \left[\frac{1}{2} N(N-1) - 1 \right] \text{ terms} \\ &\quad \vdots \end{aligned}$$

Graphs are build from the elements

$$\bullet^i \Leftrightarrow \int d\mathbf{r}_i$$

$$\overset{i}{\text{---}}\overset{j}{\text{---}} \Leftrightarrow f_{ij}.$$

Permutations of particles do not change the values of the graphs, for example

$$\int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 f_{12} f_{23} = \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 f_{13} f_{23},$$

as we can see by exchanging the integration variables \mathbf{r}_2 and \mathbf{r}_3 .

$$\begin{array}{c} 3 \\ \diagdown \quad \diagup \\ 1 \text{---} 2 \end{array} = \begin{array}{c} 3 \\ \diagup \quad \diagdown \\ 1 \text{---} 2 \end{array}$$

Examlpe:

$$\begin{aligned} \mathbf{Q}_1 &= \bullet \\ \mathbf{Q}_2 &= \bullet \text{---} \bullet \\ \mathbf{Q}_3 &= \bullet \text{---} \bullet \text{---} \bullet + \bullet \text{---} \bullet \text{---} \bullet + \bullet \text{---} \bullet \text{---} \bullet \\ &\quad + \begin{array}{c} \diagup \quad \diagdown \\ \bullet \text{---} \bullet \end{array} + \begin{array}{c} \diagdown \quad \diagup \\ \bullet \text{---} \bullet \end{array} + \begin{array}{c} \diagup \quad \diagup \\ \bullet \text{---} \bullet \end{array} + \begin{array}{c} \diagdown \quad \diagdown \\ \bullet \text{---} \bullet \end{array} \\ &= \bullet \text{---} \bullet + 3 \bullet \text{---} \bullet \text{---} \bullet + 3 \begin{array}{c} \diagup \quad \diagdown \\ \bullet \text{---} \bullet \end{array} + \begin{array}{c} \diagup \quad \diagup \\ \bullet \text{---} \bullet \end{array} + \begin{array}{c} \diagdown \quad \diagdown \\ \bullet \text{---} \bullet \end{array} \end{aligned}$$

We classify the graphs:

- in *coupled graphs* or a *clusters* one can get from every black dot (\bullet) to every black dot following a chain of lines (---).
- in *uncoupled graphs* there are parts that are not connected by a line (---).

It is easy to see that an uncoupled graph can be factorized as the product of its coupled parts.

The sum of graphs of l coupled points is called an *l-cluster*.

We define q_l so that it is the sum of all l -clusters, e.g.

$$\begin{aligned} q_1 &= \int d\mathbf{r} = V \\ q_2 &= \int \int d\mathbf{r}_1 d\mathbf{r}_2 f_{12} \\ q_3 &= \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 (3f_{12}f_{13} + f_{12}f_{23}f_{13}). \end{aligned}$$

One can show that

$$Q_N = \sum_{\{\nu_l\}} \delta \left(N, \sum_l l \nu_l \right) \frac{N!}{\prod_l (l!)^{\nu_l}} \prod_l \frac{q_l^{\nu_l}}{\nu_l!}.$$

Here

- ν_l tells the number of l -clusters.
- $\sum_{\{\nu_l\}} = \sum_{\nu_1=0}^{\infty} \sum_{\nu_2=0}^{\infty} \sum_{\nu_3=0}^{\infty} \dots$
- $\delta \left(N, \sum_l l \nu_l \right)$ restricts the number of the integration variables (black dots \bullet) to N .

- $\frac{N!}{\prod_l (l!)^{\nu_l}}$ tells how many ways there are to pick the clusters from the set of N points.
- Everyone of the possible $\nu_l!$ permutations of the l -clusters gives an identical contribution and must be counted only once. That's why the divisor $\nu_l!$ in the factor $\frac{q_l^{\nu_l}}{\nu_l!}$.

Denote

$$\xi = \frac{z}{\lambda_T^3}.$$

The grand canonical partition function is now

$$\begin{aligned} Z(T, V, \mu) &= \sum_N \frac{1}{N!} \xi^N Q_N \\ &= \sum_{\{\nu_l\}} \prod_l \left[\frac{q_l^{\nu_l}}{\nu_l! (l!)^{\nu_l}} \right] \times \\ &\quad \sum_N \frac{1}{N!} \xi^N N! \delta \left(N, \sum_l l \nu_l \right) \\ &= \sum_{\{\nu_l\}} \prod_l \left[\frac{q_l^{\nu_l}}{\nu_l! (l!)^{\nu_l}} \right] \xi^{\sum_l l \nu_l} \\ &= \sum_{\{\nu_l\}} \prod_l \frac{1}{\nu_l!} \left[\frac{q_l}{l!} \xi^l \right]^{\nu_l} \\ &= \prod_l \sum_{\nu_l=0}^{\infty} \frac{1}{\nu_l!} \left[\frac{q_l}{l!} \xi^l \right]^{\nu_l} = \prod_l e^{\frac{q_l}{l!} \xi^l}. \end{aligned}$$

We end up with the *cumulant expansion* of the grand canonical partition sum:

$$Z(T, V, \mu) = \exp \left[\sum_{l=0}^{\infty} \frac{1}{l!} \xi^l q_l \right].$$

Virial expansion

In the cumulant expansion every q_l is proportional to the volume V . We define the *cluster integral* b_l depending only on temperature so that

$$\begin{aligned} b_l &= \frac{1}{l!} \frac{1}{V} q_l \\ &= \frac{1}{l!} \frac{1}{V} \int d\mathbf{r}_1 \dots \int d\mathbf{r}_l \left[\prod_{i < j} (1 + f_{ij}) \right]_{\text{coupled graphs}}. \end{aligned}$$

Now

$$\omega(z, T) = \frac{1}{V} \ln Z(T, V, \mu) = \sum_{l=1}^{\infty} \xi^l b_l(T).$$

For the density we get

$$\rho = z \frac{\partial \omega}{\partial z} = \sum_{l=1}^{\infty} l \xi^l b_l(T).$$

We solve ξ as the power series of the density ρ , substitute it into the expression of ω and collect equal powers of ρ together and end up with the *virial expansion*

$$p = k_B T \omega(z, T) = k_B T [\rho + B_2(T) \rho^2 + B_3(T) \rho^3 + \dots].$$

The virial coefficients $B_n(T)$ are now functions of the cluster integrals $\{b_l(T) | l \leq n\}$, e.g.

$$\begin{aligned} B_2(T) &= -b_2(T) = \frac{1}{2} \int d\mathbf{r} [1 - e^{-\beta v(r)}] \\ B_3(T) &= 4b_2^2 - 2b_3 \\ B_4(T) &= -20b_2^3 + 18b_2b_3 - 3b_4. \end{aligned}$$

Second virial coefficient

We suppose that

- the interaction has a *hard core*, i.e. the interaction is strongly repulsive when $r \lesssim \sigma$.
- on the average, the interaction is attractive when $r \gtrsim \sigma$, but the temperature is so high that $\beta v(r) \ll 1$ there.

Now

$$e^{-\beta v(r)} \approx \begin{cases} 0, & \text{when } r \lesssim \sigma \\ 1 - \beta v(r), & \text{when } r \gtrsim \sigma, \end{cases}$$

and

$$\begin{aligned} B_2 &= 2\pi \int_0^\infty dr r^2 [1 - e^{-\beta v(r)}] \\ &\approx 2\pi \int_0^\sigma dr r^2 + 2\pi \int_\sigma^\infty dr r^2 \beta v(r) \\ &= b - \frac{a}{T}. \end{aligned}$$

Here

$$\begin{aligned} b &= \frac{2\pi}{3} \sigma^3 \\ a &= -2\pi \int_\sigma^\infty dr r^2 v(r) > 0. \end{aligned}$$

With these approximations we end up with the van der Waals equation of state.

For hard spheres the virial coefficients can be calculated exactly. Denoting

$$b_0 = \frac{2\pi}{3} \sigma^3$$

we get

n	B_n
2	b_0
3	$\frac{5}{8} b_0^2$
4	$0.287 b_0^3$
5	$0.110 b_0^4$
6	$0.039 b_0^5$

Low density gas

We write

$$Q_N = \int d\mathbf{r}_1 \dots \int d\mathbf{r}_{N-1} e^{-\beta \sum_{i < j}^{N-1} v_{ij}} \times \int d\mathbf{r}_N e^{-\beta \sum_i^{N-1} v(r_{iN})}.$$

With the help of Mayer's functions the last integrand is

$$\begin{aligned} \exp \left[-\beta \sum_i^{N-1} v_{iN} \right] &= \prod_i^{N-1} [1 + f_{iN}] \\ &= 1 + \sum_i^{N-1} f(r_{iN}) \\ &\quad + \sum_{i < j}^{N-1} f(r_{iN}) f(r_{jN}) + \dots \end{aligned}$$

Choose randomly two particles, i and j say. Now

- the function $f(r_{iN})$ deviates from zero only in the range of the interaction.
- the term $f(r_{iN}) f(r_{jN})$ can deviate from zero only if the particle j is in the range of the particle i (the particle N must also be in that range).
- the probability that the particle j is in the range of the particle i is $\propto \frac{1}{V}$.
- if the particle j is in the range of the particle i , then the integral over the variable \mathbf{r}_N is $\propto 1$, since the function f has a short range.

We see, that

$$\int d\mathbf{r}_N \sum_{i < j}^{N-1} f(r_{iN}) f(r_{jN}) \propto \sum_{i < j}^{N-1} \frac{1}{V} = \mathcal{O} \left(\frac{N^2}{V} \right).$$

In the low density limit we get

$$\begin{aligned} \int d\mathbf{r}_N e^{-\beta \sum_i^{N-1} v_{iN}} &= V + (N-1) \int d\mathbf{r} f(r) \\ &\quad + \mathcal{O} \left(\frac{N^2}{V} \right) \\ &\approx V + (N-1) \int d\mathbf{r} f(r). \end{aligned}$$

Iterating we have

$$\begin{aligned} Q_N &\approx \int d\mathbf{r}_1 \dots \int d\mathbf{r}_{N-2} e^{-\beta \sum_{i < j}^{N-2} v_{ij}} \times \\ &\quad \left[V + (N-2) \int d\mathbf{r} f(r) \right] \times \\ &\quad \left[V + (N-1) \int d\mathbf{r} f(r) \right] \\ &\approx \dots \approx V^N \prod_{n=0}^{N-1} \left[1 + \frac{n}{N} \rho \int d\mathbf{r} f(r) \right], \end{aligned}$$

where $\rho = N/V$. Now

$$\lim_{x \rightarrow 0} \left(1 + \frac{j}{N} x\right) \left(1 + \frac{N-j}{N} x\right) \approx \left(1 + \frac{x}{2}\right)^2$$

so

$$\lim_{x \rightarrow 0} \prod_{n=0}^{N-1} \left[1 + \frac{nx}{N}\right] \approx \left[1 + \frac{x}{2}\right]^N \approx e^{\frac{xN}{2}},$$

i.e. in the low density limit

$$Q_N \approx V^N e^{\frac{1}{2} N \rho \int d\mathbf{r} f(r)} = Q_N^{(0)} e^{\frac{1}{2} N \rho \int d\mathbf{r} f(r)}.$$

Here $Q_N^{(0)} = V^N$ is Q_N for the ideal gas. Since the canonical partition sum was

$$Z_N = \frac{1}{N! \lambda_T^{3N}} Q_N,$$

the energy can be written like

$$\begin{aligned} F(T, V, N) &= -k_B T \ln Z_N \\ &= F_0(T, V, N) - \frac{N^2 k_B T}{2V} \int d\mathbf{r} f(r), \end{aligned}$$

where $F_0(T, V, N)$ is the free energy of the ideal gas. The equation of state is now

$$\begin{aligned} p &= -\frac{\partial F}{\partial V} = -\frac{\partial F_0}{\partial V} - \frac{N^2 k_B T}{2V^2} \int d\mathbf{r} f(r) \\ &= \frac{N k_B T}{V} \left[1 - \frac{1}{2} \rho \int d\mathbf{r} f(r)\right]. \end{aligned}$$

Comparing with the virial expansion we see that the second virial coefficient is

$$B_2 = -\frac{1}{2} \int d\mathbf{r} f(r) = \frac{1}{2} \int d\mathbf{r} [1 - e^{-\beta v(r)}].$$

Correlation functions

Static linear response

Let \hat{H}_0 be the Hamiltonian of a system in the equilibrium and

$$\hat{\rho}_0 = \frac{1}{Z_0} e^{-\beta \hat{H}_0}$$

the corresponding density operator. We disturb the system with external time independent fields a_α , which couple to observables \hat{A}_α of the system:

$$\hat{H} = \hat{H}_0 - \sum_{\alpha} \hat{A}_{\alpha} a_{\alpha}.$$

The corresponding density operator is

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

where

$$Z = \text{Tr} e^{-\beta \hat{H}} = \text{Tr} e^{-\beta(\hat{H}_0 - \sum_{\alpha} \hat{A}_{\alpha} a_{\alpha})}.$$

Now

$$\begin{aligned} \frac{\partial Z}{\partial a_{\alpha}} &= \beta \text{Tr} \hat{A}_{\alpha} e^{-\beta(\hat{H}_0 - \sum_{\alpha} \hat{A}_{\alpha} a_{\alpha})} \\ &= \beta Z \langle \hat{A}_{\alpha} \rangle \end{aligned}$$

and

$$\begin{aligned} \frac{\partial^2 Z}{\partial a_{\alpha} \partial a_{\beta}} &= \beta^2 \text{Tr} \hat{A}_{\alpha} \hat{A}_{\beta} e^{-\beta(\hat{H}_0 - \sum_{\alpha} \hat{A}_{\alpha} a_{\alpha})} \\ &= \beta^2 Z \langle \hat{A}_{\alpha} \hat{A}_{\beta} \rangle, \end{aligned}$$

when we suppose that \hat{H}_0 , \hat{A}_{α} and \hat{A}_{β} commute.

