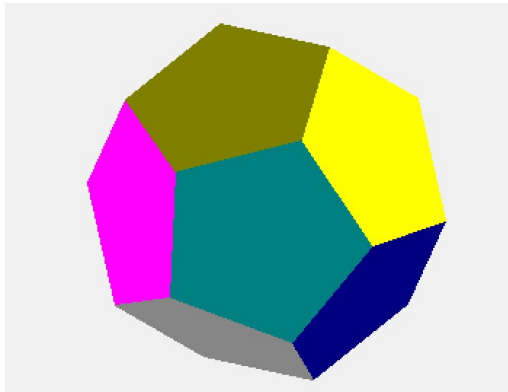


# Statistical Mechanics

## 1



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## Acknowledgement

The task of classical statistical mechanics is to give a theoretical foundation of the empirical laws of thermodynamics, and enable us to compute the functions of state, i.e. temperature  $T$ , pressure  $P$ , energy  $E$  and entropy  $S$ , when the mechanical constitution of the system is statistically defined.

In 1968 I attended a series of post graduate lectures given by Professor C. Møller on Statistical Mechanics at the Niels Bohr Institute in Copenhagen Denmark.

His notes in Danish were from 1962, written on a typewriter, belonging to that period, and supplied with hand written formulas and drawings.

In spite of this, I still find his presentation of the subject, although on a quite stringent theoretical ground is more comprehensible than i.e. Landau and Lifshitz's classic book on Statistical mechanics.

This presentation relies heavily on the lecture notes by professor Møller. Some less important parts have been omitted, and some sections have been elaborated to strengthen the clarity. At the same time it is adapted to a more modern approach of text books in theoretical physics, without losing its original rigor.

I have translated his lectures to English, because I think that the English spoken physicist community, should benefit from Professor Møller's excellent Lectures.

August 2016

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## 1. Review of analytical mechanics in Lagrange's formulation

Analytical mechanics is characterized by describing a mechanical system by generalized coordinates usually denoted:  $q_1, q_2, q_3, \dots, q_n$ . Differentiating with respect to time is indicated with a bullet above the variable e.g.  $\dot{q} = dq/dt$ , so that  $\dot{q}_1, \dot{q}_2, \dot{q}_3, \dots, \dot{q}_n$  represents the generalized velocities. Using the Lagrange approach, the kinetic energy is written as:

$$T = T(\dot{q}_1, \dot{q}_2, \dot{q}_3, \dots, \dot{q}_n, q_1, q_2, q_3, \dots, q_n),$$

and the potential energy:

$$U = U(q_1, q_2, q_3, \dots, q_n)$$

and Lagrange function  $L$  is defined as:

$$(1.1) \quad L = T - U$$

The Euler-Lagrange equations of motion are

$$(1.2) \quad \frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = 0$$

The generalized momentum is defined by the equation:

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

**Example:** For a particle with Cartesian coordinates  $(x, y, z)$ , having the kinetic energy

$$T = \frac{1}{2}mv^2 = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \quad \text{and the potential energy } U = U(r)$$

$$\frac{\partial L}{\partial \dot{q}} = m\dot{q} \quad \text{or} \quad \frac{\partial L}{\partial \dot{x}} = m\dot{x} = p_x$$

$m\dot{q}$  is the generalized momentum in the  $q$  direction, likewise

$$F_q = \frac{\partial L}{\partial q} = -\frac{\partial U}{\partial q}$$

is the generalized force in the  $q$  direction.

For a single particle, the Euler-Lagrange equations then become:

$$\frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} = 0 \quad \Leftrightarrow \quad -\frac{\partial U}{\partial q} - m\ddot{q} = 0 \quad \Leftrightarrow \quad F_q = m\ddot{q},$$

This is the familiar Newtonian equation of motion for a particle.

If we differentiate the Lagrangian with respect to time, and if the Lagrangian does not explicitly depend on time, ( the partial derivative  $\frac{\partial L}{\partial t} = 0$ ), the derivative can be written:

$$(1.5) \quad \frac{dL}{dt} = \sum_i \frac{\partial L}{\partial q_i} \dot{q}_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i$$

According to Lagrange's equation:  $\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = 0$ , we can replace  $\frac{\partial L}{\partial q_i}$  with  $\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i}$  to get:

$$\frac{dL}{dt} = \sum_i \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) \dot{q}_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i = \sum_i \frac{d}{dt} \left( \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} \right)$$

So

$$(1.6) \quad \frac{dL}{dt} = \sum_i \frac{d}{dt} \left( \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} \right)$$

Subtracting the left side from the last expression we obtain

$$(1.7) \quad \frac{d}{dt} \left( \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L \right) = 0$$

Hence we see that the quantity  $\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L$  remains constant during the motion of any closed system. For this reason we identify it with the energy  $H$  of the system.

$$(1.8) \quad H = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L$$

We want to establish, that  $H$  actually is equal to our usual perception of the concept of energy, as the sum of kinetic and potential energy:  $H = T + U$ , and for that purpose we need to apply Euler's theorem for a homogenous function of order  $n$ .

According to Euler's theorem, (which is proven below), we have

$$(1.9) \quad \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} = \sum_i \dot{q}_i \frac{\partial T}{\partial \dot{q}_i} = 2T, \quad \text{since } \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial T}{\partial \dot{q}_i}$$

$$(1.10) \quad H = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L(q_i, \dot{q}_i) = 2T(q_i, \dot{q}_i) - (T(q_i, \dot{q}_i) - U(q_i)) = T(q_i, \dot{q}_i) + U(q_i)$$

This concludes the Lagrangian approach to the total energy of a system, expressed by the Hamilton function.

### 1.1 Lemma. Eulers theorem for an homogenous function

We restrict ourselves to prove Eulers theorem for a function of two variables, the generalization to several variables is straightforward.

A real function  $f(x,y)$  is said to be homogenous of order  $n$ , if it fulfils the condition:

$$(1.11) \quad f(tx,ty) = t^n f(x,y)$$

If we put  $x_1 = tx$  and  $y_1 = ty$ , then

$$f(tx,ty) = f(x_1,y_1) = t^n f(x,y).$$

Differentiating each of the last two expressions separately with respect to  $t$ , gives:

$$\frac{df}{dt} = nt^{n-1} f(x,y) = \frac{\partial f}{\partial x_1} \frac{\partial x_1}{\partial t} + \frac{\partial f}{\partial y_1} \frac{\partial y_1}{\partial t} = x \frac{\partial f}{\partial x_1} + y \frac{\partial f}{\partial y_1}$$

because  $x_1 = x$ , and  $y_1 = y$  for  $t = 1$ , we find, putting  $t = 1$  in the last equation.

$$(1.12) \quad nf(x,y) = x \frac{\partial f}{\partial x_1} + y \frac{\partial f}{\partial y_1} = x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y}$$

Euler's theorem can easily be generalized to a homogenous function of  $n$  variables, if

$$f(tx_1,tx_2,tx_3,\dots,tx_n) = t^n f(x_1,x_2,x_3,\dots,x_n)$$

Then

$$nf(x_1,x_2,x_3,\dots,x_n) = \sum_{k=1}^n x_k \frac{\partial f}{\partial x_k}$$

Since the kinetic energy is a quadratic form in the velocities  $\dot{q}_i$

$$T = \sum_{i=1}^n \sum_{j=1}^n b_{ij} \dot{q}_i \dot{q}_j$$

It is homogenous of order 2, since  $T(t\dot{q}) = t^2 T(\dot{q})$ , so according to Euler's theorem:

$$\sum_{k=1}^n \dot{q}_k \frac{\partial T}{\partial \dot{q}_k} = 2T \quad \text{or} \quad T = \frac{1}{2} \sum_{k=1}^n \dot{q}_k \frac{\partial T}{\partial \dot{q}_k}$$

One should notice that Euler's theorem also applies, when the velocities are replaced with the generalized momenta, since the mass part will cancel in the expression.

## 1.2 Hamilton's equations

The formulation of the laws of mechanics in terms of the Lagrangian, and Lagrange's equations derived from it, presupposes that the mechanical state of the system is described by its generalized coordinates and velocities.

This is not the only description however. The statistical mechanics, it is more advantageous to attach to a description in terms of generalized coordinates  $q_i$  and generalized momenta  $p_i$ . The question therefore arises of the form of the equations of motion corresponding to that formulation of the laws of mechanics.

The passage from one set of independent variables to another, can be effected by a so called *Legendre's transformation*.

