

Boltzmann equation and H-Theorem

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Microscopic description

- ▶ Generalized coordinates and conjugate momenta: $\mathbf{q}_i, \mathbf{p}_i, i = 1, \dots, N$. In total: $6N$ variables.
- ▶ Hamiltonian of the system $\mathbf{H}(\{\mathbf{q}\}, \{\mathbf{p}\})$.
- ▶ Equations of motion: $\dot{\mathbf{q}}_i = \frac{\partial H}{\partial p_i}$ and $\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial q_i}$ for $i = 1, \dots, N$.

Postulate of both equilibrium and nonequilibrium statistical mechanics

All intensive macroscopic properties of a given system can be described in terms of the microscopic state of that system.

Density function

- ▶ Number of points in the phase space goes to infinity.
- ▶ The distribution of points throughout the phase space becomes continuous.
- ▶ Describe this with a density function $F_N(\{\mathbf{q}\}, \{\mathbf{p}\}, t)$. F_N should be symmetric in the \mathbf{q}_i and the \mathbf{p}_i (similarity of molecules).

- ▶ Normalisation: $\int \prod_{i=1}^N d\mathbf{q}_i d\mathbf{p}_i F_N(\{\mathbf{q}\}, \{\mathbf{p}\}, t) = 1$.

An ensemble average of a macroscopic property $G(\{\mathbf{q}\}, \{\mathbf{p}\})$ can be defined as:

$$\langle G(t) \rangle := \int \prod_{i=1}^N d\mathbf{q}_i d\mathbf{p}_i G(\{\mathbf{q}\}, \{\mathbf{p}\}) F_N(\{\mathbf{q}\}, \{\mathbf{p}\}, t) \quad (1)$$

Liouville equation

- ▶ How does F_N change with time?

$$\frac{dF_N}{dt} = \frac{\partial F_N}{\partial t} + \sum_{i=1}^N \left[\frac{\partial F_N}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{\partial F_N}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right] = 0. \quad (2)$$

Idea of the proof: Use uniqueness of the solutions of the Hamilton equations.

- ▶ If F_N - constant along a trajectory in the phase space, it's also every function of F_N . Of specific interest will be the function $H(t) := \int_{\Gamma} d\mathbf{x} F_N \ln F_N = \text{const.}$

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- ▶ We define the R-particle distribution function as follows:

$$F_R(\mathbf{x}_1, \dots, \mathbf{x}_R, t) := \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N F_N(\mathbf{x}_1, \dots, \mathbf{x}_R, \dots, \mathbf{x}_N, t) \quad (3)$$

- ▶ We also define the mass density as $f(\mathbf{x}_1, t) := NmF_1(\mathbf{x}_1, t)$, where m is the mass of a single particle.
- ▶ How do the evolution equations for the reduced distribution functions look like?

- ▶ We start with the case $R = N$, where we have the Liouville equation from above:

$$\frac{\partial F_N}{\partial t} + \sum_{i=1}^N \left[\frac{\partial F_N}{\partial \mathbf{q}_i} \cdot \frac{\mathbf{p}_i}{m} + \frac{\partial F_N}{\partial \mathbf{p}_i} \cdot \mathbf{F}_i \right] = 0, \quad (4)$$

where $\mathbf{F}_i = \dot{\mathbf{p}}_i$ is the force, acting on the i -th particle.

- ▶ For an arbitrary R we can integrate Eq.4 over the phases $\mathbf{x}_{R+1}, \dots, \mathbf{x}_N$. We have:

$$\int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N \frac{\partial F_N}{\partial t} = \frac{\partial}{\partial t} \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N F_N = \frac{\partial F_R}{\partial t} \quad (5)$$

$$\begin{aligned} \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N \sum_{i=1}^N \frac{\mathbf{p}_i}{m} \cdot \frac{\partial F_N}{\partial \mathbf{q}_i} &= \sum_{i=1}^R \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{q}_i} \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N F_N \\ &+ \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N \sum_{i=R+1}^N \frac{\mathbf{p}_i}{m} \cdot \frac{\partial F_N}{\partial \mathbf{q}_i} \end{aligned} \quad (6)$$