We define the *static linear response function* $\chi_{\alpha\beta}$ so that

$$\begin{aligned} \chi_{\alpha\beta} &= \frac{\partial \langle \hat{A}_{\alpha} \rangle}{\partial a_{\beta}} = \frac{1}{\beta} \frac{\partial}{\partial a_{\beta}} \frac{1}{Z} \frac{\partial Z}{\partial a_{\alpha}} \\ &= \frac{1}{\beta Z} \frac{\partial^2 Z}{\partial a_{\alpha} \partial a_{\beta}} - \frac{1}{\beta Z^2} \frac{\partial Z}{\partial a_{\alpha}} \frac{\partial Z}{\partial a_{\beta}} \\ &= \beta \langle \hat{A}_{\alpha} \hat{A}_{\beta} \rangle - \beta \langle \hat{A}_{\alpha} \rangle \langle \hat{A}_{\beta} \rangle. \end{aligned}$$

We can thus write

$$\delta \langle \hat{A}_{\alpha} \rangle = \sum_{\beta} \chi_{\alpha\beta} \delta a_{\beta},$$

where

$$\begin{aligned} \chi_{\alpha\beta} &= \beta \langle (\hat{A}_{\alpha} - \langle \hat{A}_{\alpha} \rangle) (\hat{A}_{\beta} - \langle \hat{A}_{\beta} \rangle) \rangle \\ &= \langle \delta \hat{A}_{\alpha} \delta \hat{A}_{\beta} \rangle. \end{aligned}$$

Notes:

- $\chi_{\alpha\beta}$ tells how much the expectation value of the observable \hat{A}_{α} changes when the observable \hat{A}_{β} is influenced by one unit of disturbance.
- The response functions are related to the *correlations* of the fluctuations of observables. The correlation C_{AB} of the observables \hat{A} and \hat{B} is defined to be

$$C_{AB} = \langle \delta \hat{A} \delta \hat{B} \rangle,$$

where $\delta \hat{A} = \hat{A} - \langle \hat{A} \rangle$ is the fluctuating part of the observable \hat{A} .

- The *correlation functions* $\langle \delta \hat{A}_{\alpha} \delta \hat{A}_{\beta} \rangle$ can be calculated in the limit $\{a_{\alpha} = 0\}$. The responses $\chi_{\alpha\beta}$ are determined, in the limit of infinitesimal disturbances, by the undisturbed density matrix $\hat{\rho}_0$.
- The theory of linear responses can be generalized for dynamic disturbances.

- In spite of the possible incommutability of the operators \hat{A}_α , \hat{A}_β and \hat{H}_0 the results are exact in the classical mechanics. In quantum mechanics the incommutability must be taken into account. One can show that the response function can be written as

$$\chi_{\alpha\beta} = \left\langle \delta \tilde{A}_\beta^{(\hat{A}_\beta)} \delta \hat{A}_\alpha \right\rangle,$$

where the operator $\tilde{A}^{(\hat{B})}$ is

$$\tilde{A}^{(\hat{B})} = \hat{A} + \frac{1}{2!} [\hat{A}, \hat{B}] + \frac{1}{3!} [[\hat{A}, \hat{B}], \hat{B}] + \dots$$

Particle density

Let $\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \dots, \hat{\mathbf{r}}_N$ be position operators, i.e.

$$\hat{\mathbf{r}}_i \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \mathbf{r}_i \psi(\mathbf{r}_1, \dots, \mathbf{r}_N).$$

The *number density operator* is

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \hat{\mathbf{r}}_i).$$

For example, in the pure state $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ we get

$$\begin{aligned} \langle \hat{\rho}(\mathbf{r}) \rangle &= \sum_i \int d\mathbf{r}_1 \dots \int d\mathbf{r}_{i-1} \int d\mathbf{r}_{i+1} \dots \int d\mathbf{r}_N \\ &\quad |\psi(\mathbf{r}_1, \dots, \mathbf{r}_{i-1}, \mathbf{r}, \mathbf{r}_{i+1}, \dots, \mathbf{r}_N)|^2. \end{aligned}$$

When the particles are identical bosons or fermions $|\psi|^2$ is symmetric under permutations $\mathbf{r}_i \leftrightarrow \mathbf{r}_j$, so

$$\langle \hat{\rho}(\mathbf{r}) \rangle = N \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2.$$

We supposed that the system is closed into the volume V and ψ normalized. Then

$$\begin{aligned} \int_V \langle \hat{\rho}(\mathbf{r}) \rangle d\mathbf{r} &= N \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N |\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 \\ &= N. \end{aligned}$$

In general, we have

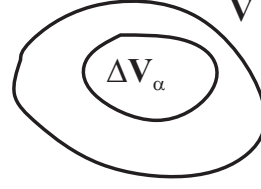
$$\begin{aligned} \int d\mathbf{r} \hat{\rho}(\mathbf{r}) &= \sum_{i=1}^N \int_V d\mathbf{r} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \\ &= \sum_{i=1}^N 1 = N, \end{aligned}$$

so we can write

$$\hat{N} = \int d\mathbf{r} \hat{\rho}(\mathbf{r}).$$

Density-density response function

We divide the volume V into elements ΔV_α .



Let

$$\hat{N}_\alpha = \int_{\Delta V_\alpha} d\mathbf{r} \hat{\rho}(\mathbf{r}) = N_\alpha$$

be the number of particles in the element ΔV_α .

Let a_α be a field coupling to \hat{N}_α . The Hamiltonian of the system is

$$\begin{aligned} \hat{H} &= \hat{H}_0 - \sum_\alpha \hat{N}_\alpha a_\alpha \\ &= \hat{H}_0 - \sum_\alpha \int_{\Delta V_\alpha} d\mathbf{r} \hat{\rho}(\mathbf{r}) a_\alpha. \end{aligned}$$

In the continuum limit we get

$$\begin{aligned} \hat{H} &= \hat{H}_0 - \int_V d\mathbf{r} \hat{\rho}(\mathbf{r}) a(\mathbf{r}) \\ &= \hat{H}_0 - \sum_i \int d\mathbf{r} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) a(\mathbf{r}) \\ &= \hat{H}_0 - \sum_i a(\hat{\mathbf{r}}_i). \end{aligned}$$

Thus the field $-a(\mathbf{r})$ is a *1-particle potential*.

The state sum Z can be thought to be a function of variables $\{a_\alpha\}$ or a functional of the function $a(\mathbf{r})$:

$$Z = Z(\{a_\alpha\}) \xrightarrow{\text{continuum}} Z[a(\mathbf{r})].$$

Now

$$\langle \hat{N}_\alpha \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial a_\alpha}$$

and in the continuum limit

$$\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle = \frac{1}{\beta} \frac{\delta \ln Z}{\delta a(\mathbf{r})}.$$

We define the *density-density response function* χ so that

$$\chi_{\alpha\beta} = \frac{\partial \langle \hat{N}_\alpha \rangle}{\partial a_\beta} \approx \beta \langle \delta \hat{N}_\alpha \delta \hat{N}_\beta \rangle$$

and in the continuum limit

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}') &= \frac{\delta \langle \hat{\rho}(\mathbf{r}) \rangle}{\delta a(\mathbf{r}')} \\ &\approx \beta \langle \delta \hat{\rho}(\mathbf{r}) \delta \hat{\rho}(\mathbf{r}') \rangle. \end{aligned}$$

Here

$$\delta \hat{\rho}(\mathbf{r}) = \hat{\rho}(\mathbf{r}) - \langle \hat{\rho}(\mathbf{r}) \rangle = \hat{\rho}(\mathbf{r}) - \rho(\mathbf{r})$$

is the fluctuation of the density.

The approximativity of the last formulas is due to the non commutativity the Hamiltonian with the operators $\delta \hat{\rho}(\mathbf{r})$ and $\delta \hat{\rho}(\mathbf{r}')$.

Pair correlation function

We restrict to homogeneous matter. Then

$$\langle \hat{\rho}(\mathbf{r}) \rangle = \rho(\mathbf{r}) = \rho.$$

Let us consider the function

$$\begin{aligned} \langle \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') \rangle &= \sum_i \langle \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \delta(\mathbf{r}' - \hat{\mathbf{r}}_i) \rangle \\ &\quad + \sum_{i \neq j} \langle \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \delta(\mathbf{r}' - \hat{\mathbf{r}}_j) \rangle \\ &= \delta(\mathbf{r} - \mathbf{r}') \langle \hat{\rho}(\mathbf{r}) \rangle \\ &\quad + \sum_{i \neq j} \langle \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \delta(\mathbf{r}' - \hat{\mathbf{r}}_j) \rangle. \end{aligned}$$

We define the *pair correlation function* $g(\mathbf{r} - \mathbf{r}')$ so that

$$\langle \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') \rangle = \rho \delta(\mathbf{r} - \mathbf{r}') + \rho^2 g(\mathbf{r} - \mathbf{r}')$$

or

$$\rho^2 g(\mathbf{r} - \mathbf{r}') = \sum_{i \neq j} \langle \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \delta(\mathbf{r}' - \hat{\mathbf{r}}_j) \rangle.$$

It can be shown that in a homogenous pure state $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of N particles one has

$$g(\mathbf{r} - \mathbf{r}') = \frac{N(N-1)}{\rho^2} \times \int d\mathbf{r}_3 \cdots \int d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2.$$

We see that

- $g(\mathbf{r} - \mathbf{r}')$ is proportional to the probability for finding two different particles at the points \mathbf{r} and \mathbf{r}' .
- since simultaneous events far away from each other cannot be correlated we have

$$\lim_{|\mathbf{r} - \mathbf{r}'| \rightarrow \infty} \langle \hat{A}(\mathbf{r}) \hat{B}(\mathbf{r}') \rangle \longrightarrow \langle \hat{A}(\mathbf{r}) \rangle \langle \hat{B}(\mathbf{r}') \rangle$$

so

$$\lim_{|\mathbf{r} - \mathbf{r}'| \rightarrow \infty} g(\mathbf{r} - \mathbf{r}') = 1.$$

The function

$$G^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(\mathbf{r}_1 - \mathbf{r}_2)$$

is called the *pair distribution function*. Distribution functions of higher rank are defined analogously. In particular, for a pure state the distribution function of rank (degree) n is

$$\begin{aligned} G^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) &= \\ N(N-1)(N-2) \cdots (N-n+1) \times \\ \int d\mathbf{r}_{n+1} \cdots \int d\mathbf{r}_N |\psi(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{r}_{n+1}, \dots, \mathbf{r}_N)|^2. \end{aligned}$$

The pair correlation function (like the higher rank functions) can be generalized for nonhomogenous systems, for example, in a pure state we have

$$\begin{aligned} \rho(\mathbf{r}) \rho(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') &= \\ N(N-1) \int d\mathbf{r}_3 \cdots \int d\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2. \end{aligned}$$

Compressibility

In the classical limit the density-density response function is

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}') &= \beta \langle \delta \hat{\rho}(\mathbf{r}) \delta \hat{\rho}(\mathbf{r}') \rangle \\ &= \beta \langle (\hat{\rho}(\mathbf{r}) - \rho)(\hat{\rho}(\mathbf{r}') - \rho) \rangle \\ &= \beta \langle \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') \rangle - \beta \rho^2 \\ &= \beta [\rho \delta(\mathbf{r} - \mathbf{r}') + \rho^2 g(\mathbf{r} - \mathbf{r}')] - \beta \rho^2 \end{aligned}$$

or

$$\chi(\mathbf{r} - \mathbf{r}') = \beta \rho \delta(\mathbf{r} - \mathbf{r}') + \beta \rho^2 [g(\mathbf{r} - \mathbf{r}') - 1].$$

Its Fourier transform

$$\chi(\mathbf{q}) = \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} \chi(\mathbf{r})$$

is

$$\chi(\mathbf{q}) = \beta \rho + \beta \rho^2 \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} [g(\mathbf{r}) - 1].$$

The *structure function* $S(\mathbf{q})$ is defined so that

$$\begin{aligned} S(\mathbf{q}) &= \frac{1}{N} \langle \delta \hat{\rho}(\mathbf{q}) \delta \hat{\rho}(-\mathbf{q}) \rangle \\ &= 1 + \rho \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} [g(\mathbf{r}) - 1]. \end{aligned}$$

Now

$$\begin{aligned} \delta \hat{\rho}(\mathbf{q})^\dagger &= \left[\int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} \delta \hat{\rho}(\mathbf{r}) \right]^\dagger \\ &= \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \delta \hat{\rho}(\mathbf{r}) = \delta \hat{\rho}(-\mathbf{q}), \end{aligned}$$

so $S(\mathbf{q})$ is a real and non negative function of the variable q .