In the present case the transformation is as follows: We write the total differential of the Lagrangian  $L = T - U$ , as a function of generalized coordinates and velocities.

$$(1.13) \quad dL = \sum_i \frac{\partial L}{\partial q_i} dq_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i$$

Since  $\dot{p}_i = \frac{\partial L}{\partial q_i}$  by Lagrange's equation, and  $p_i = \frac{\partial L}{\partial \dot{q}_i}$  by definition of the generalized momentum

(1.13) can also be written

$$(1.14) \quad dL = \sum_i \dot{p}_i dq_i + \sum_i p_i d\dot{q}_i$$

Writing the second term in (1.6) as:

$$(1.15) \quad \sum_i p_i d\dot{q}_i = d\left(\sum_i p_i \dot{q}_i\right) - \sum_i \dot{q}_i dp_i$$

Taking the differential to the left hand side, and reversing the signs, we obtain:

$$(1.16) \quad d\left(\sum_i p_i \dot{q}_i - L\right) = -\sum_i \dot{p}_i dq_i + \sum_i \dot{q}_i dp_i$$

In (1.8) we identified  $\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L$  with the Hamilton function  $H$ , that is the energy of the system,

and (1.16) can then be written as a total differential of the Hamilton function  $H$ .

$$(1.17) \quad H = -\sum_i \dot{p}_i dq_i + \sum_i \dot{q}_i dp_i$$

From this equation immediately follow the Hamiltonian Canonical Equations i.e. the equations of motion:

$$(1.18) \quad \frac{dq_k}{dt} = \frac{\partial H(p, q, a)}{\partial p_k} \quad \frac{dp_k}{dt} = -\frac{\partial H(p, q, a)}{\partial q_k}$$

Where the  $a$ 's are parameters belonging to the external forces on the system.  $q_k$  is the generalized coordinate, and the generalized momenta are defined as:

$$(1.19) \quad p_k = \frac{\partial H(q, \dot{q})}{\partial \dot{q}_k} = \frac{\partial T(q, \dot{q})}{\partial \dot{q}_k}$$

**Example:** For a particle with Cartesian coordinates  $(x, y, z)$ , having the kinetic energy

$$T = \frac{1}{2}mv^2 = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \quad , \text{ and the potential energy } U(x, y, z)$$

We find:

$$\frac{dq_k}{dt} = \frac{\partial H(p, q, a)}{\partial p_k} = \frac{p_k}{m} \quad \quad \quad \frac{dp_k}{dt} = -\frac{\partial H(p, q, a)}{\partial q_k} = -\frac{\partial U}{\partial q_k}$$

Corresponding to the Newtonian equation of motion

## 2. Foundation of statistical mechanics

Let us consider a system of  $r$  particles with the masses:  $m_1, m_2, m_3, \dots, m_r$  having the Cartesian coordinates  $(x_i, y_i, z_i)$ , and the generalized coordinates:  $q_1, q_2, q_3, \dots, q_n = q$  (shorthand notation) The coordinates may have imposed some constraints, so that  $n < 3r$ .

There consist certain relations between the Cartesian and the generalized coordinates:

$$x_i = x_i(q), \quad y_i = y_i(q), \quad z_i = z_i(q)$$

From which it follows:

$$(2.1) \quad \dot{x}_i = \sum_{k=1}^n \frac{\partial x_i}{\partial q_k} \dot{q}_k \quad \dot{y}_i = \sum_{k=1}^n \frac{\partial y_i}{\partial q_k} \dot{q}_k \quad \dot{z}_i = \sum_{k=1}^n \frac{\partial z_i}{\partial q_k} \dot{q}_k$$

The kinetic energy is:

$$(2.2) \quad T = \sum_{k=1}^r \frac{1}{2} m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) = \left( \sum_{i=1}^r \left( \sum_{k=1}^n \frac{1}{2} m_i \frac{\partial x_i}{\partial q_k} \dot{q}_k \right) \right)^2 + \left( \sum_{i=1}^r \left( \sum_{k=1}^n \frac{1}{2} m_i \frac{\partial y_i}{\partial q_k} \dot{q}_k \right) \right)^2 + \left( \sum_{i=1}^r \left( \sum_{k=1}^n \frac{1}{2} m_i \frac{\partial z_i}{\partial q_k} \dot{q}_k \right) \right)^2$$

$$T = \sum_{j=1}^n \sum_{k=1}^n d_{jk} \dot{q}_j \dot{q}_k$$

Where  $d_{jk}$  is a positive definite quadratic form, where the coefficients  $d_{ij}$  do no depend explicitly on  $q_i, i = 1 \dots n_i$  The generalized momenta are given by:

$$p_k = \frac{\partial H}{\partial \dot{q}_k} = \frac{\partial T}{\partial \dot{q}_k} \quad k = 1 \dots n$$

From which it follows that the generalized momenta are a linear function of the generalized velocities.



$$(2.3) \quad p_k = 2 \sum_{j=1}^n d_{kj} \dot{q}_j \quad k=1 \dots n$$

These linear equations can (in principle) be solved for the  $\dot{q}_j$  to give:

$$\dot{q}_j = \dot{q}_j(p, q)$$

When inserted in (2.2), the kinetic energy can then be expressed as a function of  $p$  and  $q$ .

$$T = T(p, q)$$

It is a well known fact from classical mechanics, that if the positions and the velocities of a system of particles are known at a certain time, and forces that act on the particles are also known as a function of position, then through the equations of motion the position and velocity of the particles can be precisely predicted at any later time.

This is called the *determinism* in classical physics.

We have here assumed that all forces in question, internal forces as well as external forces are conservative, that is, they can be derived by a potential.

The external forces are thought to be given by some parameters  $a$ , so that the potential energy can be written as.

$$U = U(q_1, q_2, q_3, \dots, q_n, a_1, a_2, \dots, a_m)$$

If  $dA$  denotes the work, that the system forces exert, when the system changes its configuration from  $(p, q)$  to  $(p+dp, q+dq)$ , then we have:

$$(2.4) \quad dA = \sum_{k=1}^n \frac{\partial U}{\partial q_k} dq_k$$

Whereas in (1.3)

$$F_k = - \frac{\partial U}{\partial q_k}$$

Is the generalized force component in the direction of  $q_k$ .

Similarly

$$A_k = - \frac{\partial U}{\partial a_k}$$

is the  $k$ 'th component of the generalized force, which the system performs on the surroundings. The Hamilton function  $H$ , that is, the energy in generalized coordinates, is given by:

$$(2.5) \quad H = T(p, q) + U(q, a)$$

And the equations of motion is written in the canonical form:

$$(2.6) \quad \frac{dq_k}{dt} = \frac{\partial H(p, q, t)}{\partial p_k} \quad \frac{dp_k}{dt} = -\frac{\partial H(p, q, t)}{\partial q_k}$$

### 2.7 Example. Uniform circular motion.

In a uniform circular motion driven by a potential  $U(r) = -\frac{\alpha}{r}$ , the Hamilton function is  $H = \frac{p^2}{2m} - \frac{\alpha}{r}$ , and we therefore get:

$$\frac{dq_k}{dt} = \frac{\partial H(p, q, t)}{\partial p_k} = \frac{p}{m} = v \quad \frac{dp_k}{dt} = -\frac{\partial H(p, q, t)}{\partial q_k} = -\frac{\alpha}{r^2}$$

As we should.

The mechanical state of the system is completely determined, when the values for the  $2n$  variables  $(p, q) = (p_1, p_2, p_3, \dots, p_n, q_1, q_2, q_3, \dots, q_n)$ , called the *mechanical phase* of the system are known. The phase of the system changes, according to (2.6).

The phase space is a space spanned by the  $2n$  variables.  $(p, q)$ , and the infinitesimal volume element is given by:

$$(2.8) \quad dV = dpdq = dp_1 dp_2 dp_3 \cdots dp_n \cdot dq_1 dq_2 dq_3 \cdots dq_n$$

If we have a subspace  $\Omega$ , confined by the points in phase space imposed by a hyper surface  $f(p_1, p_2, p_3, \dots, p_n, q_1, q_2, q_3, \dots, q_n) = \text{const}$ , the volume of  $\Omega$  is given by the  $2n$  dimensional integral.

$$(2.9) \quad V_\Omega = \iiint \dots \int_{f(p_1, p_2, p_3, \dots, p_n, q_1, q_2, q_3, \dots, q_n) = \text{const}} dp_1 dp_2 dp_3 \cdots dp_n \cdot dq_1 dq_2 dq_3 \cdots dq_n$$

## 3. Gibb's ensembles

If we have a system where the thermodynamic state is known, it does not mean that the mechanical phase is known in detail. If we have two systems having the same Hamilton function being in the same thermodynamic state, we shall in general find that they do not have the same mechanical phase.

We may only speak of a *probability* that the phase of the system is in a certain volume  $\Omega$  of phase space.

It is our aim to define these probabilities more precisely. At a certain time, we consider an ensemble of huge number of systems with the same Hamilton function, and in the same thermodynamic state.

This means that the thermodynamic state functions are the same, and that the external conditions also are the same. If we (hypothetically) measure the mechanical phase of all these  $N$  systems and depict their phases as a point in the  $2n$  dimensional phase space, we get the distribution of systems in phase space. Let the number of points in a volume  $\Omega$  be  $N_\Omega$ . Then the probability of finding a system in  $\Omega$  is:

$$(3.1) \quad P_\Omega = \lim_{N \rightarrow \infty} \frac{N_\Omega}{N}$$

That  $P_\Omega$  actually represent a probability of physical significance, we may not know in advance, and drawing consequences from this probability function can only be justified by experience, comparing results belonging to the world of physical realities.

If we let  $\Omega$  shrink into an infinitesimal volume element  $dV = dpdq$ , then we can define  $P(p,q)dpdq$  as the probability of finding the phase of the system in the volume element  $dV$ .

The probability of finding the system in a phase space volume  $\Omega$  is then

$$(3.2) \quad P(\Omega) = \int \int \int \dots \int P(p,q) dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

Where the integrals are extended over the volume  $\Omega$ .

The integral over the total phase space of the probabilities must normalize to one.

$$(3.3) \quad \int \int \int \dots \int P(p,q) dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = 1$$

We shall also define a *density function*  $D(p,q)$ . If there are a total of  $N$  systems in the ensemble, then the statistical density of systems lying in a volume element  $dV$  around  $(p,q)$  is:

$$D(p,q) = N \cdot P(p,q)$$

#### 4. Liouville's theorem

We shall then consider how the systems depicted as point in the  $2n$  phase space will develop in time.

Let us assume that some system points at  $t = t_0$  occupy a volume  $\Omega_0$  in phase space. At a later time  $t$  the same points occupy a volume  $\Omega_t$ . Liouville's theorem states, that the two volumes are equal.