The second term on the R.H.S. in Eq.6 can be made vanish, even if the volume of the system is finite, for example, when there are only elastic collisions of particles with the walls of the container. In that case, we have:

$$\begin{aligned}
 & F_N(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_i, \dots, p_{i,x}, p_{i,y}, p_{i,z}, t) \\
 & = F_N(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_i, \dots, -p_{i,x}, p_{i,y}, p_{i,z}, t), \quad \forall i : \mathbf{q}_i \in d\mathbf{S} \perp x
 \end{aligned} \tag{7}$$

and thus, when integrated over $p_{i,x}$, the second term on the R.H.S. of Eq.6 becomes zero. We have:

$$\int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N \sum_{i=1}^N \frac{\mathbf{p}_i}{m} \cdot \frac{\partial F_N}{\partial \mathbf{q}_i} = \sum_{i=1}^R \frac{\mathbf{p}_i}{m} \cdot \frac{\partial F_R}{\partial \mathbf{q}_i} \tag{8}$$

For conservative central intermolecular forces, we have:

$$\mathbf{F}_i = - \sum_{j=1 \neq i}^N \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \quad (9)$$

and the last term on the R.H.S. of the Liouville equation for F_N , when integrated as above, becomes:

$$\begin{aligned} - \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N \sum_{i,j=1}^N \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial F_N}{\partial \mathbf{p}_i} &= \sum_{i,j=1}^R \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N F_N \\ &- \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N \sum_{\substack{1 \leq i \leq R \\ R+1 \leq j \leq N}}^N \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial F_N}{\partial \mathbf{p}_i} \\ &- \int d\mathbf{x}_{R+1} \dots d\mathbf{x}_N \sum_{\substack{R+1 \leq i \leq N \\ 1 \leq j \leq N}}^N \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial F_N}{\partial \mathbf{p}_i} \end{aligned} \quad (10)$$

The last term on the R.H.S. vanishes. The second term can be written as:

$$-(N - R) \int dx_{R+1} \sum_{i=1}^R \frac{\partial \phi_{iR+1}}{\partial \mathbf{q}_i} \cdot \frac{\partial F_{R+1}}{\partial \mathbf{p}_i}(\mathbf{x}_1, \dots, \mathbf{x}_{R+1}, t) \quad (11)$$

When we combine all of the results, we get the equation for F_R :

$$\begin{aligned} & \frac{\partial F_R}{\partial t} + \sum_{i=1}^R \frac{\mathbf{p}_i}{m} \cdot \frac{\partial F_R}{\partial \mathbf{q}_i} - \sum_{i,j=1}^R \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial F_R}{\partial \mathbf{p}_j} \\ & = (N - R) \int dx_{R+1} \sum_{i=1}^R \frac{\partial \phi_{iR+1}}{\partial \mathbf{q}_i} \cdot \frac{\partial F_{R+1}}{\partial \mathbf{p}_i}. \end{aligned} \quad (12)$$

Equation 12 is called the BBGKY (Bogoliubov, Born, H.S. Green, Kirkwood and Yvon) hierarchy of equations.

Boltzmann gas limit

The Boltzmann equation is exact in the so called Boltzmann gas limit (BGL). This is described by three conditions:

- ▶ the density is sufficiently low so that only binary collisions need to be considered
- ▶ the spatial dependence of gas properties is sufficiently slow so that collisions can be thought of as being localised in the physical space
- ▶ the interparticle potential is of sufficiently short range so that the first statement is meaningful.

Conditions on the parameters of the gas

This means, for the particle number N , the mass of each particle m and for a parameter σ which characterises the range of the interparticle forces (σ^2 would be then the cross section):

$$\begin{aligned} N &\longrightarrow \infty \\ m &\longrightarrow 0 \\ \sigma &\longrightarrow 0 \\ N\sigma^2 &= \text{const} \\ Nm &= \text{const} \end{aligned} \tag{13}$$

Note that this limit also describes ideal gas, because the total volume of the particles $N\sigma^3 \rightarrow 0$.

Grad's derivation

Consider the truncated distributions:

$$\begin{aligned} F_1^\sigma &:= \int_{D_1} d\mathbf{y}_2 \dots d\mathbf{y}_N F_N \\ F_2^\sigma &:= \int_{D_2} d\mathbf{y}_3 \dots d\mathbf{y}_N F_N, \end{aligned} \tag{14}$$

where D_i is the part of the physical space where $|\mathbf{q}_j - \mathbf{q}_1| \geq \sigma$ for $j = i, \dots, N$ is fulfilled.