According to the definition of the response we have

$$\delta \langle \hat{\rho}(\mathbf{r}) \rangle = \int d\mathbf{r}' \chi(\mathbf{r} - \mathbf{r}') \delta a(\mathbf{r}').$$

Its Fourier transform is

$$\delta \rho(\mathbf{q}) = \chi(\mathbf{q}) \delta a(\mathbf{q}).$$

We suppose that $\delta a(\mathbf{r}')$ is constant. Then we can interpret that

$$\delta a(\mathbf{r}') = \delta \mu$$

is a change in the chemical potential, so

$$\delta \rho(\mathbf{r}) = \frac{\delta N}{V} = \delta \mu \int d\mathbf{r}' \chi(\mathbf{r} - \mathbf{r}') = \delta \mu \lim_{q \rightarrow 0} \chi(\mathbf{q}).$$

We see that

$$\lim_{q \rightarrow 0} \chi(\mathbf{q}) = \frac{1}{V} \left(\frac{\partial N}{\partial \mu} \right)_{T,V}.$$

It follows from Maxwell's relations that

$$\left(\frac{\partial N}{\partial \mu} \right)_{T,V} = \frac{1}{V} N^2 \kappa_T,$$

where κ_T is the compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N}.$$

Thus we get

$$\lim_{q \rightarrow 0} \chi(\mathbf{q}) = \rho^2 \kappa_T$$

or

$$1 + \rho \int d\mathbf{r} [g(\mathbf{r}) - 1] = \rho k_B T \kappa_T.$$

Fluctuation dissipation theorem

We suppose that fields $a_\alpha(t)$ are time dependent. Then also the Hamiltonian

$$\hat{H}(t) = \hat{H}_0 - \sum_{\alpha} \hat{A}_{\alpha} a_{\alpha}(t)$$

depends on time.

Let

$$\hat{A}(t) = e^{\frac{i}{\hbar} \hat{H}_0 t} \hat{A} e^{-\frac{i}{\hbar} \hat{H}_0 t}$$

be the Heisenberg picture of the operator \hat{A} . We use the notation

$$\langle \dots \rangle^0 = \text{Tr } \hat{\rho}_0 \dots$$

for expectation values in undisturbed states.

It can be shown that in the linear limit one gets

$$\begin{aligned} \delta A_{\alpha}(t) &\equiv \text{Tr } \delta \hat{\rho}(t) \hat{A}_{\alpha} \\ &= \sum_{\beta} \int_{-\infty}^{\infty} dt' \chi_{\alpha\beta}(t-t') a_{\beta}(t'), \end{aligned}$$

where

$$\chi_{\alpha\beta}(t-t') = \frac{i}{\hbar} \theta(t-t') \left\langle \left[\hat{A}_{\alpha}(t), \hat{A}_{\beta}(t') \right] \right\rangle^0.$$

Because

$$[\delta \hat{A}, \delta \hat{B}] = [\hat{A} - \langle \hat{A} \rangle, \hat{B} - \langle \hat{B} \rangle] = [\hat{A}, \hat{B}],$$

we can in fact write

$$\chi_{\alpha\beta}(t-t') = \frac{i}{\hbar} \theta(t-t') \left\langle \left[\delta \hat{A}_{\alpha}(t), \delta \hat{A}_{\beta}(t') \right] \right\rangle^0,$$

i.e. the response function depends only on the fluctuating parts of the operator.

The Fourier transform with respect to time is defined as

$$\chi_{\alpha\beta}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \chi_{\alpha\beta}(t).$$

The inverse transform is then

$$\chi_{\alpha\beta}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \chi_{\alpha\beta}(\omega).$$

We rewrite the response function as

$$\chi_{\alpha\beta}(t-t') = 2i\theta(t-t') \chi''_{\alpha\beta}(t-t'),$$

where

$$\chi''_{\alpha\beta}(t-t') = \frac{1}{2\hbar} \left\langle \left[\delta \hat{A}_{\alpha}(t), \delta \hat{A}_{\beta}(t') \right] \right\rangle^0.$$

It can be shown that $\chi_{\alpha\beta}(\omega)$ is analytic in the half plane $\text{Im}\omega \geq 0$ and that

$$\chi_{\alpha\beta}(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\chi''_{\alpha\beta}(\omega')}{\omega' - \omega - i0},$$

where $i0$ stands for an infinitesimal imaginary number.

The static response or *susceptibility* is

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}(\omega = 0) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{\chi''_{\alpha\beta}(\omega)}{\omega}.$$

This is the microscopic form of thermodynamic response functions.

The time dependent correlation function $C_{\alpha\beta}(t-t')$ is defined as

$$C_{\alpha\beta}(t-t') = \left\langle \delta \hat{A}_{\alpha}(t) \delta \hat{A}_{\beta}(t') \right\rangle^0.$$

So we can write the response function like

$$\chi_{\alpha\beta}(t-t') = \frac{i}{\hbar} \theta(t-t') [C_{\alpha\beta}(t-t') - C_{\beta\alpha}(t'-t)].$$

One can show that in the frequency space one has

$$C_{\alpha\beta}(\omega) = \frac{2\hbar}{1 - e^{-\beta\hbar\omega}} \chi''_{\alpha\beta}(\omega).$$

This relation is called the *fluctuation dissipation theorem*, since

- the left side, $C_{\alpha\beta}(\omega)$, describes spontaneous fluctuations of the system.
- it can be shown that an external field oscillating with the frequency ω loses energy with the power $\omega \chi''_{\alpha\beta}(\omega)$, i.e. the right side is associated with dissipations.

Pair correlation function and equation of state

We consider homogenous matter. According to the definition of the pair correlation,

$$\rho^2 g(\mathbf{r} - \mathbf{r}') = \sum_{i \neq j} \langle \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \delta(\mathbf{r}' - \hat{\mathbf{r}}_j) \rangle,$$

we have in a classical system

$$\begin{aligned}
\rho^2 g(\mathbf{r} - \mathbf{r}') &= \frac{1}{Z_N} \sum_{i \neq j} \int d\Gamma \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) e^{-\beta H} \\
&= \frac{1}{Q_N} \sum_{i \neq j} \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_{i-1} \times \\
&\quad \int d\mathbf{r}_{i+1} \cdots \int d\mathbf{r}_{j-1} \times \\
&\quad \int d\mathbf{r}_{j+1} \cdots \int d\mathbf{r}_N e^{-\beta \sum_{k < l} v_{kl}} \\
&= \frac{N(N-1)}{Q_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta \sum_{i < j} v_{ij}}.
\end{aligned}$$

The pressure is

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

where

$$E = \langle H \rangle$$

is the expectation value of the energy.

We think that the system is bounded by an L -sided cube. then

$$p = -\frac{\partial E}{\partial V} = -\frac{1}{3L^2} \frac{\partial E}{\partial L}$$

and we can write

$$\begin{aligned}
3pV &= -L \frac{\partial E}{\partial L} = -L \lim_{\epsilon \rightarrow 0} \frac{E_{L(1+\epsilon)} - E_L}{\epsilon L} \\
&= -\lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \langle H_{L(1+\epsilon)} - H_L \rangle,
\end{aligned}$$

where $H_{\lambda L}$ stands for the Hamiltonian in a λL -sided cube and $E_{\lambda L}$ for the corresponding expectation value.

When we restrict to linear terms in ϵ we obviously have

$$E_{L(1+\epsilon)} = E_L + \langle H_{L(1+\epsilon)} - H_L \rangle_{H_L} + \mathcal{O}(\epsilon^2).$$

Here $\langle \cdots \rangle_{H_L}$ means that the expectation value is evaluated in a L -sided cube with the weight $e^{-\beta H_L}$.

The Hamiltonian $H_{L(1+\epsilon)}$ deviates from H_L only in that the coordinates x_i , y_i and z_i can have values between $[0, L(1+\epsilon)]$, while in H_L they are restricted to $[0, L]$. We rewrite the Hamiltonian $H_{L(1+\epsilon)}$ with the help of the scaled variables

$$\mathbf{r}'_i = \frac{1}{1+\epsilon} \mathbf{r}_i$$

like

$$\begin{aligned}
H_{L(1+\epsilon)} &= \sum_i \frac{\mathbf{p}'_i{}^2}{2m(1+\epsilon)^2} + \sum_{i < j} v((1+\epsilon)r'_{ij}) \\
&\approx \sum_i \frac{\mathbf{p}'_i{}^2}{2m} + \sum_{i < j} v(r'_{ij}) \\
&\quad + \epsilon \left[-2 \sum_i \frac{\mathbf{p}'_i{}^2}{2m} + \sum_{i < j} r'_{ij} v'(r'_{ij}) \right]
\end{aligned}$$

. Here we have used the relation

$$\mathbf{p}' = -i\hbar \nabla_{\mathbf{r}'} = (1+\epsilon)\mathbf{p}.$$

Since the new, primed, coordinates span the same range as the originals we can replace the new ones with the originals.

Now

$$\langle H_{L(1+\epsilon)} - H_L \rangle_{H_L} = \epsilon \left[-2 \langle T \rangle + \left\langle \sum_{i < j} r_{ij} v'(r_{ij}) \right\rangle \right],$$

where $\langle T \rangle$ is the expectation value of the energy. For the equation of state we get

$$3pV = 2 \langle T \rangle - \left\langle \sum_{i < j} r_{ij} v'(r_{ij}) \right\rangle.$$

Now the kinetic energy is same as for the ideal gas, i.e.

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

The latter term is evaluated like:

$$\begin{aligned}
\left\langle \sum_{i < j} r_{ij} v'(r_{ij}) \right\rangle &= \frac{N(N-1)}{2} \langle r_{12} v'(r_{12}) \rangle \\
&= \frac{N(N-1)}{2Q_N} \int d\mathbf{r}_1 d\mathbf{r}_2 r_{12} v'(r_{12}) \times \\
&\quad \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta \sum_{i < j} v(r_{ij})} \\
&= \frac{V}{2} \rho^2 \int d\mathbf{r}_{12} r_{12} v'(r_{12}) g(r_{12}).
\end{aligned}$$

Thus the equation of state is

$$pV = N k_B T - \frac{2\pi V}{3} \rho^2 \int dr r^3 v'(r) g(r).$$

The internal energy of the system

$$E = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{3}{2} N k_B T - \frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta}$$

can also be expressed with the help of the pair correlation. Now

$$\begin{aligned}
\frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta} &= -\frac{1}{Q_N} \sum_{k < l} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N v(r_{kl}) \times \\
&\quad e^{-\beta \sum_{i < j} v(r_{ij})} \\
&= -\frac{1}{2} \frac{N(N-1)}{Q_N} \int d\mathbf{r}_1 d\mathbf{r}_2 v(r_{12}) \times \\
&\quad \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta \sum_{i < j} v(r_{ij})} \\
&= -\frac{1}{2} \rho^2 \int d\mathbf{r}_1 d\mathbf{r}_2 v(r_{12}) g(r_{12}),
\end{aligned}$$

or the internal energy is

$$E = \frac{3}{2} N k_B T + 2\pi V \rho^2 \int dr r^2 v(r) g(r).$$

We see that the thermodynamic properties of the system are determined by the pair correlation.

Approximating the pair correlation

To evaluate the state sum Z_N we have to perform $3N$ -fold integration. Correspondingly, for the pair correlation, or for the pair distribution

$$\begin{aligned} G^{(2)}(r_{12}) &= \rho^2 g(r_{12}) \\ &= \frac{N(N-1)}{Q_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta \sum_{i<j} v(r_{ij})}, \end{aligned}$$

we need $3N - 6$ integrations. In macroscopic systems N is of order 10^{23} , so the evaluation of both of them is equally tough. Like for the partition sum one can develop approximative methods for the pair correlation.

We rewrite $G^{(2)}$ like

$$G^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{Q_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \times e^{-\beta \sum_{i \neq 1} v(r_{1i})} e^{-\beta \sum_{1 < i < j} v(r_{ij})}.$$

Its gradient with respect to \mathbf{r}_1 is

$$\begin{aligned} \nabla_1 G^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= -\frac{\beta N(N-1)}{Q_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \times \\ &\quad \left[\nabla_1 v(r_{12}) + \sum_{i>2} \nabla_1 v(r_{1i}) \right] \times \\ &\quad e^{-\beta \sum_{i<j} v(r_{ij})}. \end{aligned}$$

We employ the *three body distribution*

$$G^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{N(N-1)(N-2)}{Q_N} \int d\mathbf{r}_4 \cdots d\mathbf{r}_N e^{-\beta \sum_{i<j} v(r_{ij})}.$$

Now we can write

$$\begin{aligned} \nabla_1 G^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \\ &= -\beta \nabla_1 v(r_{12}) G^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\ &= -\beta \int d\mathbf{r}_3 \nabla_1 v(r_{13}) G^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3). \end{aligned}$$

This equation is known as the *Born-Green equation*.

Repeating the procedure described above one can derive a relation which expresses $\nabla_1 G^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ as a functional of the four body distribution $G^{(4)}$. Continuing further we would get a recursive chain of relations binding together the n - and $n+1$ -body distributions. To exploit the hierarchy of the relations we have to cut the chain somewhere.

In the *Kirkwood approximation* one supposes that

$$G^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \longrightarrow G^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rho,$$

when \mathbf{r}_3 moves far from the points \mathbf{r}_1 and \mathbf{r}_2 . Since $G^{(3)}$ is symmetric with respect to its arguments one can write

$$\begin{aligned} G^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \\ &= \frac{1}{\rho^3} G^{(2)}(\mathbf{r}_1, \mathbf{r}_2) G^{(2)}(\mathbf{r}_2, \mathbf{r}_3) G^{(2)}(\mathbf{r}_3, \mathbf{r}_1). \end{aligned}$$


This is known as the *Kirkwood approximation* or as the *superposition approximation*.