At  $t_0$  the phase space volume element is  $dV_0 = dp_{10} dp_{20} dp_{30} \dots dp_{n0} \cdot dq_{10} dq_{20} dq_{30} \dots dq_{n0}$ , and at a later time, it is  $dV = dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$

The transformation between the two differentials is given by the functional or Jacoby determinant:

$$(4.1) \quad dpdq = \det\left(\frac{\partial p \partial q}{\partial p_0 \partial q_0}\right) dp_0 dq_0$$

Or when written out:

$$\begin{aligned} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = \\ \frac{\partial(p_1, p_2, p_3, \dots, p_n, q_1, q_2, q_3, \dots, q_n)}{\partial(p_{10}, p_{20}, p_{30}, \dots, p_{n0}, q_{10}, q_{20}, q_{30}, \dots, q_{n0})} dp_{10} dp_{20} dp_{30} \dots dp_{n0} \cdot dq_{10} dq_{20} dq_{30} \dots dq_{n0} \end{aligned}$$

Where

$$(4.2) \quad \frac{\partial(p_1, p_2, p_3, \dots, p_n, q_1, q_2, q_3, \dots, q_n)}{\partial(p_{10}, p_{20}, p_{30}, \dots, p_{n0}, q_{10}, q_{20}, q_{30}, \dots, q_{n0})} = \begin{vmatrix} \frac{\partial p_1}{\partial p_{10}} & \dots & \frac{\partial p_1}{\partial p_{n0}} & \frac{\partial p_1}{\partial q_{10}} & \dots & \frac{\partial p_1}{\partial q_{n0}} \\ \frac{\partial p_2}{\partial p_{10}} & \dots & \frac{\partial p_2}{\partial p_{n0}} & \frac{\partial p_2}{\partial q_{10}} & \dots & \frac{\partial p_2}{\partial q_{n0}} \\ \vdots & & \vdots & \vdots & & \vdots \\ \frac{\partial p_n}{\partial p_{10}} & \dots & \frac{\partial p_n}{\partial p_{n0}} & \frac{\partial p_n}{\partial q_{10}} & \dots & \frac{\partial p_n}{\partial q_{n0}} \\ \frac{\partial q_1}{\partial p_{10}} & \dots & \frac{\partial q_1}{\partial p_{n0}} & \frac{\partial q_1}{\partial q_{10}} & \dots & \frac{\partial q_1}{\partial q_{n0}} \\ \frac{\partial q_2}{\partial p_{10}} & \dots & \frac{\partial q_2}{\partial p_{n0}} & \frac{\partial q_2}{\partial q_{10}} & \dots & \frac{\partial q_2}{\partial q_{n0}} \\ \vdots & & \vdots & \vdots & & \vdots \\ \frac{\partial q_n}{\partial p_{10}} & \dots & \frac{\partial q_n}{\partial p_{n0}} & \frac{\partial q_n}{\partial q_{10}} & \dots & \frac{\partial q_n}{\partial q_{n0}} \end{vmatrix}$$

We shall then calculate the two integrals, corresponding to the volumes of phase space that occupy the system points at  $t_0$  and at  $t_0 + \delta t$ , where  $\delta t$ , is a small increment.

To calculate the partial derivatives in the determinant (4.2) we use the canonical equations:

$$\frac{dp_k}{dt} = -\frac{\partial H(p, q, t)}{\partial q_k} \quad \text{and} \quad \frac{dq_k}{dt} = \frac{\partial H(p, q, t)}{\partial p_k}$$

To a first order approximation we have:

$$(4.3) \quad p_k(t_0 + \delta t) = p_k(t_0) + \frac{dp_k}{dt} \delta t = p_k(t_0) - \frac{\partial H(p, q, t)}{\partial q_k} \delta t$$

or without the explicit time dependence:

$$(4.4) \quad p_k = p_{k0} + \frac{dp}{dt} \delta t = p_{k0} - \frac{\partial H(p, q, t)}{\partial q_k} \delta t$$

From which we obtain

$$(4.5) \quad \frac{\partial p_k}{\partial p_j} = \delta_{jk} - \frac{\partial^2 H(p, q, t)}{\partial q_k \partial p_j} \delta t \quad \text{and} \quad \frac{\partial p_k}{\partial q_j} = \delta_{jk} - \frac{\partial^2 H(p, q, t)}{\partial q_k \partial q_j} \delta t$$

And similarly for the coordinates  $q_k$ .

$$(4.6) \quad q_k(t_0 + \delta t) = q_k(t_0) + \frac{dq_k}{dt} \delta t = q_k(t_0) + \frac{\partial H(p, q, t)}{\partial p_k} \delta t$$

Or without the explicit time dependence:

$$(4.7) \quad q_k = q_{k0} + \frac{dq_k}{dt} \delta t = q_{k0} + \frac{\partial H(p, q, t)}{\partial p_k} \delta t$$

And consequently:

$$(4.8) \quad \frac{\partial q_k}{\partial q_j} = \delta_{jk} + \frac{\partial^2 H(p, q, t)}{\partial q_j \partial p_k} \delta t \quad \text{and} \quad \frac{\partial q_k}{\partial p_j} = \delta_{jk} + \frac{\partial^2 H(p, q, t)}{\partial p_j \partial p_k} \delta t$$

When inserted in the determinant (4.2), we find.

$$(4.9) \quad Det(p, q) = \frac{\partial(p_1, p_2, p_3, \dots, p_n, q_1, q_2, q_3, \dots, q_n)}{\partial(p_{10}, p_{20}, p_{30}, \dots, p_{n0}, q_{10}, q_{20}, q_{30}, \dots, q_{n0})} =$$

$$\left| \begin{array}{cccc} 1 - \frac{\partial^2 H(p, q, t)}{\partial p_1 \partial q_1} \delta t & \frac{\partial^2 H(p, q, t)}{\partial p_2 \partial q_1} \delta t & \dots & \dots \\ \frac{\partial^2 H(p, q, t)}{\partial p_2 \partial q_1} \delta t & 1 - \frac{\partial^2 H(p, q, t)}{\partial p_2 \partial q_2} \delta t & \dots & O(\delta t^2) \\ \dots & \dots & 1 - \frac{\partial^2 H(p, q, t)}{\partial p_n \partial q_n} \delta t & \dots \\ O(\delta t^2) & \dots & \dots & 1 + \frac{\partial^2 H(p, q, t)}{\partial q_n \partial p_n} \delta t \end{array} \right| =$$

$$1 - \sum_{k=1}^n \frac{\partial^2 H(p, q, t)}{\partial p_k \partial q_k} \delta t + \sum_{k=1}^n \frac{\partial^2 H(p, q, t)}{\partial q_k \partial p_k} \delta t + O(\delta t^2) = 1 + O(\delta t^2)$$

This means that the derivative of the determinant  $\lim_{\delta t \rightarrow 0} \frac{\Delta Det(p, q)}{\delta t} = \lim_{\delta t \rightarrow 0} \frac{O(\delta t^2)}{\delta t} = 0$  for all values of  $t$ , and it therefore follows that it is constant = 1 independent of  $t$ .

From this, it then follows:

$$(4.10) \quad V_\Omega = \int \int \int \dots \int dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n =$$

$$\int \int \int \dots \int \frac{\partial(p_1, p_2, p_3, \dots, p_n, q_1, q_2, q_3, \dots, q_n)}{\partial(p_{10}, p_{20}, p_{30}, \dots, p_{n0}, q_{10}, q_{20}, q_{30}, \dots, q_{n0})} dp_{10} dp_{20} dp_{30} \dots dp_{n0} \cdot dq_{10} dq_{20} dq_{30} \dots dq_{n0} =$$

$$\int \int \int \dots \int 1 \cdot dp_{10} dp_{20} dp_{30} \dots dp_{n0} \cdot dq_{10} dq_{20} dq_{30} \dots dq_{n0} = V_{\Omega_0}$$

As a consequence, all phase points, which lie within  $\Omega_0$  at time  $t_0$  lie within  $\Omega$  at time  $t$ , and the phase space volumes of  $\Omega_0$  and  $\Omega$  are the same, according to (4.10).

This on the other hand implies that the density  $D(p, q, t)$  of systems points in a phase space volume is constant independent of time.  $D(p, q, t) = D(p, q)$ . In other words:

**The density  $D(p, q)$  is an integral to the equations of motion.**

This can however also be inferred from the differential equation:

$$(4.11) \quad \frac{dD}{dt} = \frac{\partial D}{\partial t} + \sum_{k=1}^n \left( \frac{\partial D}{\partial q_k} \dot{q}_k + \frac{\partial D}{\partial p_k} \dot{p}_k \right)$$

Where stability means that  $\frac{\partial D}{\partial t} = 0$ . Using the Hamilton canonical equations:

$$\frac{dq_k}{dt} = \frac{\partial H(p, q, t)}{\partial p_k} \quad \frac{dp_k}{dt} = -\frac{\partial H(p, q, t)}{\partial q_k}$$

(4.11) can be written as:

$$(4.12) \quad \frac{dD}{dt} = \frac{\partial D}{\partial t} + \sum_{k=1}^n \left( \frac{\partial D}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial D}{\partial p_k} \frac{\partial H}{\partial q_k} \right) = \frac{\partial D}{\partial t} + \sum_{k=1}^n \{D, H\}_k$$

The Poisson parenthesis  $\{D, H\}_k$  is defined by

$$\frac{\partial D}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial D}{\partial p_k} \frac{\partial H}{\partial q_k}$$

If  $F$  is a physical expression, that does not explicitly depend on time i.e.  $\frac{\partial D}{\partial t} = 0$ , then  $F$  is an integral to the equations of motion, if the Poisson parenthesis vanish:

$$(4.13) \quad \frac{dF}{dt} = 0 \quad \Leftrightarrow \quad \{H, F\} = 0 \quad \Leftrightarrow \quad \frac{\partial F}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial F}{\partial p_k} \frac{\partial H}{\partial q_k} = 0$$

If (4.12) reduces to  $\{H, D\} = 0$ , that is, the density is a integral to the equations of motion.