In the BGL we can replace F_1, F_2 by F_1^σ, F_2^σ in the Liouville equation and we get:

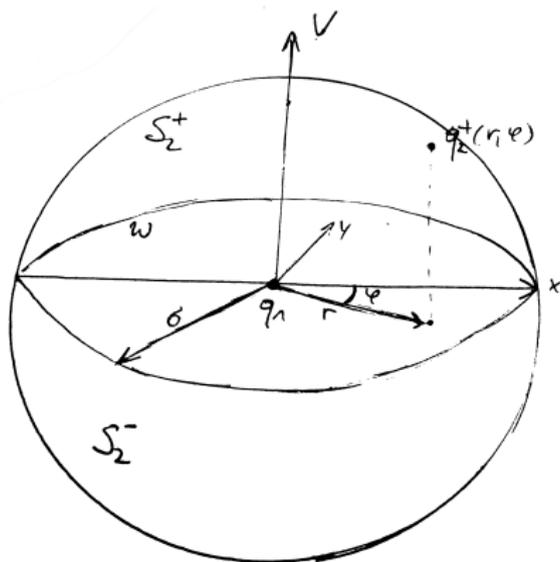
$$\begin{aligned} \frac{\partial F_1^\sigma}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial F_1^\sigma}{\partial \mathbf{q}_1} + (N-1) \oint_{S_2} d\mathbf{v}_2 d\mathbf{S}_2 \cdot (\mathbf{v}_1 - \mathbf{v}_2) F_2^\sigma \\ - (N-1) \frac{\partial}{\partial \mathbf{v}_1} \cdot \int_{|\mathbf{q}_2 - \mathbf{q}_1| > \sigma} d\mathbf{y}_2 \phi'_{12} F_2^\sigma = 0, \end{aligned} \tag{15}$$

where S_2 is the surface of the sphere $|\mathbf{q}_2 - \mathbf{q}_1| = \sigma$ and

$$\phi'_{12} := \frac{\partial \phi_{12}}{\partial \mathbf{q}_1}.$$

If $\mathbf{V} = \mathbf{v}_2 - \mathbf{v}_1$ is the relative velocity, one can introduce a plane perpendicular to it with origin \mathbf{q}_1 so that the two half-spheres S_2^+ and S_2^- are projected onto a disc with area element $d\omega = r dr d\varphi$. We exchange the integration over the sphere in Eq.15 for integration over the disc:

$$\frac{\partial F_1}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial F_1}{\partial \mathbf{q}_1} = N \int d\omega d\mathbf{v}_2 V [F_2(\mathbf{y}_1, \mathbf{y}_2^+, t) - F_2(\mathbf{y}_1, \mathbf{y}_2^-, t)] \quad (16)$$



Now, we use the *Stoßzahlansatz* (collision number assumption), due to Boltzmann, which states that:

$$F_2(\mathbf{y}_1, \mathbf{y}_2, t) = F_1(\mathbf{y}_1, t)F_1(\mathbf{y}_2, t) \quad (17)$$

to get the final Boltzmann equation:

$$\begin{aligned} & \frac{\partial f}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f}{\partial \mathbf{q}_1} \\ &= \frac{1}{m} \int d\omega d\mathbf{v}_2 V [f(\mathbf{q}_1, \bar{\mathbf{v}}_1, t)f(\mathbf{q}_1, \bar{\mathbf{v}}_2, t) - f(\mathbf{q}_1, \mathbf{v}_1, t)f(\mathbf{q}_1, \mathbf{v}_2, t)], \end{aligned} \quad (18)$$

where we denoted with $\bar{\mathbf{v}}_1, \bar{\mathbf{v}}_2$ the velocities after the collision.

Eq.18 is called the Boltzmann equation. The R.H.S. is a functional of f , which is called the collision term:

$$J[f] := \frac{1}{m} \int d\omega d\mathbf{v}_2 V [\bar{f}_1 \bar{f}_2 - f_1 f_2]. \quad (19)$$

A motivation for the assumptions

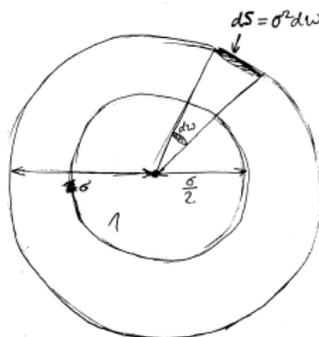
The total number of molecules, which can target the surface element dS , is:

$$\sigma^2 d\omega |\mathbf{V} \cdot \mathbf{e}| \Delta t \cdot f(\mathbf{q}_1, \mathbf{v}_2, t) d\mathbf{v}_2. \quad (20)$$