One can also derive diagram expansions for the pair correlation. Since $g(\mathbf{r})$ is a non negative function it can be written as

$$g(\mathbf{r}) = e^{-\beta v(\mathbf{r}) + B(\mathbf{r})}.$$

We define the graphical elements:

$$\begin{aligned} \circ^{\mathbf{r}} &\Leftrightarrow \text{free variable } \mathbf{r} \\ \bullet^{\mathbf{r}} &\Leftrightarrow \int d\mathbf{r} \\ \mathbf{r} \text{ --- } \mathbf{r}' &\Leftrightarrow h(\mathbf{r}, \mathbf{r}') = g(\mathbf{r} - \mathbf{r}') - 1. \end{aligned}$$

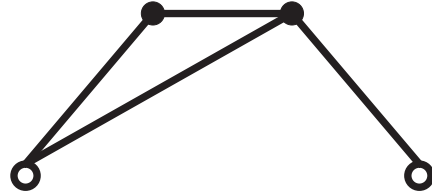


$$= \int d\mathbf{r}_1 h(\mathbf{r}, \mathbf{r}_1) h(\mathbf{r}_1, \mathbf{r}').$$

In the relevant graphs

- there are two white points $\circ^{\mathbf{r}}$ and $\circ^{\mathbf{r}'}$ together with one or more black points, $\bullet^{\mathbf{r}_i}$.
- there is no direct link (—) from one white point to the other white point.
- there is a path from every point to every other point, i.e. they are connected.

One can show that $B(\mathbf{r})$ is the sum of all these graphs.



Thus this graph expansion of $B(\mathbf{r})$ depends on the pair correlation $g(\mathbf{r})$. Provided that we can sum the graph expansion, we can solve g iteratively:

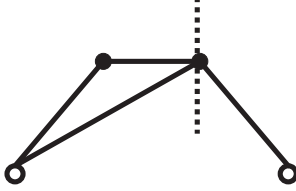
1. guess $g(\mathbf{r})$.
2. evaluate $B(\mathbf{r})$ using the graph expansion.
3. new $g(\mathbf{r})$ is now

$$g(\mathbf{r}) = e^{-\beta v(\mathbf{r}) + B(\mathbf{r})}.$$

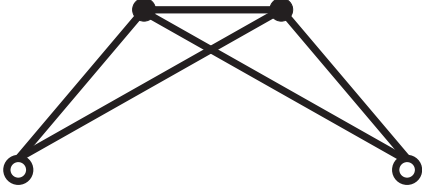
4. if the new and old ones deviate from each other remarkably we continue from 2.

We divide the graphs in the expansion of $B(r)$ into two classes:

- *nodal graphs* are such diagrams that can be splitted into two or more uncoupled parts by cutting them at some black point.



- *bridge or elementary diagrams* cannot be separated in parts by cutting them at any black point.



We rewrite the pair correlation as

$$g(r) = e^{-\beta v(r) + N(r) + E(r)},$$

where $N(r)$ is the sum of the nodal diagrams $E(r)$ the sum of the elementary diagrams.

The *HNC* (*HyperNetted Chain*) approximation assumes that $E(r)$ is insignificant, i.e.

$$g(r) \approx e^{-\beta v(r) + N(r)}.$$

It can be shown that the nodal diagrams can be summed. They satisfy the *Ornstein-Zernike relation*

$$N(r) = \rho \int d\mathbf{r}' [g(|\mathbf{r} - \mathbf{r}'|) - 1 - N(|\mathbf{r} - \mathbf{r}'|)] [g(\mathbf{r}') - 1].$$

Via Fourier transformation we end up with the algebraic relation

$$\tilde{N}(k) = \frac{(S(k) - 1)^2}{S(k)},$$

where $S(k)$ is the structure function and

$$\tilde{N}(k) = \rho \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} N(r).$$

Jastrow's theory

Although the previous cumulant expansion and approximative methods for the pair correlation are valid only for a classical system it turns out that these methods are useful also in quantum mechanical systems.

We consider *the ground state* of N identical particles (the temperature is $T = 0$), so the system is in a pure quantum state Ψ .

We suppose that, due to the interactions, the particles are strongly correlated, i.e. the independent particle model is not applicable. A good guess for the ground state wave function is then the function, known as the *Jastrow trial*,

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) \prod_{1 \leq i < j \leq N} f(|\mathbf{r}_i - \mathbf{r}_j|).$$

Here the *pair correlation*

$$f_{ij} = f(|\mathbf{r}_i - \mathbf{r}_j|)$$

describes the mutual correlation between the particles. Since the factor

$$F = \prod_{1 \leq i < j \leq N} f_{ij}$$

is symmetric with respect to the exchange of particles the possible Fermionic character is embedded into the function Φ :

- for bosons

$$\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) \equiv 1.$$

- for fermions Φ is, for example, the Slater determinant of N non interacting particles and thus antisymmetric with respect to the exchange of particles.

When Φ takes care of the statistics we can suppose that in the ground state F is real (in fact we could assume that F is positive since the ground state wave function has no zeros).

The Hamiltonian operator of the system is

$$H = - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} v(|\mathbf{r}_i - \mathbf{r}_j|).$$

We evaluate its expectation value in the state

$$\Psi = F\Phi.$$

One can easily see (integrating by parts) that

$$\begin{aligned} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \Psi^* \nabla_i^2 \Psi = \\ \frac{1}{4} \int d\mathbf{r}_1 \dots d\mathbf{r}_N |\Psi|^2 \nabla_i^2 \ln F^2 \\ - \frac{1}{4} \int d\mathbf{r}_1 \dots d\mathbf{r}_N F^2 \nabla_i^2 |\Phi|^2 \\ + \int d\mathbf{r}_1 \dots d\mathbf{r}_N F^2 \Phi^* \nabla_i^2 \Phi. \end{aligned}$$

This relation is known as the *Jackson-Feenberg energy form*.

Employing the pair distribution

$$g(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{N(N-1)}{\rho^2 \langle \Psi | \Psi \rangle} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N |\Psi|^2$$

and writing

$$f_{ij}^2 = e^{u_{ij}}$$

we get for the expectation of the kinetic energy

$$\begin{aligned} \langle T \rangle &= \left\langle -\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 \right\rangle \\ &= -\frac{1}{\langle \Psi | \Psi \rangle} \frac{\hbar^2}{2m} \sum_{i=1}^N \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi^* \nabla_i^2 \Psi \\ &= -N\rho \frac{\hbar^2}{8m} \int d\mathbf{r} g(r) \nabla^2 u(r) + T_\Phi, \end{aligned}$$

where T_Φ is composed of the Fermionic terms $\int d\mathbf{r}_1 \cdots d\mathbf{r}_N F^2 \nabla_i^2 |\Phi|^2$ and $\int d\mathbf{r}_1 \cdots d\mathbf{r}_N F^2 \Phi^* \nabla_i^2 \Phi$. The expectation value of the potential energy will be correspondingly

$$\begin{aligned} \langle v \rangle &= \left\langle \frac{1}{2} \sum_{i \neq j} v_{ij} \right\rangle \\ &= \frac{1}{\langle \Psi | \Psi \rangle} \frac{1}{2} \sum_{i \neq j} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N |\Psi|^2 v_{ij} \\ &= N\rho \frac{1}{2} \int d\mathbf{r} g(r) v(r). \end{aligned}$$

Thus the energy per particle is

$$\epsilon = -\frac{\hbar^2}{8m} \rho \int d\mathbf{r} g(r) \nabla^2 u(r) + \frac{1}{2} \rho \int d\mathbf{r} g(r) v(r) + \frac{1}{N} T_\Phi.$$

Supposing that the particles are bosons the pair distribution can be written as

$$\rho^2 g(r_{12}) = \frac{N(N-1)}{\langle \Psi | \Psi \rangle} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{\sum_{i < j} u_{ij}}.$$

This is exactly the same as in the classical system. Now, however, the potential term $-\beta v_{ij}$ is replaced with the correlation factor $u_{ij} = \ln f_{ij}^2$. So, we can apply diagram expansions of classical systems. In particular we can write

$$g(r) = e^{u(r) + N(r) + E(r)},$$

where $N(r)$ is the sum of the nodal diagrams and $E(r)$ stands for the contribution of the elementary diagrams. In HNC-approximation we write

$$g(r) \approx e^{u(r) + N(r)}.$$

A corresponding approximation can be derived also for Fermionic systems but then the nodal and bridge diagrams are not composed only of black and white points and connecting links. That approximation is called

the FHNC (*Fermi HyperNetted Chain*) approximation. In the following we consider only bosonic systems. Unlike in the classical systems the function $u(r)$ is now unknown. We use the HNC equation to eliminate u from the energy expression. For one particle energy we get

$$\begin{aligned} \epsilon &\approx -\frac{\hbar^2}{8m} \rho \int d\mathbf{r} g(r) \nabla^2 \ln g(r) \\ &\quad + \frac{\hbar^2}{8m} \rho \int d\mathbf{r} g(r) \nabla^2 N(r) \\ &\quad + \frac{1}{2} \rho \int d\mathbf{r} g(r) v(r). \end{aligned}$$

Since the functions $N(r)$ and $g(r)$ are related by the Ornstein-Zernike relation

$$N(r) = \rho \int d\mathbf{r}' [g(r') - 1 - N(r')][g(|\mathbf{r} - \mathbf{r}'|) - 1],$$

one can take the energy ϵ as a functional of the pair distribution $g(r)$ only. It turns out that in fact a more convenient variable is $\sqrt{g(r)}$, so

$$\epsilon = \epsilon[\sqrt{g}].$$

As well known, the ground state wave function is that Ψ , whose expectation value

$$\langle H \rangle = \frac{1}{\langle \Psi | \Psi \rangle} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi^* H \Psi$$

is minimized. We now seek the minimum of the expectation of the Hamiltonian among all the functions of Jastrow form. Equivalently, find out such a \sqrt{g} , that the energy $\epsilon[\sqrt{g}]$ attains its minimum. A condition for the existence of the extremum is that the variation

$$\delta\epsilon = \epsilon[\sqrt{g} + \delta\sqrt{g}] - \epsilon[\sqrt{g}]$$

vanishes up to linear order in $\delta\sqrt{g}$.

A straightforward calculation shows that

$$\delta\epsilon = \int d\mathbf{r} L[\sqrt{g(r)}] \delta\sqrt{g(r)},$$

where

$$L[\sqrt{g(r)}] = -\frac{\hbar^2}{2m} \nabla^2 \sqrt{g(r)} + v(r) \sqrt{g(r)} + W(r) \sqrt{g(r)}.$$

In order $\delta\epsilon$ to vanish independent on the variation $\delta\sqrt{g}$, the coefficient L must vanish, i.e.

$$-\frac{\hbar^2}{2m} \nabla^2 \sqrt{g(r)} + v(r) \sqrt{g(r)} + W(r) \sqrt{g(r)} = 0.$$

The function $W(r)$ is the so called induced potential. Its Fourier transform is

$$\begin{aligned} W(k) &= \rho \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} W(r) \\ &= -\frac{\hbar^2 k^2}{2m} \frac{(S-1)^2 (2S+1)}{S^2}. \end{aligned}$$

Although the above *Euler-Lagrange equation* for \sqrt{g} looks like a Schrödinger equation at 0 energy it is

- strongly nonlinear since the induced potential W depends (nonlinearly) on the structure factor S , which in turn depends via the (linear) Fourier transform on $(\sqrt{g})^2$.
- solvable only numerically. There are several solution methods but they all are iterative.
- an equation for the ground state only. Even if there are more solutions the solutions associated with other energies have no physical meaning.

In the Jastrow theory the excited states are constructed explicitly. For example

- let *every* particle in the system have the momentum $\hbar k$, i.e.
- excite the particle i with the operator $e^{i\mathbf{k}\cdot\hat{\mathbf{r}}_i}$.
- every particle is excited with the *same* phase, i.e.
- if the ground state is Ψ_0 the excited state is

$$\begin{aligned}\Psi_k &= \left[\sum_{i=1}^N e^{i\mathbf{k}\cdot\hat{\mathbf{r}}_i} \right] \Psi_0 \\ &= \hat{\rho}(\mathbf{k}) \Psi_0,\end{aligned}$$

where $\hat{\rho}(\mathbf{k})$ is the Fourier transform of the density operator

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\hat{\mathbf{r}}_i - \mathbf{r}).$$

One can show that for bosons this kind of *collective excitation* Ψ_k in the long wave length (small wave vector k) limit is energetically most favorable. The excitation energy can be obtained evaluating the expectation

$$E_k = \langle H \rangle_{\Psi_k} = \frac{\langle \Psi_k | H | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle}.$$

A straightforward calculation shows that

$$E_k = E_0 + \frac{\hbar^2 k^2}{2mS(k)},$$

when E_0 is the energy of the ground state Ψ_0 . The excitation energy is thus

$$\epsilon_k = E_k - E_0 = \frac{\hbar^2 k^2}{2mS(k)}.$$

These kind of excitations and corresponding excitation energies are called *Bijl-Feynman excitations*.