(4.11) can also be written:

$$(4.14) \quad \frac{dD}{dt} = \frac{\partial D}{\partial t} + \sum_{k=1}^n \frac{\partial(D\dot{q}_k)}{\partial q_k} + \sum_{k=1}^n \frac{\partial(D\dot{p}_k)}{\partial p_k} = 0$$

Also, and not surprisingly, (4.14) has an complete analogy to the continuity equation of an incompressible fluid with density  $\rho$ , if we replace  $D$  with  $\rho$ , and the coordinates  $q$ , with the Cartesian coordinates  $x, y, z$ , and  $\rho\vec{v}$  represents then stream density or the flux.

$$(4.15) \quad \frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho\vec{v}) = \frac{\partial \rho}{\partial t} + \frac{\partial(\rho\dot{x})}{\partial x} + \frac{\partial(\rho\dot{y})}{\partial y} + \frac{\partial(\rho\dot{z})}{\partial z} = \frac{\partial \rho}{\partial t} + \frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} = 0$$

One may formally prove that the probability of finding a system in a given position in phase space is independent of the choice of coordinates, but we shall relax on the proof, since anything else would be absurd from a physical point of view.

This ends the formal treatise of statistical mechanics, and we shall now turn to its applications to theoretical thermodynamics.

## 6. Application of the statistical mechanics on thermodynamic systems

As stated earlier, even if we know the thermodynamic state completely, and also know the mechanical conditions  $(p, q)$ , the position of a system in phase space can not be determined. The best we can do is to calculate a probability density function  $P$ , which turns out to be some function of  $(p, q)$ , being the probability  $P(p, q)dpdq$  of finding the phase of a system within the  $2n$  dimensional infinitesimal volume  $dpdq$ .

Once the Hamilton function is known, we can assign a probability density function  $P(p, q)$  to every ensemble of systems all being in the same thermodynamic state.

We shall focus on systems in thermodynamic equilibrium, that is, with a well defined temperature  $T$ , and our aim is to establish a connection between the thermodynamic variables of state and the probability density function, which we write.

$$(6.1) \quad P(p, q, T, a)$$

Where  $a = a_1, a_2, \dots$  represent the external conditions on the ensemble of systems.

We shall begin by investigating the properties of a system holding a constant temperature  $T$

We know already that the density and probability density functions are constant following a system point  $(p, q)$  along its path in phase space.

$$(6.2) \quad D(p_0, q_0, t_0) = D(p, q, t) \quad \text{or} \quad P(p_0, q_0, t_0) = P(p, q, t)$$

The distribution of systems that correspond to statistical equilibrium, must however also obey  $D(p_0, q_0, t_0) = D(p, q, t_0)$ , that is, the density must be constant along each curve, and only change from curve to curve.

A system curve in phase space can theoretically be considered as the intersection of  $2n - 1$  hyper planes, having the equations  $I_1(p, q) = c_1, I_2(p, q) = c_2, \dots, I_{2n-1}(p, q) = c_{2n-1}$ . These equations are then  $2n - 1$  integrals of motion. As one of these integrals, we can always choose the energy  $H(p, q)$ .

To each set of constants  $c_1, c_2, c_3, \dots, c_{2n-1}$ , corresponds one curve in phase space.

Therefore, any time independent integral i.e. the density  $D$  or the density probability  $P$ , may be expressed by these  $2n-1$  independent integrals.

$$(6.3) \quad P = P(I_1(p, q), I_2(p, q), \dots, I_{2n-1}(p, q))$$

And we can write (6.1) as:

$$(6.4) \quad P = P(I_1(p, q), I_2(p, q), \dots, I_{2n-1}(p, q), T, a)$$

The Hamilton function is such an integral, and for other special system, one may indicate other integrals, but the only integral that is common for all system is the energy  $H$ , so we infer that.

$$(6.5) \quad P(H, T, a)$$

## 7. Determination of the probability density function

To establish an expression for the probability density function, we shall use the simple fact that two systems  $A$  and  $B$  both in thermodynamic equilibrium at the same temperature  $T$ , subsequently, when they are brought together, will be in thermodynamic equilibrium at the same temperature, provided that the interaction between the two systems is very small compared to their energy.

We shall denote all variables belonging to the system  $A$  with an index  $A$ , similar with the system  $B$ . When they are brought together the system variables are without an index.

### System $A$ :

Coordinates:  $q_A = q_{A1}, q_{A2}, q_{A3}, \dots, q_{Al}$ . (Number of degrees of freedom  $l$ )

Momenta:  $p_A = p_{A1}, p_{A2}, p_{A3}, \dots, p_{Al}$ .

Parameters:  $a_A = a_{A1}, a_{A2}, \dots$ .

Hamilton function:  $H_A = H_A(p_A, q_A, a_A)$

Probability density:  $P_A = P(H_A, T, a_A)$

### System $B$ :

Coordinates:  $q_B = q_{B1}, q_{B2}, q_{B3}, \dots, q_{Bm}$ . (Number of degrees of freedom  $m$ )

Momenta:  $p_B = p_{B1}, p_{B2}, p_{B3}, \dots, p_{Bm}$ .

Parameters:  $a_B = a_{B1}, a_{B2}, \dots$ .

Hamilton function:  $H_B = H_B(p_B, q_B, a_B)$

Probability density:  $P_B = P(H_B, T, a_B)$

### Composite system $A + B$

(Number of degrees of freedom  $n = l + m$ )

Coordinates:  $q = q_1, q_2, q_3, \dots, q_n$ .

Momenta:  $p = p_1, p_2, p_3, \dots, p_n$ .

Parameters:  $a = a_1, a_2, \dots$ .

Hamilton function:  $H = H(p, q, a) + U(q_A, q_B, a_A, a_B)$

Probability density:  $P = P(H, T, a)$

If  $V_{AB}$  is the potential of interaction between the two systems, we assume that

$$V_{AB} \ll H_A \quad \text{and} \quad V_{AB} \ll H_B$$

For this reason, the probability density is by a good approximation equal to  $P = P(H_A + H_B, T, a)$ . The probability of finding the systems  $A$  and  $B$  in the infinitesimal phase space volumes  $dp_A dq_A$  and  $dp_B dq_B$  are:

$$(7.1) \quad P(H_A, T, a_A) dp_A dq_A \quad \text{and} \quad P(H_B, T, a_B) dp_B dq_B$$

Since the two systems are independent of each other, the probability finding  $A$  in  $dp_A dq_A$  and  $B$  in  $dp_B dq_B$  is the product of the two probabilities. However since the systems are considered to be in thermodynamic equilibrium, this probability must also be equal to the probability as finding the composite system  $A + B$  in  $dp_A dq_A dp_B dq_B$ , having the same thermodynamic state.

$$(7.2) \quad P(H_A + H_B, T, a_A, a_B) dp_A dq_A dp_B dq_B = P(H_A, T, a_A) dp_A dq_A P(H_B, T, a_B) dp_B dq_B.$$



We have assumed that we have the same probability function in phase space referring to different ensembles. That this is in fact the case can be proven formally, but we relax on the proof, since otherwise the theory would be in great trouble.

The phase space volume elements cancel, and if we omit all parameters except the energy  $H$ , equation (6.6) is reduced to:

$$(7.3) \quad P(H_A + H_B) = P(H_A) \cdot P(H_B)$$

This is however the functional equation for the exponential function:  $f(x) = e^{ax}$ .

The equation is usually written:  $f(x + y) = f(x)f(y)$ .

We therefore stipulate as a working hypothesis, that the probability density function has the general form:

$$(7.4) \quad P(H, T, a) = ce^{\lambda H}$$

where  $\lambda$  must be a universal function of  $T$ , independent of the system in consideration.

The constant  $c$  will be determined by the normalization condition:

$$(7.5) \quad \int \int \int \dots \int P(H, T, a) dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = 1 \quad \Leftrightarrow$$

$$\int \int \int \dots \int ce^{\lambda H} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = 1$$

Since the integral is extended over an infinite space, the exponent  $\lambda H$  must necessarily be negative. We therefore put

$$(7.6) \quad \lambda = -\frac{1}{\theta} \quad \text{and} \quad c = e^{\frac{\psi}{\theta}}$$

and get the following expression for the probability density.

$$(7.7) \quad P = P(H, T, a) = e^{\frac{\psi - H}{\theta}} \quad \text{where } \theta = \theta(T) > 0$$

The constant  $\psi$ , can be determined by (7.5) or by the equivalent equation:

$$(7.8) \quad e^{\frac{\psi}{\theta}} = \int \int \int \dots \int e^{\frac{H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

$e^{\frac{\psi}{\theta}}$  is a function of  $T$  and the external parameters ( $a$ ), i.e. a function of the thermodynamic state. We shall later determine  $\theta$  as a function of the temperature, and it will turn out, that  $\theta = kT$ , that is, proportional to the absolute temperature  $T$ .

The probability distribution (7.7) is called the Gibb's *canonical distribution*, and the corresponding ensemble a *canonical ensemble*.

Let us consider two systems (1) and (2) both in thermodynamic equilibrium and bring them together. The probability distribution for the composite system is then:

$$(7.9) \quad P = P_1 \cdot P_2 = e^{\frac{\psi_1 + \psi_2}{\theta_1 + \theta_2} - \frac{H_1 + H_2}{\theta_1 + \theta_2}}$$

But this distribution will not correspond to thermodynamic equilibrium if  $\theta_1 \neq \theta_2$ , because in that case

$$(7.10) \quad F = \frac{H_1}{\theta_1} - \frac{H_2}{\theta_2}$$

can not, even approximately, be an integral to the equation of motion with Hamilton function  $H = H_1 + H_2 + U$ . The reason for this is, that the condition for physical variable  $F$  to be an integral to the equation of motion is that the Poisson parenthesis of  $F$  with  $H$  vanishes.

$$(7.11) \quad \{H, F\} = \frac{\partial F}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial F}{\partial p_k} \frac{\partial H}{\partial q_k}$$

And it is obvious that (7.10) does not comply.

But this is in accordance with experience, (and the second law of thermodynamics) that the thermodynamic equilibrium is disturbed, when two bodies having different temperatures are brought together.

Only when  $\theta_1 \approx \theta_2$  (7.9) will approximately correspond to statistical equilibrium.