There are $f(\mathbf{q}_1) d\mathbf{q}_1 d\mathbf{v}_1$ particles with velocity \mathbf{v}_1 . The total number of binary collisions per given time interval and per $d\mathbf{x}_1$, are:

$$\sim \sigma^2 \int |\mathbf{V} \cdot \mathbf{e}| f(\mathbf{q}, \mathbf{v}_1, t) f(\mathbf{q}_1, \mathbf{v}_2, t) d\omega d\mathbf{v}_2. \quad (21)$$

This consideration gives us a motivation for the loss term. The gain term is motivated analogously.



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Binary collisions

Now we want to investigate the collision term. In classical binary collisions there is momentum and energy conservation:

$$\begin{aligned}\mathbf{v}_1 + \mathbf{v}_2 &= \bar{\mathbf{v}}_1 + \bar{\mathbf{v}}_2 \\ v_1^2 + v_2^2 &= \bar{v}_1^2 + \bar{v}_2^2.\end{aligned}\tag{22}$$

One can easily show that the modulus of the relative velocity doesn't change. We have $V = \bar{V}$. We can also establish an explicit relation between the old and the new velocities. If $\alpha := \frac{\bar{\mathbf{v}}_1 - \mathbf{v}_1}{|\bar{\mathbf{v}}_1 - \mathbf{v}_1|}$, we have:

$$\begin{aligned}\bar{\mathbf{v}}_1 &= \mathbf{v}_1 + \alpha(\alpha \cdot \mathbf{V}) \\ \bar{\mathbf{v}}_2 &= \mathbf{v}_2 - \alpha(\alpha \cdot \mathbf{V}).\end{aligned}\tag{23}$$

The inverse transformation is:

$$\begin{aligned}\mathbf{v}_1 &= \bar{\mathbf{v}}_1 + \alpha(\alpha \cdot \bar{\mathbf{V}}) \\ \mathbf{v}_2 &= \bar{\mathbf{v}}_2 - \alpha(\alpha \cdot \bar{\mathbf{V}}).\end{aligned}\tag{24}$$

so the Jacobian is unity and we have: $d\mathbf{v}_1 d\mathbf{v}_2 = d\bar{\mathbf{v}}_1 d\bar{\mathbf{v}}_2$.

We can define the angle between \mathbf{V} and α to be θ . This is:

$$\alpha \cdot \mathbf{V} = V \cos \theta. \quad (25)$$

If there is a one-to-one correspondence between the distance of the (centres of the) two particles r and the angle θ (This is the case, for example, for repulsive potentials), we can rewrite the integration over the disc area as follows:

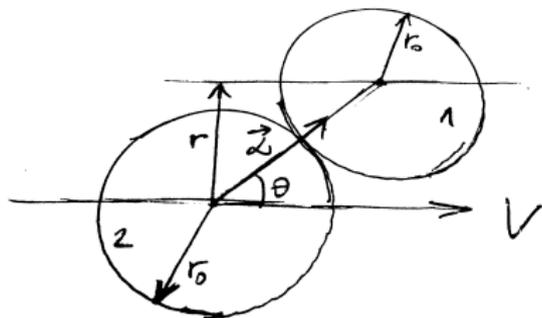
$$\begin{aligned} d\omega &= r dr d\varphi = r(\theta, V) \left| \frac{\partial r(\theta, V)}{\partial \theta} \right| d\theta d\varphi \\ &=: \frac{1}{V} B(\theta, V) d\theta d\varphi. \end{aligned} \quad (26)$$

Thus, the Boltzmann collision term becomes:

$$J[f] = \frac{1}{m} \int d\mathbf{v}_2 d\theta d\varphi B(\theta, V) [\bar{f}_1 \bar{f}_2 - f_1 f_2]. \quad (27)$$

Hard sphere molecules

If we consider hard sphere molecules of radius r_0 , the obvious geometrical relation $r = 2r_0 \sin \theta$ allows us to calculate the function $B(\theta, V)$:



$$\Rightarrow B(\theta, V) = Vr \left| \frac{\partial r}{\partial \theta} \right| = 4r_0^2 V \sin \theta \cos \theta. \quad (28)$$

