Kinetic theory II

After the introduction to kinetic theory presented in the previous lecture, I move to the key issues the theory deals with. The Boltzmann equation will be derived and the famous H theorem will be proven.

Boltzmann equation

Collisions of gas particles are of crucial importance for some gas properties. In particular, the collisions are responsible for a system's evolution towards thermodynamical equilibrium. At the beginning we are going to modify the collisionless transport equation, derived at the previous lecture, to take into account the inter-particle collisions.

- Deriving the collisionless transport equation, which is

$$\Big(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla + \mathbf{F}(\mathbf{r})\cdot\nabla_p\Big) f(t,\mathbf{r},\mathbf{p}) = 0, \tag{1}$$

  we observed what happens at the moment of time $t+\delta t$ with particles which are located at $\mathbf{r}$ and have momentum $\mathbf{p}$ at time t.

- A presence of the collisions modifies the reasoning. Our purpose is the derive the so-called collision term $C(t,\mathbf{r},\mathbf{p})$ defined as

$$C(t,\mathbf{r},\mathbf{p}) \equiv \frac{\partial f(t,\mathbf{r},\mathbf{p})}{\partial t}\bigg|_{\text{collisions}}. \tag{2}$$

- The probability per unit time that at a moment of time t and in location $\mathbf{r}$ a particle with momentum $\mathbf{p}$ collides with a particle with momentum $\mathbf{p}_1$ and that as a result of the collision the particles' momenta are $\mathbf{p}'$ i $\mathbf{p}'_1$ is written as

$$f(t,\mathbf{r},\mathbf{p})\frac{d^3p}{(2\pi)^3}\, f(t,\mathbf{r},\mathbf{p}_1)\frac{d^3p_1}{(2\pi)^3}\, W(\mathbf{p},\mathbf{p}_1|\mathbf{p}',\mathbf{p}'_1), \tag{3}$$

  where $W(\mathbf{p},\mathbf{p}_1|\mathbf{p}',\mathbf{p}'_1)$ is the transition matrix element given as

$$W(\mathbf{p},\mathbf{p}_1|\mathbf{p}',\mathbf{p}'_1) = (2\pi)^6|\mathbf{v}-\mathbf{v}_1|\,\frac{d\sigma}{d^3p'd^3p'_1}, \tag{4}$$

  where $\mathbf{v}=\frac{\mathbf{p}}{m}$, $\mathbf{v}_1=\frac{\mathbf{p}_1}{m}$ are particles' velocities and $\mathbf{v}-\mathbf{v}_1$ their relative velocity; $\frac{d\sigma}{d^3p'd^3p'_1}$ is the collision cross section. The factor $(2\pi)^6$ results from the convention where d^3p is divided by $(2\pi)^3$. The formulas (3, 4) become evident if one remembers that the collision probability equals the cross section multiplied by the flux of incoming particles.

- Since the energy and momentum are conserved in a collision there are the equalities

$$\frac{\mathbf{p}^2}{2m}+\frac{\mathbf{p}_1^2}{2m}=\frac{\mathbf{p}'^2}{2m}+\frac{{\mathbf{p}'_1}^2}{2m}, \qquad \mathbf{p}+\mathbf{p}_1=\mathbf{p}'+\mathbf{p}'_1. \tag{5}$$

  Consequently, out of six momentum components of $\mathbf{p}'$ and $\mathbf{p}'_1$ only two of them are not determined by Eqs. (5). The cross section $\frac{d\sigma}{d^3p'd^3p'_1}$ can be thus expressed in the center-of-mass frame as $\frac{d\sigma}{d\Omega}$. To get the relation let us compute the quantity

$$\delta\Big(\frac{\mathbf{p}^2}{2m}+\frac{\mathbf{p}_1^2}{2m}-\frac{\mathbf{p}'^2}{2m}-\frac{{\mathbf{p}'_1}^2}{2m}\Big)\,\delta^{(3)}(\mathbf{p}+\mathbf{p}_1-\mathbf{p}'-\mathbf{p}'_1)\;d^3p'd^3p'_1.$$