Density fluctuations and correlation length

Let's consider the canonical partition sum

$$Z_N = e^{-\beta F_N} = \text{Tr}_N e^{-\beta \hat{H}},$$

where F_N is the free energy. We divide the volume into elements V_α , whose particle numbers are

$$N_\alpha = 0, 1, 2, \dots$$

Let $\delta(\hat{N}_\alpha, N_\alpha)$ be an operator satisfying

$$\delta(\hat{N}_\alpha, N_\alpha) |N\rangle = \begin{cases} |N\rangle, & \text{if } \hat{N}_\alpha |N\rangle = N_\alpha |N\rangle \\ 0, & \text{if } \hat{N}_\alpha |N\rangle \neq N_\alpha |N\rangle, \end{cases}$$

i.e. $\delta(\hat{N}_\alpha, N_\alpha)$ is the Kronecker delta function. The identity operator operating in the volume element α can be written as

$$\hat{I}_\alpha = \sum_{N_\alpha=0}^{\infty} \delta(\hat{N}_\alpha, N_\alpha).$$

The identity operator of the whole system can be written, for example, as

$$\begin{aligned}\hat{I} &= \prod_{\alpha} \hat{I}_\alpha = \prod_{\alpha} \left[\sum_{N_\alpha=0}^{\infty} \delta(\hat{N}_\alpha, N_\alpha) \right] \\ &= \sum_{\{N_\alpha\}} \prod_{\alpha} \delta(\hat{N}_\alpha, N_\alpha).\end{aligned}$$

Here $\sum_{\{N_\alpha\}}$ stands for the summation over all possible configurations, i.e.

$$\sum_{\{N_\alpha\}} [\dots] = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \dots [\dots].$$

The partition sum is now

$$\begin{aligned}Z_N &= \text{Tr}_N e^{-\beta \hat{H}} \\ &= \text{Tr}_N \sum_{\{N_\alpha\}} \prod_{\alpha} \delta(\hat{N}_\alpha, N_\alpha) e^{-\beta \hat{H}} \\ &= \sum_{\{N_\alpha\}} \text{Tr} \prod_{\alpha} \delta(\hat{N}_\alpha, N_\alpha) e^{-\beta \hat{H}} \\ &= \sum_{\{N_\alpha\}} e^{-\beta \tilde{F}_N}.\end{aligned}$$

Here

$$\begin{aligned}e^{-\beta \tilde{F}_N} &= \text{Tr} \prod_{\alpha} \delta(\hat{N}_\alpha, N_\alpha) e^{-\beta \hat{H}} \\ &= \text{Tr}_{\{N_\alpha\}} e^{-\beta \hat{H}},\end{aligned}$$

where $\text{Tr}_{\{N_\alpha\}}$ means that in the evaluation of the trace the summation is over all microscopical degrees of freedom keeping, however, the particle numbers N_α constant and fixing for the total number

$$N = \sum_{\alpha} N_\alpha.$$

The function

$$\tilde{F}_N = \tilde{F}_N(T, V, \{N_\alpha\})$$

is the free energy or the *reduced free energy* of the configuration $\{N_\alpha\}$.

The quantity $e^{-\beta\tilde{F}_N}$ is proportional to the probability for the configuration $\{N_\alpha\}$. Thus the most probable configuration is such where the reduced free energy $\tilde{F}_N(T, V, \{N_\alpha\})$ attains its minimum.

Density functional theory

In the continuum limit the configuration $\{N_\alpha\}$ is described by the density $\rho(\mathbf{r})$ and the reduced free energy will become a functional of the density:

$$\tilde{F}_N = \tilde{F}_N[\rho].$$

Now all the microscopical degrees of the freedom are reduced to the single density distribution. This kind of model is called the *density functional theory*.

Normally the reduced free energy cannot be calculated exactly. A phenomenological method is the *Local Density Approximation, LDA*:

- the reduced free energy is the volume integral of the *free energy density* f_N .
- the free energy density at every spatial point depends only on the local particle density and its low order derivatives at that particular point.

Thus the energy functional of the system is

$$\tilde{F}_N[\rho] = \int d\mathbf{r} f_N[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla\nabla\rho(\mathbf{r}), \dots].$$

If there is an external potential $u(\mathbf{r})$, there is the additional term $\int d\mathbf{r} u(\mathbf{r})\rho(\mathbf{r})$ in the functional.

As we noted above the most probable configuration corresponds to the minimum of the reduced free energy. We restrict to homogenous systems so that the constant density ρ_0 minimizes the functional $\tilde{F}_N[\rho]$. Let

$$\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$$

be a small deviation from the constant density. The simplest model for the variation of the energy functional is

$$\tilde{F}_N[\delta\rho] = \int d\mathbf{r} \left[f_0 + \frac{1}{2} f_1 (\delta\rho(\mathbf{r}))^2 + \frac{1}{2} f_2 (\nabla\delta\rho(\mathbf{r}))^2 \right],$$

where f_0 , f_1 and f_2 are constants independent on the position \mathbf{r} (but can depend on the temperature and the constant density ρ_0). In the expansion

- there is no linear term in the variation $\delta\rho$, since according to the hypothesis ρ_0 minimizes the energy.
- due to the minimum condition the coefficients f_1 and f_2 must be positive.

- the gradient term $(\nabla\rho)^2$ favors slowly varying densities, so the wave lengths of the density fluctuations cannot be arbitrary short. At points \mathbf{r} and \mathbf{r}' close to each other the deviations $\delta\rho(\mathbf{r})$ and $\delta\rho(\mathbf{r}')$ are roughly the same.
- physically the gradient term can be motivated by the tendency of the stochastic thermal motion to smooth down the density differences in close by volume elements. Thus the factor f_2 depends on the correlations of the particles in volumes close to each other.

Since the particle number is constant we have

$$\delta N = \int d\mathbf{r} \delta\rho(\mathbf{r}) = \delta\rho(\mathbf{q}=0) = 0,$$

and, with the help of the Fourier transform, the free energy can be written as

$$\tilde{F}_N = \tilde{F}_N^0 + \frac{1}{2V} \sum'_{\mathbf{q}} (f_1 + f_2 q^2) \delta\rho(\mathbf{q}) \delta\rho(-\mathbf{q}),$$

where $\sum'_{\mathbf{q}}$ means that the term $\mathbf{q}=0$ is not to be summed.

Since the variation $\delta\rho(\mathbf{r})$ is real its Fourier transform satisfies

$$\delta\rho(-\mathbf{q}) = \delta\rho(\mathbf{q})^*,$$

so

$$\delta\rho(\mathbf{q}) \delta\rho(-\mathbf{q}) = |\delta\rho(\mathbf{q})|^2.$$

The physical meaning of this term is that $\langle \delta\rho(\mathbf{q}) \delta\rho(-\mathbf{q}) \rangle$, as we recall, describes density correlations. the probability for the fluctuation $\delta\rho$ is now

$$\begin{aligned} P[\delta\rho] &\propto e^{-\beta\tilde{F}_N} \\ &\propto \exp \left[-\frac{1}{2k_B T V} \sum'_{\mathbf{q}} (f_1 + f_2 q^2) |\delta\rho(\mathbf{q})|^2 \right]. \end{aligned}$$

Correlation length

Since the distribution $P[\delta\rho]$ derived above is of Gaussian shape one can directly read from it the correlation function

$$\begin{aligned} \langle \delta\rho(\mathbf{q}) \delta\rho(-\mathbf{q}) \rangle &= \frac{k_B T V}{f_1 + f_2 q^2} \\ &= \frac{k_B T V}{f_2} \frac{1}{q^2 + q_c^2}, \end{aligned}$$

where

$$q_c^2 = \frac{f_1}{f_2}.$$

The density-density response $\chi(\mathbf{q})$ was defined so that

$$\chi(\mathbf{q}) = \beta \rho S(\mathbf{q}) = \frac{\beta}{V} \langle \delta\rho(\mathbf{q}) \delta\rho(-\mathbf{q}) \rangle,$$

when $S(\mathbf{q})$ is the structure factor. So we get

$$\chi(\mathbf{q}) = \frac{1}{f_2} \frac{1}{q^2 + q_c^2}.$$

Its inverse Fourier transform is

$$\chi(r) = \frac{1}{f_2} \frac{1}{4\pi r} e^{-r/\xi}.$$

The parameter

$$\xi = \frac{1}{q_c} = \sqrt{\frac{f_2}{f_1}}$$

is the *correlation length*.

Since we had $\lim_{\mathbf{q} \rightarrow 0} \chi(\mathbf{q}) = \rho^2 \kappa_T$ we must have

$$f_1 = \frac{1}{\rho^2 \kappa_T},$$

so

$$f_2 = \frac{\xi^2}{\rho^2 \kappa_T}.$$

The pair correlation $h(r) = g(r) - 1$ can be written with the help of the density-density response (excluding the autocorrelation proportional to δ -function) as

$$h(r) = \frac{1}{\beta \rho^2} \chi(r).$$

We see that

$$h(r) = \frac{k_B T \kappa_T}{\xi^2} \frac{1}{4\pi r} e^{-r/\xi}.$$

Note The results are characteristically qualitative because they are derived using a nonmicroscopic model.

Scattering in medium

We consider the scattering of photons or massive particles in a medium. One can show that the intensity of the elastic scattering is proportional to the structure factor, i.e.

$$I(\mathbf{k}, \mathbf{q}) \propto S(\mathbf{q}) = \frac{1}{N} \langle \delta \hat{\rho}(\mathbf{q}) \delta \hat{\rho}(-\mathbf{q}) \rangle.$$

Here \mathbf{k} is the wave vector of the incoming particle and \mathbf{q} its change due to the scattering, i.e. the wave vector of the scattered particle is

$$\mathbf{k}' = \mathbf{k} - \mathbf{q}.$$

Since the scattering is elastic we have

$$|\mathbf{k}'| = |\mathbf{k}|.$$

The intensity of the inelastic scattering in turn is proportional to the dynamic structure factor:

$$I(\mathbf{k}; \mathbf{q}, \omega) \propto S(\mathbf{q}, \omega),$$

where \mathbf{q} the change in wave vector and $\hbar\omega$ in the energy.

When the temperature approaches the critical point from above the isothermal compressibility κ_T diverges, i.e. an infinitesimal change in the pressure causes an finite change in the volume. Then

$$f_1 = \frac{1}{\rho^2 \kappa_T^{\text{critical point}}} \longrightarrow 0.$$

On the other hand, there is no reason to assume that, for example, the correlations would become independent on the wave vector at the critical point, as would happen if

$$f_2 = \frac{\xi^2}{\rho^2 \kappa_T^{\text{critical point}}} \longrightarrow 0.$$

That's why we can suppose the correlation length ξ diverges at the critical point.

Consider elastic scattering of light. When the scattering angle is θ the change in the wave vector is

$$q = 2k \sin \frac{\theta}{2},$$

the wave length being

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

We see that the intensity is

$$I(\theta) \propto \frac{1}{f_1 + f_2 q^2} \propto \frac{1}{\sin^2 \frac{\theta}{2} + \left(\frac{\lambda}{4\pi\xi} \right)^2}.$$

Then at the critical point

$$I(\theta) \propto \frac{1}{\sin^2 \frac{\theta}{2}},$$

i.e. the scattering intensity is strongly peaked at forward directions and the total cross section ($\propto \int d\Omega I(\theta)$) diverges. Thus the radiation cannot pass through the medium: in the vicinity of the critical point transparent matter becomes opaque. The phenomenon is called the *critical opalescence*.

Discrete interaction models

We first consider interaction between atomic spins in a solid. Assuming that the atoms are bound to their lattice sites the spin degrees of freedom are independent on other degrees of freedom, that is

$$H \approx H_{\text{spin}} + H_{\text{other}}.$$

Now the state sum can be factorized:

$$Z = \text{Tr} e^{-\beta H} \approx Z_{\text{spin}} Z_{\text{other}}.$$

In the case where the factorization is not complete one can define the spin Hamiltonian

$$\begin{aligned} H_{\text{spin}} &= H(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_N) = H(\{\mathbf{s}_i\}) \\ &= -\frac{1}{\beta} \ln \text{Tr}_{\{\mathbf{s}_i\}} e^{-\beta H}. \end{aligned}$$

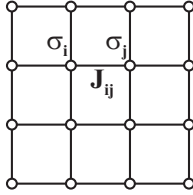
Here $\text{Tr}_{\{\mathbf{s}_i\}}$ means that the trace is evaluated keeping the spin configuration fixed. The total partition function is

$$Z = \text{Tr}^{\text{spin}} e^{-\beta H(\{\mathbf{s}_i\})},$$

where now the trace is over spins.

In the spin model

- the most important interactions are between nearest neighbours.
- the interactions are associated with the *links* connecting the lattice points.
- the spins associated with *the lattice points* are the dynamical variables.



In some cases it is possible to construct spin models also for continuum systems by discretizing the field variables. We denote the lattice points by i, j, \dots . If the spin quantum number of the particles in the model is s , the state sum is

$$\begin{aligned} Z &= \sum_{\{\sigma_i\}} e^{-\beta H(\{\mathbf{s}_i\})} \\ &= \sum_{\sigma_1=-s}^s \dots \sum_{\sigma_N=-s}^s e^{-\beta H(\{\mathbf{s}_i\})}. \end{aligned}$$

Heisenberg's model

In the external field \mathbf{B}_0 the Hamiltonian according to the Heisenberg model is

$$H = -\frac{1}{2} \sum_{ij} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j - \gamma \mathbf{B}_0 \cdot \sum_i \mathbf{s}_i$$

when the magnetic moment of the particles is

$$\boldsymbol{\mu}_i = \gamma \mathbf{s}_i.$$

We use notation $\langle ij \rangle$ for such spins i, j , which are closest neighbours of each other and count this kind of pair only once. We suppose further that the interactions do not depend on the lattice sites, i.e. $J_{ij} = J$. Then

$$H = -J \sum_{\langle ij \rangle} \mathbf{s}_i \cdot \mathbf{s}_j,$$

when the external field is $\mathbf{B}_0 = 0$.

Ferromagnetic coupling $J > 0$

The interaction favors parallel spins. One can easily see that the state

$$\bigotimes_i |\sigma_i = s\rangle = |s, s, \dots, s\rangle,$$

where the spins at all lattice points are parallel is the ground state.