If the statistical equilibrium shall be maintained for all systems and all kinds of mutual interaction, one is lead to the conclusion that the probability density can depend only on the energy of the system.

## 8. Mean value of and fluctuations in the energy of the Gibb's ensemble

From (7.8) it is seen, that a body at a certain temperature does not necessarily have a definite energy. On the contrary the energy is given by a probability distribution function (7.7).

In the empirical thermodynamic one nevertheless often describes a system as having a certain internal energy  $E = E(T, a)$ , which is a function of the thermodynamic state.

$E$  can not however be identified with  $H$ , which is a function of the undefined mechanical state  $(p, q)$ .

On the other hand the mean value of  $H$ , taken over the ensemble may be identified with  $E$ .

$$(8.1) \quad \bar{H} = \int \int \int \dots \int H e^{-\frac{H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

As a preperation to evaluate the mean of  $H$ , we shall first evaluate the mean of the kinetic energy  $T$ . (not to confuse with the temperature  $T$ )

According to Euler's theorem, which applies to any quadratic form in  $p_k$ .

$$(8.2) \quad T = \frac{1}{2} \sum_{k=1}^n p_k \frac{\partial T}{\partial p_k}$$

Furthermore

$$\int e^{\frac{\psi-H}{\theta}} \frac{\partial T}{\partial p_k} dp_k = \int e^{\frac{\psi-H}{\theta}} \frac{\partial H}{\partial p_k} dp_k = -\theta e^{\frac{\psi-H}{\theta}} \quad \left( \text{Since } \frac{\partial T}{\partial p_k} = \frac{\partial H}{\partial p_k} \right)$$

This result we shall apply, when calculating the mean value of the kinetic energy.

$$(8.3) \quad \bar{T} = \sum_{k=1}^n \int \int \dots \int T e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

Using Euler's theorem

$$(8.4) \quad \bar{T} = \frac{1}{2} \sum_{k=1}^n \int \int \dots \int p_k \frac{\partial T}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

Where the limits of integration all go from  $-\infty$  to  $+\infty$ .

We first look at the integral with respect to  $p_k$ , which we do by partial integration.

$$(8.5) \quad \int_{-\infty}^{\infty} p_k \frac{\partial T}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_k = \int_{-\infty}^{\infty} p_k d(-\theta e^{\frac{\psi-H}{\theta}}) = -\theta \left[ p_k e^{\frac{\psi-H}{\theta}} \right]_{-\infty}^{\infty} + \theta \int_{-\infty}^{\infty} e^{\frac{\psi-H}{\theta}} dp_k$$

The first term on the right hand side vanishes, and the final integral is equal to 1, by the normalization condition. When inserted in (8.4), then by definition of the probability distribution function.

$$(8.6) \quad \int_{-\infty}^{\infty} p_k \frac{\partial T}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_1 dp_2 \dots dp_3 dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = \theta$$

It then follows:  $\bar{T} = \frac{1}{2} \sum_{k=1}^n \int \int \dots \int p_k \frac{\partial T}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = \frac{n}{2} \theta$

$$(8.7) \quad \bar{T} = \frac{n}{2} \theta$$

This is **the principle of equipartition**, also known from the kinetic theory of gasses.

We proceed to calculate the square of the standard deviation of  $T$ .

$$(8.8) \quad \sigma^2(T) = (\overline{T - \bar{T}})^2 = \overline{T^2} - \bar{T}^2$$

This can be calculated by the same means as (8.4).

$$(8.9) \quad \overline{T^2} = \frac{1}{2} \sum_{k=1}^n \int \int \dots \int T^2 e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

$$\overline{T^2} = \frac{1}{2} \sum_{k=1}^n \iint \dots \int T p_k \frac{\partial T}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

For simplicity we extract the integral over  $p_k$ :

$$\begin{aligned} \int T p_k \frac{\partial T}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_k &= -\theta \int T p_k d(e^{\frac{\psi-H}{\theta}}) && \text{(since } \frac{\partial T}{\partial p_k} = \frac{\partial H}{\partial p_k} \text{)} \\ &= \left[ -\theta T p_k e^{\frac{\psi-H}{\theta}} \right]_{-\infty}^{\infty} + \theta \int \frac{\partial(T p_k)}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_k \end{aligned}$$

The first term vanishes, and we do the integral as we did before, now implying the full sum and integration over all variables:

$$\begin{aligned} \theta \int \frac{\partial(T p_k)}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_k &= \theta \int (p_k \frac{\partial T}{\partial p_k} + T) e^{\frac{\psi-H}{\theta}} dp_k = \\ (8.10) \quad \theta \int p_k \frac{\partial T}{\partial p_k} e^{\frac{\psi-H}{\theta}} dp_k + \theta \int T e^{\frac{\psi-H}{\theta}} dp_k &= n \frac{\theta}{2} \overline{T} + \theta \overline{T} \end{aligned}$$

$$(8.11) \quad \sigma^2(T) = \overline{(T - \overline{T})^2} = \overline{T^2} - \overline{T}^2 = n \frac{\theta}{2} \overline{T} + \theta \overline{T} - \overline{T}^2 = \overline{T}^2 - \frac{2}{n} \overline{T}^2 - \overline{T}^2 = \frac{2}{n} \overline{T}^2$$

And consequently:

$$(8.12) \quad \frac{\sigma^2(T)}{\overline{T}^2} = \frac{\overline{(T - \overline{T})^2}}{\overline{T}^2} = \frac{2}{n}$$

This means that the probability, when measuring the kinetic energy of a system, to find a value which deviates more than  $\overline{T}$  from the mean is equal to  $\sqrt{\frac{2}{n}}$ .

For thermodynamic systems the number of particles is usually of the order of Avogadro's number  $N_A = 6,0 \cdot 10^{23}$ , so usually the deviations from the mean are immensely small, and this result will not alter even if we alter the deviation to 1/10,000 of  $\overline{T}$ .

To obtain similar results for the total energy  $H$ , we start out from the equation (7.8):

$$e^{\frac{\psi}{\theta}} = \iiint \dots \int e^{\frac{H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

Which defines  $\psi$  as a function of the temperature and the external parameters ( $a$ ).

Taking the differential of this equation gives.

$$e^{\frac{\psi}{\theta}} \left( -\frac{d\psi}{\theta} + \frac{\psi}{\theta^2} d\theta \right) = \iiint \dots \int e^{\frac{H}{\theta}} \left( \frac{H}{\theta^2} d\theta - \frac{1}{\theta} \sum_{i=1}^m \frac{\partial H}{\partial a_i} da_i \right) dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

Multiplying the equation by  $-\theta e^{\frac{\psi}{\theta}}$ , we get:

$$\begin{aligned}
 d\psi &= \frac{\psi}{\theta} d\theta - \frac{d\theta}{\theta} \int \int \int \dots \int H e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n - \\
 &\sum_{l=1}^m da_l \int \int \int \dots \int \sum_{l=1}^m \left(-\frac{\partial H}{\partial a_l} da_l\right) e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n \Leftrightarrow \\
 d\psi &= \frac{\psi - \bar{H}}{\theta} d\theta - \sum_{l=1}^m \left(-\frac{\partial \bar{H}}{\partial a_l} da_l\right) \Leftrightarrow \\
 (8.13) \quad d\psi &= \frac{\psi - \bar{H}}{\theta} d\theta - \sum_{l=1}^m \bar{A}_l da_l \quad \text{where} \quad A_l = -\frac{\partial H}{\partial a_l}
 \end{aligned}$$

$A_l$  is the  $l$ 'th component of the generalized force, on which the system act on the environment. For simplicity we define  $\bar{\eta}$ , the probability exponent as:

$$(8.14) \quad \bar{\eta} = \frac{\psi - \bar{H}}{\theta}$$

Then

$$d\psi = \bar{\eta} d\theta - \sum_{l=1}^m \bar{A}_l da_l$$

From which it follows that  $\psi$  is a function of the variable  $\theta$  and the external parameters  $a_l$ .

$$(8.15) \quad \bar{\eta} = \frac{\partial \psi}{\partial \theta} \quad \text{and} \quad \bar{A}_l = -\frac{\partial \psi}{\partial a_l}$$

From

$$\bar{\eta} = \frac{\partial \psi}{\partial \theta}$$

and

$$\bar{\eta} = \frac{\psi - \bar{H}}{\theta} \Leftrightarrow \bar{H} = \psi - \theta \bar{\eta}$$

we find

$$(8.15) \quad \bar{H} = \psi - \theta \frac{\partial \psi}{\partial \theta}$$

From the definition of the mean of  $H$  we have,

$$(8.16) \quad \bar{H} = \sum_{k=1}^n \int \int \int \dots \int H e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

We get by a partial differentiation with respect to  $\theta$

$$\frac{\partial \bar{H}}{\partial \theta} = \sum_{k=1}^n \int \int \int \dots \int H e^{\frac{\psi-H}{\theta}} \left( -\frac{\psi-H}{\theta^2} + \frac{1}{\theta} \frac{\partial \psi}{\partial \theta} \right) dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n$$

$$(8.17) \quad \frac{\partial \bar{H}}{\partial \theta} = \left(-\frac{\psi}{\theta^2} + \frac{1}{\theta} \frac{\partial \psi}{\partial \theta}\right) \bar{H} + \frac{1}{\theta^2} \bar{H}^2$$

And according to (8.15)

$$\bar{H} = \psi - \theta \frac{\partial \psi}{\partial \theta}$$

We find

$$\bar{H}^2 = \left(\psi - \theta \frac{\partial \psi}{\partial \theta}\right) \bar{H} + \theta^2 \frac{\partial \bar{H}}{\partial \theta}$$

$$\bar{H}^2 = \bar{H}^2 + \theta^2 \frac{\partial \bar{H}}{\partial \theta} \Rightarrow \sigma^2(H) = \bar{H}^2 - \bar{H}^2 = \theta^2 \frac{\partial \bar{H}}{\partial \theta}$$

$$(8.18) \quad \sigma^2(H) = \theta^2 \frac{\partial \bar{H}}{\partial \theta}$$

and by

$$\bar{H} = \psi - \theta \frac{\partial \psi}{\partial \theta}$$

it follows

$$(8.19) \quad \frac{\partial \bar{H}}{\partial \theta} = \frac{\partial \psi}{\partial \theta} - \frac{\partial \psi}{\partial \theta} - \theta \frac{\partial^2 \psi}{\partial \theta^2} = -\theta \frac{\partial^2 \psi}{\partial \theta^2}$$