First of all we observe that the quantity is the same in any inertial reference frame because the Jacobian of Galilean transformation equals unity and because any two four-momenta which are equal in one frame remain equal in any other one, in particular in the center-of-mass frame. Consequently, we get

$$\delta\Big(\frac{\mathbf{p}^2}{2m} + \frac{\mathbf{p}_1^2}{2m} - \frac{\mathbf{p}'^2}{2m} - \frac{\mathbf{p}_1'^{\,2}}{2m}\Big)\, \delta^{(3)}(\mathbf{p} + \mathbf{p}_1 - \mathbf{p}' - \mathbf{p}_1')\; d^3p' d^3p_1' \tag{6}$$

$$= \delta\Big(\frac{\mathbf{p}_*^2}{m} - \frac{\mathbf{p}_*'^{\,2}}{2m} - \frac{\mathbf{p}_{*1}'^{\,2}}{2m}\Big)\, \delta^{(3)}(\mathbf{p}_*' + \mathbf{p}_{*1}')\; d^3p_*' d^3p_{*1}', \tag{7}$$

where the center-of-mass variables are labeled with $*$ and $\mathbf{p}_* = -\mathbf{p}_{*1}$. Taking into account that $\delta(x)\, dx = 1$, if dx includes the point $x = 0$, Eq. (7) reads

$$\delta\Big(\frac{\mathbf{p}^2}{2m} + \frac{\mathbf{p}_1^2}{2m} - \frac{\mathbf{p}'^2}{2m} - \frac{\mathbf{p}_1'^{\,2}}{2m}\Big)\, \delta^{(3)}(\mathbf{p} + \mathbf{p}_1 - \mathbf{p}' - \mathbf{p}_1')\; d^3p' d^3p_1' = \delta\Big(\frac{\mathbf{p}_*^2}{m} - \frac{\mathbf{p}_*'^{\,2}}{m}\Big)\; d^3p_*'. \tag{8}$$

Using the spherical coordinates and keeping in mind that

$$\delta\big(\phi(x)\big) = \frac{\delta(x - x_0)}{\Big|\frac{d\phi(x_0)}{dx}\Big|}, \tag{9}$$

where x_0 is the unique solution of the equation $\phi(x) = 0$, one obtains

$$\delta\Big(\frac{\mathbf{p}^2}{2m} + \frac{\mathbf{p}_1^2}{2m} - \frac{\mathbf{p}'^2}{2m} - \frac{\mathbf{p}_1'^{\,2}}{2m}\Big)\, \delta^{(3)}(\mathbf{p} + \mathbf{p}_1 - \mathbf{p}' - \mathbf{p}_1')\; d^3p' d^3p_1' = \frac{1}{2} m p_* d\Omega, \tag{10}$$

where $d\Omega$ is the solid angle. Finally, we get the desired relation

$$\frac{d\sigma}{d^3p' d^3p_1} = \frac{2}{m p_*}\, \delta\Big(\frac{\mathbf{p}^2}{2m} + \frac{\mathbf{p}_1^2}{2m} - \frac{\mathbf{p}'^2}{2m} - \frac{\mathbf{p}_1'^{\,2}}{2m}\Big)\, \delta^{(3)}(\mathbf{p} + \mathbf{p}_1 - \mathbf{p}' - \mathbf{p}_1') \frac{d\sigma}{d\Omega}. \tag{11}$$

We note that using Eq. (10), the relation (11) provides the expected identity

$$\frac{d\sigma}{d^3p' d^3p_1'}\, d^3p' d^3p_1' = \frac{d\sigma}{d\Omega}\, d\Omega. \tag{12}$$

- The expression

$$\int \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3}\, f(t, \mathbf{r}, \mathbf{p})\, f(t, \mathbf{r}, \mathbf{p}_1)\, W(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}_1'), \tag{13}$$

tells us how fast the particles with momentum $\mathbf{p}$ disappear from the system due to collisions schematically denoted as $(\mathbf{p},\, \mathbf{p}_1) \to (\mathbf{p}',\, \mathbf{p}_1')$. However, the particles with momentum $\mathbf{p}$ also appear in the system due to the inverse process $(\mathbf{p}',\, \mathbf{p}_1') \to (\mathbf{p},\, \mathbf{p}_1)$. Consequently, the collision term (2) is

$$\begin{aligned} C(t, \mathbf{r}, \mathbf{p}) \;\; = \;\; \int \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3} \Big[& f(t, \mathbf{r}, \mathbf{p}')\, f(t, \mathbf{r}, \mathbf{p}_1')\, W(\mathbf{p}', \mathbf{p}_1' | \mathbf{p}, \mathbf{p}_1) \\ & - f(t, \mathbf{r}, \mathbf{p})\, f(t, \mathbf{r}, \mathbf{p}_1)\, W(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}_1') \Big]. \end{aligned} \tag{14}$$