Let z be the *coordination number* of the lattice (the number of nearest neighbours at each lattice point). For example, in the cubical lattice $z = 6$ and in the two dimensional square lattice $z = 4$. It is easy to see that the ground state energy is

$$E_0 = -N \frac{z}{2} J s^2.$$

Since the scalar product $\mathbf{s}_i \cdot \mathbf{s}_j$ is invariant under rotations the Hamiltonian of the system is also rotationally invariant. The ground state

- does not obey the symmetry of the Hamiltonian. It is said that a *spontaneous symmetry break* has occurred.
- is very degenerated. Rotating all spins equally we end up with a state with the same energy.

Antiferromagnetic coupling $J < 0$

The interaction favors neighbours with opposite spins. Supposing that opposite configurations were possible for all nearest neighbours the classical ground state energy were

$$E_0 = N \frac{z}{2} J s^2.$$

This kind state of alternating spins,

$$\bigotimes_i |\sigma_i = \pm s\rangle = |s, -s, s, \dots\rangle,$$

is, however, not a quantum mechanical eigenstate of the operator

$$\begin{aligned} H &= -J \sum_{\langle ij \rangle} \mathbf{s}_i \cdot \mathbf{s}_j \\ &= -\frac{J}{2} \sum_{\langle ij \rangle} [(\mathbf{s}_i + \mathbf{s}_j)^2 - \mathbf{s}_i^2 - \mathbf{s}_j^2] \end{aligned}$$

since the spin pairs are not coupled to eigenstates of the operator

$$\mathbf{s}_{ij}^2 = (\mathbf{s}_i + \mathbf{s}_j)^2.$$

The correct eigenstate can be solved only in the one dimensional system (so called *Bethe's Ansatz* method).

Ising's model

We simplify the Heisenberg model by restricting the spin quantum number to the case $s_i = \frac{1}{2}$ and taking into account only the z components. Then

$$H = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i,$$

where $\sigma_i = \pm 1$ and h is proportional to the external magnetic field.

The Ising model can be solved (i.e. the partition function evaluated) exactly for one and two dimensional systems. Analogical to Ising's model are for example

- *binary mixture* composed of two species of atoms, A ja B , where each lattice point is occupied by either A or B type atom.
- *lattice gas*, where at each lattice point there either is an atom or is nothing.

Potts' model

We let the spin take q different values,

$$\sigma_i = 1, 2, \dots, q,$$

but only the neighbouring spins in the same spin state are allowed to interact, i.e.

$$H = -J \sum_{\langle ij \rangle} \delta(\sigma_i, \sigma_j).$$

We see that this *Potts model* reduces to Ising's model when $q = 2$.

When the coupling is ferromagnetic ($J > 0$) the ground state is such that every spin is in the same state. The ground state is thus q -foldly degenerated. Hence at certain low temperature the system transforms to a phase where one of the values of the variable is dominant. The number of these ordered phases is q .

Spin glass

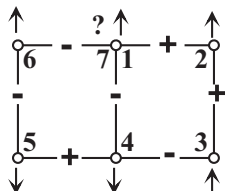
In the spin glass either the positions of atoms or their interactions (or both) vary randomly. For simplicity we assume that the spin glass Hamiltonian is of the form

$$H = - \sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j,$$

where the couplings J_{ij} are random quantities. The simplest choice is

$$J_{ii} = \pm J$$

the sign being stochastic. This is known as *Ising's spin glass*. In a system of this type there are *frustrations* i.e. going around a closed path along links setting the spins so that the energy of each link is minimized the last spin direction will differ from the one we started with. That's why all interactions cannot be minimized simultaneously and the ground state cannot be determined.



XY model

We confine the spins in the Heisenberg model to a two dimensional plane, i.e.

$$\mathbf{s}_i = s_{ix}\mathbf{i} + s_{iy}\mathbf{j}.$$

When the spins are treated classically the *XY model* Hamiltonian can be written as

$$H = -J \sum_{\langle ij \rangle} \cos \theta_{ij},$$

where $\theta_{ij} = \theta_i - \theta_j$ is the angle between neighbour spins. If the coupling is ferromagnetic, $J > 0$, all spins are parallel in the ground state. Then we can assume that at low temperatures the angles θ_i vary slowly as a function of the position. Thus one can write

$$\theta(\mathbf{r}_i + a\mathbf{i}) - \theta(\mathbf{r}_i) \approx a \frac{\partial \theta(x, y)}{\partial x}$$

and

$$\cos \theta_{ij} \approx 1 - \frac{1}{2} \theta_{ij}^2 \approx 1 - \frac{1}{2} a^2 \left(\frac{\partial \theta}{\partial x} \right)^2.$$

In the continuum limit we get the field theoretic model

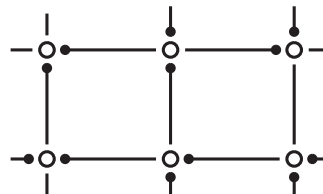
$$H \approx E_0 + \frac{1}{2} K \int \int \mathrm{d}x \, \mathrm{d}y \, |\nabla \theta|^2.$$

Vertex models

In the vertex models the dynamical variables are associated with the links and the interactions to the lattice points common to the links. As an example we consider models for crystalline phases of water (H_2O) (*ice models*):

- in the ice the oxygen atoms correspond to the lattice points.
- the links binding oxygen atom pairs are *hydrogen bonds*.
- the hydrogen bond is unsymmetric: the hydrogen ion is always closer to one of the atoms.
- the state of the hydrogen bond can be described by the two valued spin variable $\sigma_{ij} = \pm 1$.
- the hydrogen ions must satisfy so called *ice conditions*: each oxygen atom must have exactly two hydrogen as neighbours. The water molecules of the ice are thus binded together by weak hydrogen bonds.

We approximate the ice structure with two dimensional square lattice. There are 6 possible link configuration for each lattice point. We have a so called *6 vertex model*.



Let θ_i be the ice condition for the lattice point i :

$$\theta_i = \begin{cases} 1, \text{condition satisfied} \\ 0, \text{condition not satisfied.} \end{cases}$$

A suitable Hamiltonian for the system is such that the energy of the forbidden configurations is infinite, e.g.

$$H = \lim_{U \rightarrow \infty} \sum_i U(1 - \theta_i).$$

Now the energy of an allowed configuration is zero. One can also associate different energy ϵ_k with each vertex type k . The total energy of the lattice, in an allowed configuration, is

$$E = \sum_{k=1}^6 N_k \epsilon_k.$$

Here N_k is the total number of the k type vertices. One can easily see that the state sum is

$$Z = \sum_{\{\sigma_{ij}\}} e^{-\beta \sum_{k=1}^6 N_k \epsilon_k} \prod_i \theta_i.$$

Phase transitions

Lee-Yang theory

A phase transition happens at an exactly determined temperature which depends on the density, pressure and other intensive properties of the system. Since the state variables behave differently on each side of the transition point the partition sum must be non analytic at the transition point. The energy spectrum $\{E_n\}$ of finite number particles in a finite volume is discrete so the state sum

$$Z_N = \sum_n e^{-\beta E_n}$$

is a positive and, on the positive real axis $\beta > 0$ and in the neighbourhood of it, an analytic function of its argument β . In this kind of a system there can be no sharp phase transition point. Phase transition can thus occur only in the *thermodynamic limit* where

$$V \rightarrow \infty \text{ and } N \rightarrow \infty \text{ but } \frac{N}{V} \rightarrow \rho = \text{constant}.$$

The model by Lee and Yang explains how the analytic state sum develops toward non-analytic form when we approach the thermodynamic limit. We consider a system of hard spheres confined in the volume V . Let V_0 be the volume of one sphere. Then

$$N_m \approx \frac{V}{V_0}$$

is the maximum number of spheres. The state sum

$$Z_G(T, V, \mu) = \sum_{N=0}^{N_m} z^N Z(T, V, N)$$

is a polynomial of degree N_m of the fugacity

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

We use the shorthand notation

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

Let $\xi_1, \xi_2, \dots, \xi_{N_m}$ be the zeros of the polynomial $Z(z)$. Since $Z(0) = 1$, we have, according to the fundamental theorem of algebra,

$$Z(z) = \prod_{n=1}^{N_m} \left(1 - \frac{z}{\xi_n}\right).$$

Because $Z(z)$ is real when z is real the zeros must occur as conjugate pairs, i.e. for every root ξ_n there must be the root ξ_n^* .

When we approach the thermodynamic limit the number of zeros of the partition function $Z(z)$ tends to infinity. One can assume that the real axis remains clean of the zeros excluding, maybe, some separate points. In the

vicinity of those points the density of zeros is very high and the function $Z(z)$ non-analytic.

Let's suppose that the zeroes of the partition function $Z(z)$ close to the real axis condense on the curve C . The function $Z(z)$ is analytic on both sides of the curve but its analytic properties are different on different sides.

When the zeros lying on the curve C condense to continuum we can write

$$\begin{aligned}\ln Z(z) &= \sum_n \ln \left(1 - \frac{z}{\xi_n}\right) \\ &\rightarrow \int_C d\xi w(\xi) \ln \left(1 - \frac{z}{\xi}\right).\end{aligned}$$

Here

$$dn = d\xi w(\xi)$$

is the number of zeroes on the arc $d\xi$ of the curve. The density $w(\xi)$ is $\propto N_m \propto V$ and so an extensive quantity. From this expression for the partition function one can clearly see that $Z(z)$ is not analytic if z happens to lie on the curve formed by the zeroes.

As an example we consider the state sum which in the vicinity of z_0 behaves like

$$Z(z) \approx e^{\Phi(z)} \cosh \left[\frac{\pi}{b} (z - z_0) \right],$$

where $\Phi(z)$ is analytic. The zeroes of the state sum are then at the points

$$\xi_n = z_0 + ib \left(n + \frac{1}{2} \right), \quad n = 0, \pm 1, \pm 2, \dots$$

Since

$$\ln Z(z) = \Phi(z) + \ln \cosh \left[\frac{\pi}{b} (z - z_0) \right]$$

is extensive the argument $\pi/b(z - z_0)$ must be extensive. The only possibility is that $1/b \propto V$. We denote

$$b = \frac{v_0}{V},$$

so in the thermodynamic limit

$$V \rightarrow \infty \text{ or } b \rightarrow 0 \text{ but } v_0 = \text{constant}$$

we get

$$\begin{aligned}\frac{1}{V} \ln Z &= \frac{1}{V} \Phi(z) + \frac{1}{V} \ln \cosh \left[\frac{\pi V}{v_0} (z - z_0) \right] \\ &\rightarrow \begin{cases} \frac{1}{V} \Phi(z) + \frac{1}{V} \ln \frac{1}{2} + \frac{\pi}{v_0} (z_0 - z), & z < z_0 \\ \frac{1}{V} \Phi(z) + \frac{1}{V} \ln \frac{1}{2} + \frac{\pi}{v_0} (z - z_0), & z > z_0. \end{cases}\end{aligned}$$

Because in the grand canonical ensemble we have

$$\begin{aligned}pV &= k_B T \ln Z \\ N &= z \frac{\partial \ln Z}{\partial z},\end{aligned}$$

we see that now

$$\begin{aligned}pV &= k_B T \Phi(z) + \frac{\pi}{v_0} k_B T V |z - z_0| \xrightarrow{z \rightarrow z_0} k_B T \Phi(z_0) \\ N &= z \frac{\partial \Phi(z)}{\partial z} + \pi \frac{V}{v_0} z \operatorname{sgn}(z - z_0).\end{aligned}$$

We are thus dealing with a typical first order phase transition where the density jump is

$$\Delta \rho = \frac{2\pi z_0}{v_0}.$$

Isings model

Practically the only exactly solvable models are the one and two dimensional models by Ising.

We consider one dimensional chain of spins

$$\begin{array}{ccccccc} \uparrow & \uparrow & \downarrow & \uparrow & & \downarrow & \\ 1 & 2 & 3 & 4 & \cdots & N, \end{array}$$

where we apply periodic boundary conditions, i.e. we set

$$\sigma_{N+1} = \sigma_1.$$

The Hamiltonian operator of the system is then

$$\begin{aligned}H &= -J \sum_{i=1}^N \sigma_i \sigma_{i+1} - h \sum_{i=1}^N \sigma_i \\ &= -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} - J \sigma_N \sigma_1 - h \sum_{i=1}^N \sigma_i,\end{aligned}$$

where each spin variable can attain the values

$$\sigma_i = \pm 1.$$

The state sum is

$$\begin{aligned}Z &= \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_N} e^{\beta J \sum_{i=1}^N \sigma_i \sigma_{i+1} + \beta h \sum_{i=1}^N \sigma_i} \\ &= \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_N} \prod_{i=1}^N e^{\beta J \sigma_i \sigma_{i+1} + \frac{1}{2} \beta h (\sigma_i + \sigma_{i+1})}.\end{aligned}$$

We define the 2×2 transition matrix T so that

$$T_{\sigma\sigma'} = e^{\beta J \sigma \sigma' + \frac{1}{2} \beta h (\sigma + \sigma')},$$

where $\sigma, \sigma' = \pm 1$. The state sum can now be written as

$$\begin{aligned}Z &= \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_N} T_{\sigma_1 \sigma_2} T_{\sigma_2 \sigma_3} \cdots T_{\sigma_N \sigma_1} \\ &= \sum_{\sigma_1} (T^N)_{\sigma_1 \sigma_1} = \operatorname{Tr} T^N.\end{aligned}$$

Looking at the matrix

$$T = \begin{pmatrix} e^{\beta J + \beta h} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J - \beta h} \end{pmatrix}$$

we see that the transition matrix is symmetric. Thus its eigenvalues

$$\lambda^\pm = e^{\beta J} \left[\cosh(\beta J) \pm \sqrt{\sinh^2(\beta h) + e^{-4\beta J}} \right],$$

are real. Let S be a orthoganal matrix diagonalizing T (composed of the eigenvectors of T), i.e.