So that

$$\sigma^2(H) = -\theta^3 \frac{\partial^2 \psi}{\partial \theta^2}$$

Using

$$\sigma^2(H) = \theta^2 \frac{\partial \bar{H}}{\partial \theta}$$

and changing the variable from  $\theta$  to the kinetic energy  $T = \frac{n}{2} \theta \Leftrightarrow \theta = \frac{2T}{n}$  we get:

$$\sigma^2(H) = \theta^2 \frac{\partial \bar{H}}{\partial \theta} = \frac{4\bar{T}^2}{n^2} \frac{2}{n} \frac{\partial \bar{H}}{\partial \bar{T}}$$

Arriving at

$$(8.20) \quad \frac{\sigma^2(H)}{\bar{T}^2} = \frac{2}{n} \frac{\partial \bar{H}}{\partial \bar{T}}$$

Generally  $\frac{\partial \bar{H}}{\partial \bar{T}}$  is of order 1, so we can draw the same conclusions about the fluctuations in the total energy as for the kinetic energy. Even if  $\frac{\partial \bar{H}}{\partial \bar{T}}$  is very large in some small temperature interval, it will not change the conclusions about the fluctuations significantly.

Temperature and mechanical phase are *complementary* in the sense of Niels Bohr.

The temperature is a statistical concept based on a probability distribution of an ensemble, whereas the mechanical phase of the individual systems are unknown. On the other hand, if the mechanical phase is well known, it does not make sense to talk about the probability of finding the system in that mechanical phase (since it is known), and consequently it makes no sense to talk about temperature.

### 9. Fluctuations in the external components of force on an arbitrary system

Differentiation of the equation

$$\int \int \int \dots \int e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = 1$$

With respect to the external parameters  $a_l$  gives:

$$(9.1) \quad \int \int \int \dots \int \left( \frac{\partial \psi}{\partial a_l} - \frac{\partial H}{\partial a_l} \right) e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = 0$$

Integrating the two terms separately gives:

$$(9.2) \quad A_l = -\frac{\partial \bar{H}}{\partial a_l} = -\frac{\partial \psi}{\partial a_l}$$

Now differentiating (9.1) with respect to  $a_k$  gives:

$$\int \int \int \dots \int \left( \frac{\partial^2 \psi}{\partial a_l \partial a_k} - \frac{\partial^2 H}{\partial a_l \partial a_k} + \frac{1}{\theta} \left( \frac{\partial \psi}{\partial a_l} - \frac{\partial H}{\partial a_l} \right) \left( \frac{\partial \psi}{\partial a_k} - \frac{\partial H}{\partial a_k} \right) \right) e^{\frac{\psi-H}{\theta}} dp_1 dp_2 dp_3 \dots dp_n \cdot dq_1 dq_2 dq_3 \dots dq_n = 0$$

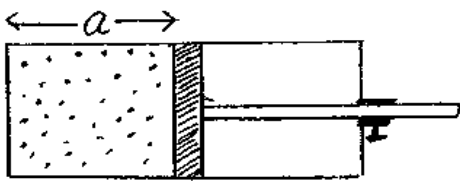
Then using (9.2)

$$(9.3) \quad \overline{(A_l - \bar{A}_l)(A_k - \bar{A}_k)} = \theta \left( \frac{\partial^2 \bar{H}}{\partial a_l \partial a_k} - \frac{\partial^2 \psi}{\partial a_l \partial a_k} \right) \quad (l, k) = (1, 2, \dots, m)$$

By differentiating (9.1) with respect to  $\theta$ , we find in a similar manner.

$$(9.4) \quad \overline{(A_l - \bar{A}_l)(H - \bar{H})} = -\theta^2 \frac{\partial^2 \psi}{\partial a_l \partial \theta} = \theta^2 \frac{\partial \bar{A}_l}{\partial \theta} = -\theta^2 \frac{\partial \bar{\eta}}{\partial a_l}$$

### 10. Determination of $\theta$ as a function of absolute temperature



Let us consider an ideal gas, consisting of  $n$  particles with equal masses  $m$ , (since the extension to a mixture of gasses is trivial). They move freely in a container supplied with a piston that can be pushed in and out without friction. The Cartesian coordinates of the  $i$ 'th particle is  $(x_i, y_i, z_i) \quad i = 1 \dots n$ ,

And the generalized coordinates and momenta are:  $q_i \quad i = 1 \dots 3n$  and  $p_i \quad i = 1 \dots 3n$ .

The kinetic energy is:

$$(10.1) \quad T = \frac{1}{2} m \sum_{k=1}^n (\dot{x}_k^2 + \dot{y}_k^2 + \dot{z}_k^2)$$

and the associated momenta are:

$$(p_{xk}, p_{yk}, p_{zk}) = (m\dot{x}_k, m\dot{y}_k, m\dot{z}_k)$$

The surroundings are the walls of the container and the piston. Their influences on the system consist of the impact of the particles with the walls, where the particles are recoiled at a very large acceleration. This may be represented by a potential for the  $i$ 'th particle given by:

$$(10.2) \quad U_i = U(x_i, y_i, z_i, a)$$

Where  $(a)$  represent the surroundings. We have assumed that the potential has the same form for all particles. The total potential  $U$  is then the sum of all the potentials  $U_i$ .

There might be an interactive potential between the individual particles, but for an ideal gas, it can safely be neglected. We assume that the system is in thermodynamic equilibrium having the same overall temperature. The corresponding probability density is then:

$$(10.3) \quad P = e^{\frac{\psi-H}{\theta}} = e^{\frac{\psi-T-U}{\theta}} \quad (\text{Here } T \text{ stands for the kinetic energy})$$

We begin by calculating  $\psi$  as function of  $\theta$  and  $a$ .

$$(10.4) \quad e^{\frac{\psi}{\theta}} = \iiint \dots \int e^{-\frac{\frac{1}{2}m \sum_{k=1}^n (\dot{x}_k^2 + \dot{y}_k^2 + \dot{z}_k^2) + \sum_{k=1}^n U(x_k, y_k, z_k)}{\theta}} m dx_1 m dy_1 m dz_1 \dots m dx_n m dy_n m dz_n dx_1 dy_1 dz_1 \dots dx_n dy_n dz_n$$

The integration over  $x_i$  can be done, if we introduce the variable  $t = \sqrt{\frac{m}{2\theta}} \dot{x}_i$

$$(10.5) \quad \int_{-\infty}^{\infty} e^{-\frac{m\dot{x}_i^2}{2\theta}} m dx_i = \sqrt{2m\theta} \int_{-\infty}^{\infty} e^{-t^2} dt = \sqrt{2\pi m\theta}$$

The same integration is performed over all the other velocity variables.

The potential  $U_i = U(x_i, y_i, z_i, a) = 0$ , except at the walls, where it is extremely large, but it does not contribute to the integral, so the integration over the coordinates gives:

$$(10.6) \quad \iiint e^{-\frac{U(x_i, y_i, z_i, a)}{\theta}} dx_i dy_i dz_i = \iiint e^0 dx_i dy_i dz_i = V$$

Where  $V$  is the volume of the container. We thus have according to (10.4):

$$(10.7) \quad e^{\frac{\psi}{\theta}} = (2\pi m\theta)^{\frac{3n}{2}} V^n$$

Or when taking the logarithm on both sides



$$(10.8) \quad \psi = -n\theta \ln(V(2\pi m\theta)^{\frac{3}{2}})$$

If  $D$  is the area of the piston and  $a$  is of the distance from the bottom of the cylinder to the piston, then the volume  $V = Da$ , and according to (10.2)

$$\bar{A}_l = -\frac{\partial \psi}{\partial a_l}$$

The force on the piston is

$$(10.9) \quad \bar{A} = -\frac{\partial \psi}{\partial a} = -D \frac{\partial \psi}{\partial V} = \frac{nD\theta}{V}$$

One may also from (9.3) calculate the square of the standard deviation.

$$(10.10) \quad (\overline{A - \bar{A}})^2 = \theta \left( \frac{\partial^2 H}{\partial^2 a} - \frac{\partial^2 \psi}{\partial^2 a} \right)$$

Since  $V = Da$ , we get, using (9.4):

$$\overline{(A_l - \bar{A}_l)(H - \bar{H})} = -\theta^2 \frac{\partial^2 \psi}{\partial a_l \partial \theta} = \theta^2 \frac{\partial \bar{A}_l}{\partial \theta} = -\theta^2 \frac{\partial \bar{\eta}}{\partial a_l}$$

$$(10.11) \quad \frac{\partial^2 \psi}{\partial a^2} = D^2 \frac{\partial}{\partial V} (-n\theta) \frac{1}{V} = \frac{D^2 n \theta}{V^2}$$

Since the kinetic energy  $T$  does not explicitly depend on the coordinates  $q_i$ , and  $U = \sum_{i=1}^n U_i$  we have

$$\frac{\partial^2 H}{\partial a^2} = \sum_{i=1}^n \frac{\partial^2 U_i}{\partial a^2}$$

And furthermore the factor  $e^{-\frac{T}{\theta}}$  can be put outside both integrals and cancel each other.

$$(10.12) \quad \frac{\partial^2 U}{\partial a^2} = \frac{\iiint \dots \int \frac{\partial^2 U}{\partial a^2} e^{-\frac{U}{\theta}} dx_1 dy_1 \dots dz_n}{\iiint \dots \int e^{-\frac{U}{\theta}} dx_1 dy_1 \dots dz_n}$$