- Assuming that the collision processes are invariant under the time inversion, we have

$$W(\mathbf{p}', \mathbf{p}'_1|\mathbf{p}, \mathbf{p}_1) = W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}'_1) \tag{15}$$

and the collision term (14) simplifies to

$$\begin{aligned} C(t, \mathbf{r}, \mathbf{p}) \;\; = \;\; & \int \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p'_1}{(2\pi)^3} \Big[f(t, \mathbf{r}, \mathbf{p}') \, f(t, \mathbf{r}, \mathbf{p}'_1) \\ & - f(t, \mathbf{r}, \mathbf{p}) \, f(t, \mathbf{r}, \mathbf{p}_1) \Big] W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}'_1), \end{aligned} \tag{16}$$

which is used further on.

- Taking into account the relations (4) and (11), the collision term (16) can be written as

$$C(t, \mathbf{r}, \mathbf{p}) = \int \frac{d^3p_1}{(2\pi)^3} \, d\Omega \, |\mathbf{v} - \mathbf{v}_1| \, \frac{d\sigma}{d\Omega} \Big[f(t, \mathbf{r}, \mathbf{p}') \, f(t, \mathbf{r}, \mathbf{p}'_1) - f(t, \mathbf{r}, \mathbf{p}) \, f(t, \mathbf{r}, \mathbf{p}_1) \Big]. \tag{17}$$

- The kinetic equation

$$\Big(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla + \mathbf{F}(\mathbf{r}) \cdot \nabla_p \Big) f(t, \mathbf{r}, \mathbf{p}) = C(t, \mathbf{r}, \mathbf{p}), \tag{18}$$

with the collision term (17) is known as the <u>Boltzmann equation</u>.

Entropy

- In kinetic theory the entropy is defined as

$$S(t) \equiv -k_B \int \frac{d^3r \, d^3p}{(2\pi)^3} \, f(t, \mathbf{r}, \mathbf{p}) \ln[\hbar^3 f(t, \mathbf{r}, \mathbf{p})], \tag{19}$$

where the Planck constant is introduced to make the argument of the logarithm dimensionless. As seen, the entropy is, in general, time dependent.

- Using the equilibrium distribution function

$$f^{\rm eq}(\mathbf{p}) = \Big(\frac{2\pi}{m k_B T} \Big)^{3/2} \frac{N}{V} \, e^{-\frac{\mathbf{p}^2}{2 m k_B T}}, \tag{20}$$

the entropy (19) equals

$$S = N k_B \ln \Big[\frac{V}{N} \Big(\frac{m k_B T}{2\pi \hbar^2} \Big)^{\frac{3}{2}} \Big] + \frac{3}{2} N k_B, \tag{21}$$

which agrees with the <u>ideal gas entropy</u> obtained within the Gibbs statistical mechanics.

H-theorem

The H-theorem is historically the first attempt to understand the second principle of thermodynamics and it still remains of fundamental importance[1].

- The H-theorem states that the entropy (19) is a non-decreasing function of time, if the distribution function obeys the Boltzmann equation (18).
- To prove the theorem we compute at first the time derivative of the entropy (19)

$$\frac{dS(t)}{dt} = -k_B \int \frac{d^3r\, d^3p}{(2\pi)^3} \frac{\partial f(t,\mathbf{r},\mathbf{p})}{\partial t} \big[\ln[\hbar^3 f(t,\mathbf{r},\mathbf{p})] + 1\big]. \tag{22}$$