$$T = S^{-1} \begin{pmatrix} \lambda^+ & 0 \\ 0 & \lambda^- \end{pmatrix} S.$$

Now

$$T^N = S^{-1} \begin{pmatrix} (\lambda^+)^N & 0 \\ 0 & (\lambda^-)^N \end{pmatrix} S$$

and, due to the cyclic property of the trace,

$$\begin{aligned} Z &= \text{Tr } T^N = \text{Tr } S S^{-1} \begin{pmatrix} (\lambda^+)^N & 0 \\ 0 & (\lambda^-)^N \end{pmatrix} \\ &= (\lambda^+)^N + (\lambda^-)^N. \end{aligned}$$

The logarithm of the state sum is

$$\begin{aligned} \ln Z &= \ln \left[(\lambda^+)^N + (\lambda^-)^N \right] \\ &= N \ln \lambda^+ + \ln \left[1 + \left(\frac{\lambda^-}{\lambda^+} \right)^N \right]. \end{aligned}$$

Since in the thermodynamic limit, $N \rightarrow \infty$,

$$\left(\frac{\lambda^-}{\lambda^+} \right)^N \rightarrow 0,$$

holds we get

$$\lim_{N \rightarrow \infty} \ln Z \rightarrow N \left[\ln \lambda^+ + \frac{1}{N} \left(\frac{\lambda^-}{\lambda^+} \right)^N \right] \xrightarrow{N \rightarrow \infty} N \ln \lambda^+.$$

Just like in the free spin system the free energy is interpreted as the magnetic Gibbs function. Its value per spin is

$$\begin{aligned} \frac{G}{N} &= -\frac{k_B T}{N} \ln Z \\ &= -J \\ &\quad -k_B T \ln \left[\cosh(\beta h) + \sqrt{\sinh^2(\beta h) + e^{-4\beta J}} \right]. \end{aligned}$$

The equilibrium values of other thermodynamic variables can be calculated from the Gibbs function. In particular, the average of the spin variable is

$$\begin{aligned} \sigma &\equiv \langle \sigma_i \rangle = \frac{1}{N\beta} \frac{\partial \ln Z}{\partial h} = -\frac{\partial G/N}{\partial h} \\ &= \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + e^{-4\beta J}}}. \end{aligned}$$

The expectation value σ is an *order parameter* of the system: $\sigma = 0$ corresponds to completely stochastically oriented spins whereas $|\sigma| = 1$ corresponds to the case where all spins are ordered themselves parallelly. The order parameter σ is analogous to the magnetization M of the free spin system when h corresponds to the magnetic field H . The susceptibility is analogically

$$\chi = \frac{\partial M}{\partial H} \Leftrightarrow \frac{\partial \sigma}{\partial h}.$$

In the weak field limit $h \rightarrow 0$ we get then

$$\chi = \left. \frac{\partial \sigma}{\partial h} \right|_{h=0} = \frac{1}{k_B T} e^{\frac{2J}{k_B T}}.$$

When the coupling is ferromagnetic ($J > 0$) the system magnetizes strongly at low temperatures. When the external field is removed the system returns to the disordered state $\sigma = 0$: there is no *spontaneous symmetry break*.

If the coupling is antiferromagnetic ($J < 0$) the polarization is damped exponentially.

The one dimensional Ising chain is thus a paramagnetic system without any phase transitions. However, since it does not obey Curie's law it is not a Curie paramagnet. *Two dimensional Ising model* can be solved exactly generalizing the transition matrix method (Onsager, 1944). It turns out that in this case there is a phase transition at the temperature

$$T_c = \frac{2J}{\ln(1 + \sqrt{2})} \approx 2.269 J.$$

The specific heat diverges logarithmically at the critical point $T = T_c$ and the phase transition is continuous.

Monte Carlo methods

Because, in general, interacting systems can not be solved analytically numerical methods are of great value. An important class of numerical methods, *Monte Carlo methods*, handles interacting systems using stochastic simulations. Suitable simulations for continuum systems, like ^3He - ^4He -liquids and electron gas, are mostly based on *Green's function Monte Carlo*.

In discretized systems one can often apply *Metropolis'* *Monte Carlo method*:

- Let the possible configurations of the system be

$$j \in J = \{1, 2, \dots, K\}$$

and $E(j)$ the corresponding energies.

- Form a chain j_1, j_2, \dots, j_n of configurations.
- Choose the next configuration, $(n+1)$ 'th, in the chain drawing randomly from the set J of the possible configurations. The drawn configuration, j' , will be

- accepted if $\Delta E = E(j') - E(j_n) < 0$.
- accepted with the probability $\propto e^{-\beta \Delta E}$ if $\Delta E > 0$.
- When the length N of the chain $\{j_n\}$ increases ($N \rightarrow \infty$) the probability for each configuration j approaches

$$P(j) \propto e^{-\beta E(j)}.$$

- The chain is thus a canonical ensemble which can be used to evaluate expectation values.

Note The method assumes that the energy eigenstates of the system are known. So it can be applied for handling of e.g. Isings models and all classical systems. If the energy states are unknown the quantization must be included in the simulation.

Critical phenomena

In a second order phase transition the system normally goes from a higher temperature phase to a lower temperature phase with less symmetry. We say that a *symmetry is broken spontaneously*. For example, ferromagnetic material will get polarized below a certain critical temperature. The spin rotation symmetry is broken. The amount of the symmetry break is described by an *order parameter*, which is usually assigned to the expectation value of some observable of the system. In the ferromagnetic system a suitable order parameter is the magnetization \mathbf{m} . In the symmetric phase $\mathbf{m} = 0$ and in the ordered, i.e. symmetry breaking phase $\mathbf{m} \neq 0$. Let the order parameter be m and h the external field coupling to the corresponding observable. We consider the system close to the critical point $T = T_c$. When we denote

$$\tau = T - T_c,$$

the critical point is at origin of the (τ, h) -plane. Since the critical point is a singular point of thermodynamic potentials we divide them into regular and singular parts. For example, we write

$$\begin{aligned} F(T, m) &= F_0(T, m) + F_s(T, m) \\ G(T, h) &= G_0(T, h) + G_s(T, h) = F - hm, \end{aligned}$$

where the functions F_0 and G_0 are regular at the vicinity of the point $(\tau = 0, h = 0)$ whereas the functions F_s and G_s are singular there. Their differentials are

$$\begin{aligned} dF(T, m) &= -S dT + h dm \\ dG(T, h) &= -S dT - m dh. \end{aligned}$$

Critical exponents

Close to the critical point the singular parts are (with great accuracy) proportional to some powers of the thermodynamical quantities τ and h . The *critical exponents* or the *critical indeces* are defined as follows:

- α, α' determine the singular part of the specific heat so that

$$\begin{aligned} C_h &= -T \left(\frac{\partial^2 G}{\partial T^2} \right)_h \\ &= \begin{cases} K \tau^{-\alpha}, & \text{when } T > T_c \\ K' (-\tau)^{-\alpha'}, & \text{when } T < T_c. \end{cases} \end{aligned}$$

In practice we have $\alpha' = \alpha$.

- β tells how the order parameter behaves:

$$m(T) = \begin{cases} 0, & \text{when } T > T_c \\ K (-\tau)^\beta, & \text{when } T < T_c. \end{cases}$$

- γ, γ' are related with the susceptibility:

$$\begin{aligned} \chi &= \left(\frac{\partial m}{\partial h} \right)_T = - \left(\frac{\partial^2 G}{\partial h^2} \right)_T \\ &= \begin{cases} K \tau^{-\gamma}, & \text{when } T > T_c \\ K' (-\tau)^{-\gamma'}, & \text{when } T < T_c. \end{cases} \end{aligned}$$

Within the experimental accuracy $\gamma' = \gamma$.

- δ tells how the order parameter depends on the external field h at the critical temperature $T = T_c$:

$$m(T_c, h) = K h^{1/\delta}.$$

- ν determines the dependence of the correlation length on the temperature,

$$\xi = K |\tau|^{-\nu}.$$

The index ν is not actually a thermodynamic quantity since it is related with the microscopical parameter ξ .

Scaling theory

A *scalable* equation is such that it remains invariant under the scale transformations if the units of measurements are selected by scaling them properly. As an example we consider *Navier-Stokes'* equation of flow:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = \mathbf{f} - \frac{1}{m\rho} \nabla p + \nu \nabla^2 \mathbf{v},$$

where \mathbf{v} is the velocity, ρ the density, p the pressure and \mathbf{f} the force. The coefficient

$$\nu = \frac{\eta}{m\rho}$$

is the kinematic viscosity and η the viscosity. Let T , L , V and M be the dimensional units of the time, length, velocity and mass. With the help of the corresponding measures t' , \mathbf{r}' , \mathbf{v}' and m' (for example the mass is $m = m'M$) the Navier-Stokes equation takes the form

$$\frac{\partial \mathbf{v}'}{\partial t'} + (\mathbf{v}' \cdot \nabla') \mathbf{v}' = \mathbf{f}' - \frac{1}{m'\rho'} \nabla' p' + \frac{1}{R} \nabla'^2 \mathbf{v}'.$$

The parameter R is the dimensionless *Reynolds number*

$$R = \frac{L^2}{T\nu} = \frac{VL}{\nu} = \frac{m\rho VL}{\eta},$$

which characterizes the flow: if $R \lesssim 10 \dots 100$, the flow is usually laminar and if $R \gtrsim 10 \dots 100$, it's turbulent. Looking at the Navier-Stokes equation written using the measurement numbers we see that the behaviour of the system is dictated by the Reynolds number. If one can go from a system S to a system S_1 by scaling the measuring units so that the Reynolds number remains fixed, the equation describing the system as well as its solution remain also invariant. We say that the systems S ja S_1 are *similar*.

As a concrete example we consider two systems which are composed of same material, i.e.

$$\rho = \rho_1 \text{ ja } \nu = \nu_1.$$

We scale the linear measure by the factor s i.e.

$$L_1 = sL.$$

If we want the systems to be similar the Reynolds number must stay invariant. For example

$$R = \frac{L^2}{T\nu} = \frac{L_1^2}{T_1\nu_1} = \frac{s^2 L^2}{s_T T \nu},$$

so the scaling factor of the time s_T must be

$$s_T = s^2.$$

Let A and A_1 be some dimensional units of measure corresponding to similar systems S and S_1 . It turns out that all scaling laws are of the form

$$A_1 = s^{-d_a} A,$$

where d_a is a rational number.

Scaling hypothesis

In dense matter (liquid, solid, ...)

- the microscopical length scale is determined by the distance between atoms or molecules.
- when macroscopic properties are considered the microscopic structure is invisible.
- the only macroscopically essential parameter related to microscopical properties is the correlation length ξ , because in the vicinity of the critical point it grows macroscopically large.

We can thus assume that when we approach the critical point the classical similarity will hold:

- Consider two systems of same material with correlation lengths ξ and ξ_1 .
- The correlation length tells the scale of the fluctuations, i.e. the scale of structure of the matter (provided that we cannot observe the atomic structure).
- When the systems are observed using such magnifications that ξ and ξ_1 seem to be of equal length (and possibly adjusting sampling frequencies) no differences between the systems can be found.

Since the correlation length at the critical point is infinite all sizes of fluctuations related to the order parameter are present. Except the atomic scale, there is no natural measure of length in the system. Thus the system looks similar no matter what scale is used, the system is *self similar*. The self similarity assumption is formulated mathematically as the *scaling hypothesis*:

- The singular parts of all thermodynamic potentials scale as exponential functions of the correlation length ξ only.

- The quantity A behaves in the vicinity of the critical point like

$$A \propto \xi^{-d_A},$$

where d_A is the *scaling dimension* of A .

The scaling dimension of the correlation length is then obviously $d_\xi = -1$. Further, we see that the scaling dimension of the quantity $A^x B^y \dots$ is

$$d_{(A^x B^y \dots)} = x d_A + y d_B + \dots$$

Because the critical index ν was defined so that

$$\xi \propto |\tau|^{-\nu},$$

the scaling dimension of the temperature is

$$d_\tau = \nu^{-1}.$$

The scaling dimensions of the most important quantities are

- *Correlation length ξ* : We saw above that

$$d_\xi = -1.$$

- *Temperature τ* : We had

$$d_\tau = \frac{1}{\nu}.$$

- *Length ℓ* : Since the correlation length determines the length scale of the system ℓ scales like ξ i.e.

$$d_\ell = -1.$$

- *Wave vector q* : The wave vector is inversely proportional to the length so

$$d_q = 1.$$

- *Order parameter m* : The index β was defined so that $m \propto (-\tau)^\beta$, so

$$d_m = \beta d_\tau = \frac{\beta}{\nu}.$$

- *Free energy G* : Scale transformation do not affect the free energy of the system, so

$$d_G = 0.$$

- *Free energy per volume element g* : Since $g = G/V$, we have

$$d_g = d_G - d_V = -d d_\ell = d,$$

when d is the spatial dimension.