As before the denominator gives  $V^n$ , since we integrate over the volume  $V$  of the cylinder, and  $U = 0$ , except at the walls. Concerning the potential  $U_i(x_i, y_i, z_i, a)$  we shall simply assume, that it, within a tiny interval  $\delta$  grows to a very large value  $U_0$ , at the walls of the container, and that the position of the piston is given by  $a$ . We further assume that the direction of  $a$  is the direction of the  $x$ -axis, so that the potential  $U_i$  is a function of  $(x_i - a)$ . It then follows:

$$\frac{\partial^2 U_i}{\partial a^2} = \frac{\partial^2 U_i}{\partial x_i^2} \quad \text{and} \quad \frac{\partial^2 U}{\partial a^2} = \sum_{i=1}^n \frac{\partial^2 U_i}{\partial x_i^2}$$

Therefore we have:

$$(10.13) \quad \iiint \dots \int \frac{\partial^2 U}{\partial a^2} e^{-\frac{\sum_{k=1}^n U_k(x_k, y_k, z_k)}{\theta}} dx_1 dy_1 \dots dz_n = \sum_{i=1}^n \iiint \dots \int \frac{\partial^2 U_i}{\partial x_i^2} e^{-\frac{\sum_{k=1}^n U_k(x_k, y_k, z_k)}{\theta}} dx_1 dy_1 \dots dz_n$$

We consider now the  $i$ 'th term in this sum:

$$\iiint \dots \int \frac{\partial^2 U_i}{\partial x_i^2} e^{-\frac{\sum_{k=1}^n U_k(x_k, y_k, z_k)}{\theta}} dx_1 dy_1 \dots dz_n = V^{n-1} \iiint \dots \int \frac{\partial^2 U_i}{\partial x_i^2} e^{-\frac{U_i}{\theta}} dx_i dy_i dz_i$$

The integration over  $dydz$ , just gives a factor  $D$ , so we get:

$$(10.14) \quad V^{n-1} D \iiint \dots \int \frac{\partial^2 U_i}{\partial x_i^2} e^{-\frac{U_i}{\theta}} dx_i$$

$U_i$  is vanishing except for a very small interval  $\delta$ , and we get by a partial integration, omitting the index  $i$ .

$$\int \frac{\partial^2 U}{\partial x^2} e^{-\frac{U(x)}{\theta}} dx = \int e^{-\frac{U(x)}{\theta}} dU'(x) = \left[ e^{-\frac{U(x)}{\theta}} U'(x) \right] + \frac{1}{\theta} \int U'(x) e^{-\frac{U(x)}{\theta}} U'(x) dx$$

The first term is 0, because  $U'(x) = 0$  outside the tiny interval, and the last integral, does not depend significantly how the potential grows within the tiny interval. Since we are only interested in the magnitude, we can assume that  $U(x)$  grows linearly with  $x$ , so that:  $U'(x) = \frac{U_0}{\delta} = \text{constant}$ .

Then we find:

$$\frac{1}{\theta} \int U'(x) e^{-\frac{U(x)}{\theta}} U'(x) dx = \frac{1}{\theta} \int U'(x) e^{-\frac{U(x)}{\theta}} dU = \frac{1}{\theta} \left( \frac{U_0}{\delta} \right) \int_0^{U_0} e^{-\frac{U}{\theta}} dU = \left[ -e^{-\frac{U}{\theta}} \right]_0^{U_0} = \frac{U_0}{\delta} (1 - e^{-\frac{U_0}{\theta}}) \approx \frac{U_0}{\delta}$$

So according to (10.11), (10.12), (10.13)

$$\overline{\frac{\partial^2 H}{\partial a^2}} = \frac{\partial^2 U}{\partial a^2} = n V^{n-1} D U_0 \frac{n V^{n-1} D U_0}{V^n \delta} = \frac{n D U_0}{V \delta}$$

Then from (10.9), (10.10), (10.11)

$$(10.15) \quad \frac{(\overline{A - \bar{A}})^2}{\bar{A}^2} = \frac{\sigma^2(A)}{\bar{A}^2} = \frac{V^2 \theta}{D^2 \theta^2 n^2} \left( \frac{n D U_0}{V \delta} - \frac{D^2 \theta n}{V^2} \right) = \frac{1}{n} \left( \frac{U_0}{\delta} \frac{a}{\theta} - 1 \right)$$

When  $n$  is sufficiently large the fluctuations in the force will remain vanishingly small, even if

$$\frac{U_0}{\theta} \gg 1 \quad \text{and} \quad a \gg \delta$$

With a reasonable estimate of the parameters involved one finds:

$$(10.15) \quad \frac{\sigma^2(A)}{A^2} \approx 10^{-11}$$

In other words, we may identify  $\bar{A}$  with the force that gives rise to the pressure that the molecules exercise on the walls of the container.

In other words:  $\bar{A} = PD$ , where  $P$  is the pressure and  $D$  is the area of the piston. We therefore get, according to (10.9)  $\bar{A} = \frac{nD\theta}{V}$ , and consequently, since  $P = \frac{\bar{A}}{D}$

$$(10.16) \quad P = \frac{n\theta}{V}$$

This, we can compare to the equation of state for an ideal gas.

$$(10.17) \quad PV = nkT \quad \text{or} \quad PV = n_M RT$$

$k$  is Boltzmann's constant  $k = 1.372 \cdot 10^{-16} \text{ J/K}$ .  $n_M = \frac{n}{N_A}$  is the mole number, and  $N_A = 6.023 \cdot 10^{23}/\text{mole}$ , is Avogadro's number. From (10.13) and (10.14) we then see:

$$(10.18) \quad \theta = kT$$

For the mean value of the energy, we have from (10.15)

$$(10.19) \quad \bar{H} = \psi - \theta \frac{\partial \psi}{\partial \theta} = -n\theta \ln \left( V(2\pi m\theta)^{\frac{3}{2}} \right) - \theta \ln \left( -V(2\pi m\theta)^{\frac{3}{2}} - n\theta - \frac{3}{2} \frac{1}{\theta} \right)$$

$$(10.20) \quad \bar{H} = \frac{3}{2} nkT$$

So the internal energy is proportional to the absolute temperature, and it is independent of the external parameters (a), that is, the volume  $V$ .

This is in accordance with the experimental results of thermodynamics. Equation (10.20) is therefore considered one of the major achievements of statistical mechanics.

Furthermore the numerical value of  $\frac{3}{2}nk$  is in accordance with that for one-atomic gasses:

$$(10.21) \quad C_V = \frac{\partial \bar{H}}{\partial T} = \frac{3}{2} nk = \frac{3}{2} n_M R$$

## 11. Maxwell's velocity distribution

The probability of finding a specific molecule (1) within a volume :  $d\Omega = dp_{1x}dp_{1y}dp_{1z}dx_1dy_1dz_1$  of phase space is:

$$\begin{aligned}
 P_1 dp_{1x} dp_{1y} dp_{1z} dx_1 dy_1 dz_1 &= \\
 (11.1) \quad dp_{1x} dp_{1y} dp_{1z} dx_1 dy_1 dz_1 \cdot \int \dots \int e^{\frac{\psi - \sum_{k=1}^n \frac{1}{2m} (dp_{1x}^2 dp_{1y}^2 dp_{1z}^2) - \sum_{k=1}^n U_i(x_i, y_i, z_i)}{\theta}} dp_{2x} \dots dz_n &= \\
 C e^{\frac{-\frac{1}{2m} (dp_{1x}^2 dp_{1y}^2 dp_{1z}^2) - U_1(x_1, y_1, z_1)}{\theta}} dp_{1x} dp_{1y} dp_{1z} dx_1 dy_1 dz_1 &= \\
 e^{\frac{\psi_1 - H_1}{\theta}} dp_{1x} dp_{1y} dp_{1z} dx_1 dy_1 dz_1 &
 \end{aligned}$$

This is valid for each molecule, that is, every molecule is canonically distributed. So we may drop the index (1). Crucial for this assertion is that the mutual interaction between the molecules is vanishing. The constant  $\psi_1$  can be determined by:

$$(11.2) \quad \int e^{\frac{\psi_1 - H_1}{\theta}} dp_{1x} dp_{1y} dp_{1z} dx_1 dy_1 dz_1 = 1$$

When the number of molecules is very large, we can perceive this as an ensemble of molecules with temperature  $\theta = kT$ . The number of molecules having velocities  $(v_x, v_y, v_z)$  in the velocity volume  $dv_x dv_y dv_z$  must then be proportional to.

$$(11.3) \quad c e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z$$

Introducing polar coordinates, where  $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$ , which gives the volume element  $dV = v^2 dv \sin \theta d\theta d\varphi$ , we may after a trivial integration over the angles, write the probability of finding a molecule with speed  $v$  in the interval  $dv$ .

$$(11.4) \quad P(v) dv = c_1 e^{-\frac{mv^2}{2kT}} v^2 dv$$

Where the constant is to be determined by the condition:  $\int_0^{\infty} P(v) dv = 1$

$$(11.5) \quad c_1 \int_0^{\infty} e^{-\frac{mv^2}{2kT}} v^2 dv = 1$$

Introducing the variable:

$$x^2 = \frac{mv^2}{2kT} \Rightarrow v^2 = \frac{2kT}{m}x^2$$

$$x = \sqrt{\frac{m}{2kT}}v \Rightarrow dx = \sqrt{\frac{m}{2kT}}dv \Rightarrow dv = \sqrt{\frac{2kT}{m}}dx$$

The integral becomes:

$$(11.6) \quad c_1 \left( \frac{2kT}{m} \right)^{\frac{3}{2}} \int_0^\infty e^{-x^2} x^2 dx = 1$$

The integral is evaluated by the method of partial integration, as formulated below.