- Since the distribution function obeys the Boltzmann equation (18) we have

$$\frac{\partial f(t,\mathbf{r},\mathbf{p})}{\partial t} = -\Big(\mathbf{v}\cdot\nabla + \mathbf{F}\cdot\nabla_p\Big) f(t,\mathbf{r},\mathbf{p}) + C(t,\mathbf{r},\mathbf{p}). \tag{23}$$

- Substituting the formula (23) into Eq. (22), we get the following term with the gradient

$$\int d^3r\, \nabla f(t,\mathbf{r},\mathbf{p}) \big[\ln[\hbar^3 f(t,\mathbf{r},\mathbf{p})] + 1\big], \tag{24}$$

  which is computed performing the partial integration as

$$\int d^3r\, \nabla f(t,\mathbf{r},\mathbf{p}) \big[\ln[\hbar^3 f(t,\mathbf{r},\mathbf{p})] + 1\big] = -\int d^3r\, \nabla f(t,\mathbf{r},\mathbf{p}) = 0. \tag{25}$$

  The surface term does not show up because the distribution function is assumed to vanish at $|\mathbf{r}| \to \infty$ to give a finite number of gas particles. For the same reason the whole integral (25) vanishes. Analogously one shows that the term with the momentum gradient present in (23) also vanishes. Consequently, the time derivative (22) equals

$$\frac{dS(t)}{dt} = -k_B \int \frac{d^3r\, d^3p}{(2\pi)^3}\, C(t,\mathbf{r},\mathbf{p})\, \big[\ln[\hbar^3 f(t,\mathbf{r},\mathbf{p})] + 1\big]. \tag{26}$$

- Substituting the collision term (16) into Eq. (26), one finds

$$\frac{dS(t)}{dt} = k_B \int d^3r \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3} \left[f f_1 - f' f_1'\right] \big[\ln[\hbar^3 f] + 1\big] W(\mathbf{p},\mathbf{p}_1|\mathbf{p}',\mathbf{p}_1'), \tag{27}$$

  with the following notation

$$f \equiv f(t,\mathbf{r},\mathbf{p}), \qquad f_1 \equiv f(t,\mathbf{r},\mathbf{p}_1), \qquad f' \equiv f(t,\mathbf{r},\mathbf{p}'), \qquad f_1' \equiv f(t,\mathbf{r},\mathbf{p}_1'). \tag{28}$$

- Now we change the variables under the integral (27) in such a way that $\mathbf{p} \to \mathbf{p}_1$ and $\mathbf{p}_1 \to \mathbf{p}$ that is $\mathbf{p} \leftrightarrow \mathbf{p}_1$. Keeping in mind that $W(\mathbf{p},\mathbf{p}_1|\mathbf{p}',\mathbf{p}_1') = W(\mathbf{p}_1,\mathbf{p}|\mathbf{p}',\mathbf{p}_1')$, we get

$$\frac{dS(t)}{dt} = k_B \int d^3r \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3} \left[f f_1 - f' f_1'\right] \big[\ln[\hbar^3 f_1] + 1\big] W(\mathbf{p},\mathbf{p}_1|\mathbf{p}',\mathbf{p}_1'). \tag{29}$$

[1] The term 'H-theorem' comes from the quantity equal to the minus entropy (19) which was denoted by H. Boltzmann actually used the symbol E in his treatise *Weitere Studien über das Wärmeglechgewicht unter Gasmolekülen* (*Further studies on thermal equilibrium of gas molecules*) from 1872. The notation H was presumably introduced by Henry W. Watson in the second edition of *Kinetic Theory of Gases* from 1893.

- Summing up the left and right sides of the equations (27, 29) and dividing the result by 2, one finds

$$\frac{dS(t)}{dt} = \frac{k_B}{2} \int d^3r \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p'_1}{(2\pi)^3} [f f_1 - f' f'_1] \big[\ln[\hbar^6 f f_1] + 2 \big] W(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1). \quad (30)$$

- In the next step one changes the variables as $\mathbf{p} \leftrightarrow \mathbf{p}'$ and $\mathbf{p}_1 \leftrightarrow \mathbf{p}'_1$. Using the property $W(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1) = W(\mathbf{p}', \mathbf{p}'_1 | \mathbf{p}, \mathbf{p}_1)$, the formula (30) becomes

$$\frac{dS(t)}{dt} = \frac{k_B}{2} \int d^3r \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p'_1}{(2\pi)^3} [f' f'_1 - f f_1] \big[\ln[\hbar^6 f' f'_1] + 2 \big] W(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1). \quad (31)$$