- *Specific heat c* : Since the specific heat (density) is

$$c \approx -T_c \frac{\partial^2 g}{\partial \tau^2},$$

the scaling dimension d_c satisfies the condition

$$d_c = d_g - 2d_\tau = d - \frac{2}{\nu}.$$

Thus we have for the specific heat

$$c \propto \xi^{(2/\nu)-d} \propto |\tau|^{d\nu-2}$$

and, according to the definition of the critical index α ,

$$c \propto |\tau|^{-\alpha}.$$

Hence the critical indices are related via the *scaling law*

$$\alpha = 2 - \nu d.$$

- *Field h* : In an equilibrium the order parameter m is

$$m = -\frac{\partial g}{\partial h},$$

so

$$d_m = d - d_h.$$

For the field h we thus have

$$d_h = d - d_m = d - \frac{\beta}{\nu}.$$

The susceptibility obeys according to the definition of the index γ the relation

$$\chi = \frac{\partial m}{\partial h} \propto |\tau|^{-\gamma},$$

so

$$d_m - d_h = -\gamma d_\tau.$$

Comparing the dimension obtained from this for d_h with our earlier result we end up with the scaling law

$$\gamma = \nu d - 2\beta.$$

Further, the index δ was defined so that at the critical temperature

$$m \propto h^{1/\delta}.$$

Then we have

$$d_m = \frac{d_h}{\delta},$$

from which, using our earlier result, we get the scaling law

$$\delta = \frac{\nu d}{\beta} - 1.$$

The hard to measure index ν , which is related to the microscopical correlation length, can be eliminated from

the three scaling laws derived above. We are left with scaling laws relating thermodynamic indeces:

$$\begin{aligned}\alpha + 2\beta + \gamma &= 2 \\ \beta(\delta - 1) &= \gamma.\end{aligned}$$

Note Although the scaling laws derived above are based on phenomenological arguments they are valid within experimental accuracy.

Widom scaling

We consider the Gibbs function per primitive cell (or particle)

$$g(\tau, h) = g_0(\tau, h) + g_s(\tau, h),$$

where we have again separated the regular and singular parts from each other at the singular point ($\tau = 0, h = 0$). Its differential is

$$dg = -s d\tau - m dh,$$

when $s = S/N$ is the entropy per primitive cell (or particle). Since the order parameter m is zero at temperatures above the critical point the critical exponents related to it must come from the singular function g_s .

The function f is a *generalized homogenous function* if it satisfies the condition

$$f(\lambda^{\alpha_1} x_1, \lambda^{\alpha_2} x_2, \dots) = \lambda f(x_1, x_2, \dots).$$

According to *Widom's hypothesis* the function g_s behaves in the vicinity of the critical point like a generalized homogenous function, i.e. it *scales* like

$$g_s(\lambda^p \tau, \lambda^q h) = \lambda g_s(\tau, h),$$

when $\lambda > 0$ and p and q are system independent exponents.

Because the scaling equation holds for all positive values of λ it holds when $\lambda = h^{-1/q}$, in which case $\lambda^q h = 1$.

Thus we can write the scaling hypothesis as

$$\begin{aligned}g_s(\tau, h) &= h^{1/q} g_s\left(\frac{\tau}{h^{p/q}}, 1\right) \\ &= h^{1/q} \phi\left(\frac{\tau}{h^{p/q}}\right).\end{aligned}$$

Here we have defined

$$\phi(x) = g_s(x, 1).$$

The critical indeces can be obtained as follows

- β . Take the derivative of the scaling equation

$$g_s(\lambda^p \tau, \lambda^q h) = \lambda g_s(\tau, h),$$

with respect to the field h and recall that the order parameter is

$$m(\tau, h) = -\frac{\partial g_s(\tau, h)}{\partial h},$$

so we have the scaling condition

$$\lambda^q m(\lambda^p \tau, \lambda^q h) = \lambda m(\tau, h). \quad (*)$$

Since the order parameter is supposed to be $m \neq 0$, we have $\tau < 0$. Then we can choose λ so that $\lambda^p \tau = -1$. Setting $h = 0$ we get

$$m(\tau, 0) = (-\tau)^{(1-q)/p} m(-1, 0).$$

According to the definition we have

$$m(\tau, 0) \propto (-\tau)^\beta,$$

so

$$\beta = \frac{1-q}{p}.$$

- δ . We set in the equation (*) $\tau = 0$ and $\lambda^q = 1/h$, so

$$m(0, h) = h^{1/q-1} m(0, 1).$$

According to the definition $m(0, h) \propto h^{1/\delta}$, so

$$\delta = \frac{q}{1-q}.$$

- γ, γ' . According to the definition the susceptibility is

$$\chi(\tau, h) = \frac{\partial m(\tau, h)}{\partial h},$$

which close to the critical point behaves like

$$\chi \propto \begin{cases} \tau^{-\gamma}, & \text{when } \tau > 0 \\ (-\tau)^{-\gamma'}, & \text{when } \tau < 0. \end{cases}$$

Differentiating (*) with respect to the field h we get

$$\lambda^{2q} \chi(\lambda^p \tau, \lambda^q h) = \lambda \chi(\tau, h).$$

Setting $h = 0$ and $\lambda^p \tau = \pm 1$ we have

$$\chi(\tau, 0) = |\tau|^{-(2q-1)/p} \chi(\pm 1, 0).$$

From this we can read for γ and γ'

$$\gamma = \gamma' = \frac{2q-1}{p}.$$

- α, α' . The specific heat is

$$c_h \propto \frac{\partial^2 g}{\partial \tau^2}.$$

Differentiating the scaling equation

$$g_s(\lambda^p \tau, \lambda^q h) = \lambda g_s(\tau, h)$$

twice with respect to τ we get

$$\lambda^{2p} c_h(\lambda^p \tau, \lambda^q h) = \lambda c_h(\tau, h).$$

We set $h = 0$ and $\lambda^p \tau = \pm 1$ and compare the result with the definitions of α and α' :

$$c_h \propto \begin{cases} \tau^{-\alpha}, & \text{kun } \tau > 0 \\ (-\tau)^{-\alpha'}, & \text{kun } \tau < 0. \end{cases}$$

We see that

$$\alpha = \alpha' = 2 - \frac{1}{p}.$$

It is easy to verify that the Widom scaling hypothesis leads to the scaling laws

$$\begin{aligned}\alpha + 2\beta + \gamma &= 2 \\ \beta(\delta - 1) &= \gamma.\end{aligned}$$

Kadanoff scaling theory

Unlike the Widom scaling hypothesis the method developed by Kadanoff (1966) is based on the microscopic properties of matter.

Outlines of Kadanoffs method:

- Combine the original microscopical state variables blockwise to *block variables*.
- Determine the effective interactions between the blocks. This coarsing of the system is called the *block transform*.
- The block transforms form a semigroup, so called *renormalization group*. One can perform transforms sequentially.
- Because in a system at the critical point there is no natural length scale the transformed systems look copies of each other. Thus the critical point corresponds to a *fixed point* of the transformations.

We apply the method to the d -dimensional Ising spin system.

Block transform

We denote by i, j, \dots the original lattice points and the blocks obtained by combining them by indices I, J, \dots . The block spin σ'_I of the block I is defined so that

$$\sigma'_I = \sum_{i \in I} \sigma_i.$$

If we end up with the blocks I by scaling the length measure by the factor L , each block has L^d spins. Because in the Ising model each spin can get the values $\sigma_i = \pm 1$ the block spin can get the values

$$\sigma'_I = -L^d, -L^d + 2, \dots, L^d$$

i.e. altogether $L^d + 1$ different values.

Let H be the original Hamiltonian. We denote

$$\mathcal{H}[\sigma_i] = \beta H = -K \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i.$$

The state sum is

$$Z = e^{-\mathcal{G}} = \text{Tr} e^{-\mathcal{H}[\sigma_i]} = \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]},$$

where $\mathcal{G} = \beta G$, G is the Gibbs function. We divide the trace summation into two parts

$$\begin{aligned}Z &= \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \\ &= \sum_{\{\sigma'_I\}} \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \prod_I \delta\left(\sigma'_I, \sum_{i \in I} \sigma_i\right) \\ &= \sum_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma'_I]}.\end{aligned}$$

Here we have defined

$$\begin{aligned}e^{-\mathcal{H}[\sigma'_I]} &= \text{Tr}_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma_i]} \\ &= \sum_{\{\sigma_i\}} e^{-\mathcal{H}[\sigma_i]} \prod_I \delta\left(\sigma'_I, \sum_{i \in I} \sigma_i\right).\end{aligned}$$

As can be seen from the definition

$$\mathcal{H}[\sigma'_I] = \ln \text{Tr}_{\{\sigma'_I\}} e^{-\mathcal{H}[\sigma_i]}$$

the *Hamilton block function* $\mathcal{H}[\sigma'_I]$ is actually the *reduced free energy*. Thus it can be written as

$$\mathcal{H}[\sigma'_I] = \overline{\mathcal{H}[\sigma_i]} \Big|_{\{\sigma'_I\}} - TS|_{\{\sigma'_I\}},$$

where $\overline{\mathcal{H}[\sigma_i]} \Big|_{\{\sigma'_I\}}$ is the expectation value of the energy (the internal energy) evaluated in the block configuration $\{\sigma'_I\}$. Hence the Hamiltonian block function contains the internal entropy related to the internal variables of the blocks.

Close to the critical point, due to the scale invariance, we assume the reduced free energy to take approximately the same form as the original Hamiltonian. To achieve this we scale the range of the block spins so that

$$\sigma'_I = z \sigma_I,$$

where $\sigma_I = \pm 1$. Because the maximum of the block spin is L^d we must have $z \leq L^d$.

Critical exponents

According to Kadanoff effectively the most important values of the block variable are $\pm z$. We denote

$$\mathcal{H}_L[\sigma_I] = \mathcal{H}[z\sigma_I].$$

We let the new Hamiltonian \mathcal{H}_L to be of the same form as the original \mathcal{H} :

$$\mathcal{H}_L[\sigma_I] = -K_L \sum_{\langle IJ \rangle} \sigma_I \sigma_J - h_L \sum_I \sigma_I.$$

The parameters K_L and h_L depend now on the scale L . Let the values of the parameters at the critical point to be

$$\begin{aligned}K &= K_c \\ h &= h_c = 0.\end{aligned}$$

Since at the critical point nothing changes while scaling we must also have

$$\begin{aligned} K_L &= K_c \\ h_L &= h_c = 0. \end{aligned}$$

We consider the neighbourhood of the critical point. We suppose that $h \neq 0$, so also the corresponding scaled field satisfies $h_L \neq 0$. We write the original coupling constant as

$$K = K_c + \Delta K$$

and the corresponding scaled coupling constant as

$$K_L = K_c + \Delta K_L.$$

We now vary the scale factor L by a (small) amount δL . The relative variation of the scale is then $\delta L/L$. we can assume (as a good approximation) that the relative variations of the scaled parameters are proportional to the relative variation of the scale, i.e.

$$\begin{aligned} \frac{\delta \Delta K_L}{\Delta K_L} &= x \frac{\delta L}{L} \\ \frac{\delta h_L}{h_L} &= y \frac{\delta L}{L}, \end{aligned}$$

where x and y are constants.

When the change in the ratio is infinitesimal we get the differential equations

$$\begin{aligned} x &= \frac{\partial \ln \Delta K_L}{\partial \ln L} \\ y &= \frac{\partial \ln h_L}{\partial \ln L}, \end{aligned}$$

which after integration give

$$\begin{aligned} K_L &= K_c + L^x (K - K_c) \\ h_L &= L^y h. \end{aligned}$$

To obtain the same energy from the original and scaled Hamiltonians the coupling to the external field must satisfy the condition

$$h \sum_{i \in I} \sigma_i = h \sigma'_I = h z \sigma_I = h_L \sigma_I,$$

so the field scales like $h_L = z h$. We see that

$$z = L^y \text{ and } y \leq d.$$

The same reasoning allows us to assume that the relative deviation of the temperature from the critical point,

$$\tau = \frac{T - T_c}{T_c},$$

behaves like the relative deviation of the coupling constant K from the critical value, i.e.

$$\tau_L = L^x \tau.$$

Thus the Gibbs function per spin unit scales like

$$g(\tau_L, h_L) = g(L^x \tau, L^y h) = L^d g(\tau, h),$$

where the factor L^d is due to the fact that the new block contains L^d old spins. Writing

$$\begin{aligned} x &= p d \\ y &= q d \end{aligned}$$

we end up with the Widom scaling.

Renormalization group

Let us suppose that the Hamiltonian \mathcal{H} depends on the parameters

$$\mu = (\mu_1, \mu_2, \dots),$$

For example $\mu = (K, h)$, as above. Block transforms are now mappings in the parameter space

$$\mu \longrightarrow \mu_L.$$

Let \mathbf{R}_L be the operator corresponding to the block transform, i.e.

$$\mu \longrightarrow \mu_L = \mathbf{R}_L \mu.$$

Since the block transform is a change in the scale we must have

$$\mathbf{R}_L \mathbf{R}_{L'} = \mathbf{R}_{LL'}.$$

Furthermore, it does not matter in which order the scale transforms are performed:

$$\mathbf{R}_L \mathbf{R}_{L'} = \mathbf{R}_{L'} \mathbf{R}_L.$$

In the block transform we loose information, for example the detailed knowledge of the values of the original spin variables. Thus it is impossible to return to the original system by scaling: the operation $\mathbf{R}_{L'}$ has no inverse transformation among the operations $\{\mathbf{R}_L\}$. We see that the operations

$$\mathcal{R} = \{\mathbf{R}_L\}$$

form a *commutative semigroup* which is called the *renormalization group*.

A point μ^* which satisfies the condition

$$\mu^* = \mathbf{R} \mu^* \quad \forall \mathbf{R} \in \mathcal{R},$$

is called a *fixed point*. A system corresponding to the parameter values μ^* is at the critical point since any transformation of that systems results an exactly identical system. The set of those points that after sequential block transforms lead to the fixed point μ^* is called the *critical surface*. If the system is on the critical surface, but not at the critical point, it is at a critical point of the phase transition. However, one can still observe it using the scale where microscopical details are visible.