$$\int f(x)g'(x)dx = \int f(x)dg(x) = f(x)g(x) - \int g(x)df(x)$$

$$(11.7) \quad \int_0^\infty e^{-x^2} x^2 dx = \int_0^\infty \frac{x^2}{-2x} de^{-x^2} = -\frac{1}{2} \int_0^\infty x de^{-x^2} =$$

$$-\frac{1}{2} [xe^{-x^2}]_0^\infty + \frac{1}{2} \int_0^\infty e^{-x^2} dx = 0 + \frac{\sqrt{\pi}}{4} = \frac{\sqrt{\pi}}{4}$$

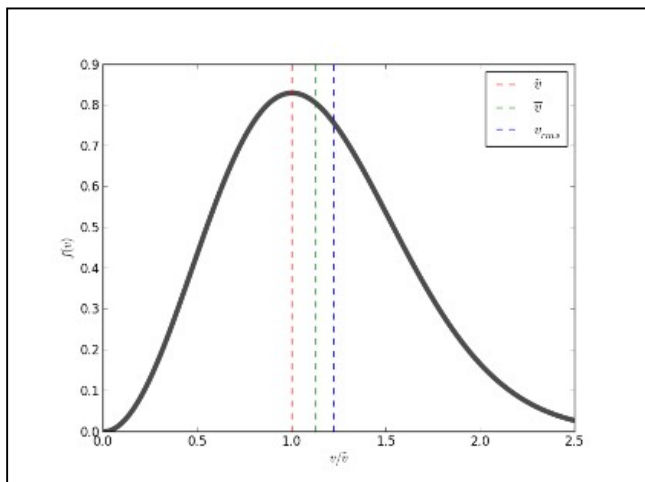
And (11.6) becomes:

$$(11.8) \quad c_1 \left( \frac{2kT}{m} \right)^{\frac{3}{2}} \frac{\sqrt{\pi}}{4} = 1 \Leftrightarrow c_1 = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{\frac{3}{2}}$$

And this finally yields the velocity distribution of Maxwell

$$(11.9) \quad P(v) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$$

A curve representing this distribution is shown below.



The most frequent speed of the molecules, that is, the value of  $v$ , where curve has its maximum, can be found by differentiating the function.

$$f(v) = v^2 e^{-\frac{mv^2}{2kT}}$$

$$f'(v) = e^{-\frac{mv^2}{2kT}} \left( -\frac{m}{2kT} 2v \right) v^2 + e^{-\frac{mv^2}{2kT}} 2v = 2ve^{-\frac{mv^2}{2kT}} \left( -\frac{m}{2kT} v^2 + 1 \right)$$

$$(11.10) \quad f'(v) = 0 \Leftrightarrow \left( -\frac{m}{2kT} v^2 + 1 \right) = 0 \Leftrightarrow v = \sqrt{\frac{2kT}{m}}$$

Inserting values for  $N$  (Nitrogen)  $M_N = 28u$ ,  $T = 300 K$  (room temperature), Boltzmann's constant  $k = 1.381 \cdot 10^{-23} J/K$  and  $m_N = 28 \cdot 1.660 \cdot 10^{-27} kg$ , we get for  $v_{most\ frequent} = 422 m/s$ .

We may also calculate the mean value of  $v$ .

$$(11.11) \quad \int_0^{\infty} vP(v)dv = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{\frac{3}{2}} \int_0^{\infty} v^3 e^{-\frac{mv^2}{2kT}} dv = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{\frac{3}{2}} \frac{1}{2} \int_0^{\infty} v^2 e^{-\frac{mv^2}{2kT}} dv^2$$

As before, we make the substitution:  $x^2 = \frac{mv^2}{2kT} \Rightarrow v^2 = \frac{2kT}{m} x^2$  to get

$$\frac{2}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{\frac{3}{2}} \left( \frac{2kT}{m} \right)^2 \int_0^{\infty} x^2 e^{-x^2} dx^2 = \frac{4}{\sqrt{\pi}} \sqrt{\frac{2kT}{m}} \int_0^{\infty} x^3 e^{-x^2} dx$$

Integrating by parts

$$\begin{aligned} \int_0^{\infty} x^3 e^{-x^2} dx &= \int_0^{\infty} \frac{x^3}{-2x} de^{-x^2} = \\ &= -\frac{1}{2} \left( \left[ x^2 e^{-x^2} \right]_0^{\infty} - 2 \int_0^{\infty} x e^{-x^2} dx \right) = 0 + \int_0^{\infty} x e^{-x^2} dx = -\frac{1}{2} \left[ e^{-x^2} \right]_0^{\infty} = \frac{1}{2} \end{aligned}$$

We find:

$$\bar{v} = \int_0^{\infty} vP(v)dv = \frac{4}{\sqrt{\pi}} \sqrt{\frac{2kT}{m}} \int_0^{\infty} x^3 e^{-x^2} dx = \frac{2}{\sqrt{\pi}} \sqrt{\frac{2kT}{m}}$$

Using the same values, as we did above, we find:  $\bar{v} = 476 m/s$ .

## 12. Perrins experiment

Let us consider a liquid, having a certain temperature, in which a large number of particles with mass  $m$  and volume  $v$  are suspended. The particles are considered microscopic i.e. they can only be observed in a microscope. Let us consider an arbitrary one of these particles. The only thing we know is that the particles are in thermodynamic equilibrium with its surroundings.

The probability of finding a particle in the phase space volume  $dp_x dp_y dp_z dx dy dz$  must therefore be given by the canonical distribution:

$$(12.1) \quad P dp_x \dots dz = e^{-\frac{\psi-H}{kT}} dp_x \dots dz$$

Since we are only interested in the position of the particle, we first integrate over the momenta. The spatial distribution is then given by:

$$(12.2) \quad P_1 dx dy dz = c_1 e^{-\frac{U(x,y,z)}{kT}} dx dy dz$$

The microscopic particle is only affected by the gravitational potential  $U(h) = m_v g h$ , where  $h$  is the height over some reference level.  $v$  is the volume of the particle and  $m_v$  is the mass of the particle, reduced by the buoyancy from the liquid with density  $\rho$ . The potential of a particle in the liquid is:

$$(12.3) \quad u(x, y, z) = (m - v\rho)gz$$

The probability of finding a particle within the volume element is then according to (12.2)

$$(12.4) \quad c_1 e^{-\frac{(m-v\rho)gz}{kT}} dx dy dz$$

The probability depends only on the vertical coordinate  $z$ , so the relative number of particles in the slice  $dz$ , can be written:

$$(12.5) \quad N(z)dz = N(0)e^{-\frac{(m-v\rho)gz}{kT}} dz \quad \Leftrightarrow \quad N(z) = N(0)e^{-\frac{(m-v\rho)gz}{kT}}$$

This formula has been experimentally verified by Perrin, who manually counted the number of particles, using a microscope. In accordance with (12.5) he found an exponential decreasing number of particle with height, and he was able to determine the logarithmic slope  $\frac{(m-v\rho)g}{kT}$ .

Doing separate experiments, he could also estimate the mass and volume of the particles.

Bringing the results together Perrin was also able to obtain a value for Boltzmann's constant  $k$ .

Since  $k = R/N_A$ , where  $R$  is the gas constant, the experiment also delivered a value for Avogadro's number  $N_A$ .

### 13. Entropy and Helmholtz's free energy

In the preceding sections, we have acquired the means to calculate the "internal energy" of a system in thermodynamic equilibrium at a temperature  $T$ , identifying the energy  $E$  with the mean of the Hamilton function  $\bar{H}$  taken over the canonical ensemble.

We shall now proceed to do the same, concerning the entropy. The entropy is only defined apart from a constant, since it is only meaningful to talk about differences in entropy between two thermodynamic states of equilibrium.

The difference in entropy, between two adjacent states is given by the first and second law of thermodynamics combined into one equation:

$$(13.1) \quad dQ = dE + dA \quad \text{and} \quad dS = \frac{dQ}{T} \quad \text{gives} \quad dS = \frac{dQ}{T} = \frac{dE + dA}{T}$$

$dA$  is the work done by the system from a reversible transition from the one state to the other. According to (9.14)

$$(13.2) \quad \bar{\eta} = \frac{\psi - \bar{H}}{kT}$$

And consequently:

$$(13.3) \quad d\psi = d\bar{H} + kTd\bar{\eta} + k\bar{\eta}dT$$

And from (9.15)

$$d\psi = \bar{\eta}kdT - \sum_{k=1}^m \bar{A}_k da_k$$

We find combining these two equations

$$(13.4) \quad \begin{aligned} -d\bar{\eta} &= \frac{d\bar{H} + \sum_{k=1}^m \bar{A}_k da_k}{kT} \quad \Leftrightarrow \\ -kd\bar{\eta} &= \frac{d\bar{H} + \sum_{k=1}^m \bar{A}_k da_k}{T} \end{aligned}$$

Comparing (13.4) with (13.1) and identifying the energy  $E$  with  $\bar{H}$ , and  $dA$  with  $\sum_{k=1}^m \bar{A}_k da_k$ , we get:

$$(13.5) \quad S = -k\bar{\eta}$$

According to (12.14)  $\bar{\eta} = \frac{1}{k} \frac{\partial \psi}{\partial T}$ , and consequently:

$$(13.6) \quad S = -\frac{\partial \psi}{\partial T}$$

In the history of thermodynamics, Helmholtz introduced a state variable  $F = E - TS$ , called the free energy. Using (13.2) it leads to:

$$(13.7) \quad \bar{\eta} = \frac{\psi - \bar{H}}{kT} \quad \Leftrightarrow \quad Tk\bar{\eta} = \psi - \bar{H} \quad \Leftrightarrow \quad -TS = \psi - E \quad \Leftrightarrow \quad \psi = E - TS$$

We can see, that  $\psi$  is actually equal to “the free energy” of Helmholtz.

The differentials in the equations refer to differences between canonical distributions. It is therefore imperative that the changes are *reversible*. That is, that both states are in thermodynamic equilibrium, the condition for well defined temperature.