- Now we sum up the left and right sides of the equations (30, 31), divide the result by 2 and we get the desired expression

$$\begin{aligned} \frac{dS(t)}{dt} &= \frac{k_B}{4} \int d^3r \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p'_1}{(2\pi)^3} \\ &\quad \times [f f_1 - f' f'_1] \big[\ln[\hbar^6 f f_1] - \ln[\hbar^6 f' f'_1] \big] W(\mathbf{p}, \mathbf{p}_1 | \mathbf{p}', \mathbf{p}'_1). \end{aligned} \quad (32)$$

- Let us define $x \equiv f f_1$ and $y \equiv f' f'_1$. Since a logarithm is a monotonously growing function, the following relations hold

$$x \geq y \quad \Rightarrow \quad \ln x \geq \ln y \qquad \text{oraz} \qquad x \leq y \quad \Rightarrow \quad \ln x \leq \ln y, \quad (33)$$

which lead to the conclusion that

$$(x - y)(\ln x - \ln y) \geq 0. \quad (34)$$

So, we see that the integrand (32) is non-negative as the transition matrix element is non-negative.

- In this way we arrive to the fundamental result

$$\frac{dS(t)}{dt} \geq 0. \quad (35)$$

The entropy (19) is a non-decreasing function of time, if the distribution function obeys the Boltzmann equation (18).

- In Lecture VII the equilibrium distribution function was introduced referring to the Gibbs statistical mechanics. One can show that the entropy is maximal for the function. However, the equilibrium distribution function can defined within the kinetic theory with no reference the Gibbs statistical mechanics. Namely, the distribution function is derived from the condition of maximal entropy. To discuss the problem a technical problem must be resolved.

Collisional invariants

- A collisional invariant is such a characteristics Φ of a single particle that the sum of characteristics of initial state particles equals the sum of characteristic of collision final state particles. In other words, the quantity is conserved. In case of binary collisions, which are taken into account the collision term of the Boltzmann equation (18), the collision invariant obeys
$$\Phi + \Phi_1 - \Phi' - \Phi_1' = 0, \tag{36}$$
where the notation (28) is used. Φ can be the particle's energy, momentum, or any conserved charge.

- We are going to prove the following equality
$$I \equiv \int \frac{d^3p}{(2\pi)^3}\, \Phi\, C(t, \mathbf{r}, \mathbf{p}) = 0. \tag{37}$$

- Using the explicit form of the collision term (16), Eq. (37) becomes
$$I = \int \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3}\, \Phi\, [f'f_1' - ff_1]\, W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}_1'). \tag{38}$$

- The proof that the integral I (37) vanishes is very similar to that one of the $H-$theorem. At the beginning we change the integration variables in Eq. (38) as $\mathbf{p} \leftrightarrow \mathbf{p}_1$ and keeping in mind that $W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}_1') = W(\mathbf{p}_1, \mathbf{p}|\mathbf{p}', \mathbf{p}_1')$, we get
$$I = \int \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3}\, \Phi_1\, [f'f_1' - ff_1]\, W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}_1'). \tag{39}$$

- Summing up the left and right sides of Eqs. (38, 39) and diving the result by 2, one finds
$$I = \frac{1}{2}\int \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3}\, [\Phi + \Phi_1]\, [f'f_1' - ff_1]\, W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}_1'). \tag{40}$$

- In the next step we change variables as $\mathbf{p} \leftrightarrow \mathbf{p}'$ and $\mathbf{p}_1 \leftrightarrow \mathbf{p}_1'$, and using the property $W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}_1') = W(\mathbf{p}', \mathbf{p}_1'|\mathbf{p}, \mathbf{p}_1)$, we obtain
$$I = \frac{1}{2}\int \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3}\, [\Phi' + \Phi_1']\, [ff_1 - f'f_1']\, W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}_1'). \tag{41}$$

- Finally we sum up Eqs. (40, 41) and divide the result by 2. Thus we get the desired expression
$$I = \frac{1}{4}\int \frac{d^3p}{(2\pi)^3} \frac{d^3p_1}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3p_1'}{(2\pi)^3}\, [\Phi + \Phi_1 - \Phi' - \Phi_1']\, [f'f_1' - ff_1]\, W(\mathbf{p}, \mathbf{p}_1|\mathbf{p}', \mathbf{p}_1') = 0, \tag{42}$$
which vanishes because of the relation (36).

Equilibrium distribution function

The entropy becomes maximal when the system reaches the state of thermodynamical equilibrium. Therefore, the equilibrium distribution function is defined as a solution of the functional equation

$$\frac{dS(t)}{dt} = 0. \tag{43}$$

- Eq. (32) clearly shows that the equation (43) is solved if

$$f f_1 = f' f_1', \tag{44}$$

or equivalently

$$\ln f + \ln f_1 - \ln f' - \ln f_1' = 0, \tag{45}$$

which means that $\ln f$ is a collisional invariant.

- Assuming that there are no external forces, we construct the equilibrium distribution function out of three collisional invariants of energy, momentum and particle number that is

$$\ln f^{\rm eq}(\mathbf{p}) = a\frac{\mathbf{p}^2}{2m} + \mathbf{b}\cdot\mathbf{p} + c, \tag{46}$$

which gives

$$f^{\rm eq}(\mathbf{p}) = \exp\big[a\frac{\mathbf{p}^2}{2m} + \mathbf{b}\cdot\mathbf{p} + c\big], \tag{47}$$

where $a,\ \mathbf{b},\ c$ are parameters.

- A physical meaning of the parameters is found computing the particle density and flux as

$$\rho = \int \frac{d^3p}{(2\pi)^3}\, f^{\rm eq}(\mathbf{p}) = \exp\big[-\frac{m\mathbf{b}^2}{2a} + c\big]\Big(-\frac{m}{2\pi a}\Big)^{3/2}, \tag{48}$$

$$\mathbf{j} = \int \frac{d^3p}{(2\pi)^3}\,\frac{\mathbf{p}}{m}\, f^{\rm eq}(\mathbf{p}) = -\frac{\mathbf{b}}{a}\exp\big[-\frac{m\mathbf{b}^2}{2a} + c\big]\Big(-\frac{m}{2\pi a}\Big)^{3/2}, \tag{49}$$

where a is assumed to be negative to guarantee an existence of the integrals (48, 49).

- Demanding that

$$\mathbf{j} = \rho\,\mathbf{u}, \tag{50}$$

where $\mathbf{u}$ is the velocity of the whole system, one finds

$$a = -\beta = -\frac{1}{k_BT}, \qquad \mathbf{b} = \frac{\mathbf{u}}{k_BT}, \qquad e^c = \rho\Big(\frac{2\pi}{mk_BT}\Big)^{3/2}. \tag{51}$$

- The equilibrium distribution function gets the form

$$\begin{aligned} f^{\rm eq}(\mathbf{p}) &= \rho\Big(\frac{2\pi}{mk_BT}\Big)^{3/2}\exp\Big[-\beta\Big(\frac{\mathbf{p}^2}{2m} - \mathbf{u}\cdot\mathbf{p} + \frac{m\mathbf{u}^2}{2}\Big)\Big] \\ &= \rho\Big(\frac{2\pi}{mk_BT}\Big)^{3/2}\exp\Big[-\frac{m(\mathbf{v}-\mathbf{u})^2}{2k_BT}\Big], \end{aligned} \tag{52}$$

where $\mathbf{v} = \frac{\mathbf{p}}{m}$.

- The distribution function (52) can be obtained from the function (20) by means of the Galilean transformation to the reference frame where the heat bath moves with the velocity $\mathbf{u}$.
- If there is an external force such that $\mathbf{F}(\mathbf{r}) = -\nabla v(\mathbf{r})$, the equilibrium distribution function is modified to

$$\begin{aligned} f^{\rm eq}(\mathbf{r},\mathbf{p}) &= \rho_0 \Big(\frac{2\pi}{mk_BT}\Big)^{3/2} \exp\Big[-\beta\Big(\frac{\mathbf{p}^2}{2m} - \mathbf{u}\cdot\mathbf{p} + \frac{\mathbf{u}^2}{2m} + v(\mathbf{r})\Big)\Big] \\ &= \rho_0 \Big(\frac{2\pi}{mk_BT}\Big)^{3/2} \exp\Big[-\beta\Big(\frac{m(\mathbf{v}-\mathbf{u})^2}{2} + v(\mathbf{r})\Big)\Big]. \end{aligned} \tag{53}$$

We note that ρ_0 is not particle density which is

$$\rho(\mathbf{r}) = \int \frac{d^3p}{(2\pi)^3}\, f^{\rm eq}(\mathbf{r},\mathbf{p}) = \rho_0 \exp[-\beta v(\mathbf{r})] \tag{54}$$

- Because of the external force the equilibrium distribution function (53) becomes position dependent.
- Finally, one easily shows that the equilibrium distribution function (53) satisfies the transport equation

$$\big(\mathbf{v}\cdot\nabla + \mathbf{F}(\mathbf{r})\cdot\nabla_p\big) f^{\rm eq}(\mathbf{r},\mathbf{p}) = 0. \tag{55}$$

Molecular chaos

- The $H-$theorem caused a very hot controversy. It was unclear how a time reversible mechanics can lead to the irreversible growth of entropy. It was soon realized that the irreversibility occurs due to the assumption of molecular chaos.
- Deriving the collision term of transport equation it was assumed that the probability to find at t and $\mathbf{r}$ two particles with momenta $\mathbf{p}$ and $\mathbf{p}_1$ is proportional

$$f(t,\mathbf{r},\mathbf{p})\, f(t,\mathbf{r},\mathbf{p}_1), \tag{56}$$

which means that the two particles are independent from each other. This is the assumption of molecular chaos which is only approximately true as inter-particle interactions create correlations in the system. For example, due to the energy and momentum conservation final state particles of a collision process are not independent from each other.

- The $H-$theorem should be formulated as follows: the entropy (19) is a non-decreasing function of time, if the distribution function obeys the Boltzmann equation (18) and the assumption of molecular chaos holds.

Dogs and fleas

In 1907 Tatiana and Paul Ehrenfest formulated a simple model to show how independence of random events leads to irreversible temporal evolution.

- There are two dogs which sleep together. $N_1(t)$ and $N_2(t)$ are numbers of fleas of the dogs.
- The fleas jump all the time and with a probability per unit time α a flea jumps from one dog to another.
- The increase of number of fleas of one dog is proportional to the number of fleas of another one. Therefore,

$$\frac{dN_1(t)}{dt} = \alpha N_2(t) - \alpha N_1(t), \tag{57}$$

$$\frac{dN_2(t)}{dt} = \alpha N_1(t) - \alpha N_2(t). \tag{58}$$

- Summing up the equations and subtracting them from each other one gets

$$\frac{d}{dt}\big(N_1(t) + N_2(t)\big) = 0 \tag{59}$$

$$\frac{d\Delta(t)}{dt} = -2\alpha\Delta(t), \tag{60}$$

  where $\Delta(t) \equiv N_1(t) - N_2(t)$.

- Eq. (59) expresses the conservation of fleas that is the total number of fleas, which is denoted as N, is constant. Eq. (60) is elementary and it gives $\Delta(t) = \Delta(0)e^{-2\alpha t}$. Thus we obtain

$$N_1(t) = \frac{1}{2}\big(N + \Delta(t)\big) = \frac{1}{2}N + \Big(N_1(0) - \frac{1}{2}N\Big)\, e^{-2\alpha t}, \tag{61}$$

$$N_2(t) = \frac{1}{2}\big(N - \Delta(t)\big) = \frac{1}{2}N + \Big(N_2(0) - \frac{1}{2}N\Big)\, e^{-2\alpha t}. \tag{62}$$

  One sees that independently of initial values $N_1(0)$ and $N_2(0)$, the system reaches the state of equilibrium with $N_1(t) = N_2(t) = \frac{1}{2}N$ after the time $t \gg \alpha^{-1}$.