The collision cross section

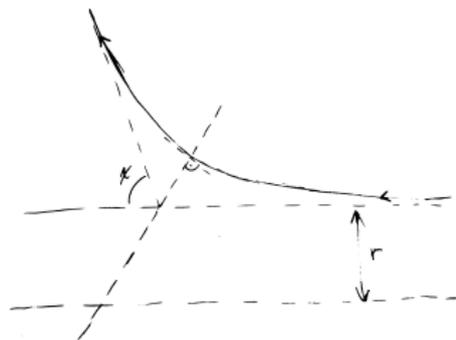
We note that the collision term can be also expressed through the cross section of the collision, which is quite obvious from the following consideration:

$$\begin{aligned}\sigma(V, \chi) \sin(\chi) d\chi d\varphi &= \sigma(V, \chi) d\Omega = r dr d\varphi \\ \Rightarrow \sigma(V, \chi) &= \frac{r}{\sin(\chi)} \frac{dr}{d\chi}.\end{aligned}\quad (29)$$

We can directly insert that in the Boltzmann equation and get:

$$J[f] = \frac{1}{m} \int d\mathbf{v}_2 d\Omega \sigma(V, \chi) V [\bar{f}_1 \bar{f}_2 - f_1 f_2] \quad (30)$$

expressed by the differential cross section.



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Symmetry properties of $J(f)$

If $\psi(\mathbf{v}_1)$ is a function of \mathbf{v}_1 , we have:

$$\begin{aligned}\int d\mathbf{v}_1 J(f)\psi(\mathbf{v}_1) &= \frac{1}{m} \int d\mathbf{v}_1 d\mathbf{v}_2 d\theta d\varphi B(\theta, V)[\bar{f}_1 \bar{f}_2 - f_1 f_2]\psi(\mathbf{v}_1) \\ &= \frac{1}{m} \int d\mathbf{v}_1 d\mathbf{v}_2 d\theta d\varphi B(\theta, V)[\bar{f}_1 \bar{f}_2 - f_1 f_2]\psi(\mathbf{v}_2) \\ &= -\frac{1}{m} \int d\mathbf{v}_1 d\mathbf{v}_2 d\theta d\varphi B(\theta, V)[\bar{f}_1 \bar{f}_2 - f_1 f_2]\psi(\bar{\mathbf{v}}_1) \\ &= -\frac{1}{m} \int d\mathbf{v}_1 d\mathbf{v}_2 d\theta d\varphi B(\theta, V)[\bar{f}_1 \bar{f}_2 - f_1 f_2]\psi(\bar{\mathbf{v}}_2).\end{aligned}\tag{31}$$

Thus, we can write the L.H.S. of Eq.31 as:

$$\int d\mathbf{v}_1 J(f)\psi(\mathbf{v}_1) = \frac{1}{4} \int d\mathbf{v}_1 J(f)(\psi(\mathbf{v}_1) + \psi(\mathbf{v}_2) - \psi(\bar{\mathbf{v}}_1) - \psi(\bar{\mathbf{v}}_2)).\tag{32}$$

We can directly see that for every quantity, for which:

$$\psi(\mathbf{v}_1) + \psi(\mathbf{v}_2) = \psi(\bar{\mathbf{v}}_1) + \psi(\bar{\mathbf{v}}_2), \quad (33)$$

the collision term is already zero. This is true for the number of particles ($\psi(\mathbf{v}_1) = 1$), the momentum ($\psi(\mathbf{v}_1) = \mathbf{v}_1$) and the energy ($\psi(\mathbf{v}_1) = v_1^2$) due to number, momentum and energy conservation in a binary collision. Functions, which satisfy Eq.33 are called summational invariants.

Actually, one can show that an arbitrary summational invariant can be written as:

$$\psi(\mathbf{v}_1) = A \frac{1}{2} m v_1^2 + \mathbf{B} \cdot m \mathbf{v}_1 + C. \quad (34)$$

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We recover some macroscopic quantities of a system from it's mass density function $f(\mathbf{q}_1, \mathbf{v}_1, t)$:

$$\text{The density: } \rho(\mathbf{q}, t) = \int d\mathbf{v}_1 f(\mathbf{q}_1, \mathbf{v}_1, t) \quad (35)$$

$$\text{The fluid velocity: } \mathbf{u}(\mathbf{q}, t) = \frac{1}{\rho} \int d\mathbf{v}_1 \mathbf{v}_1 f(\mathbf{q}_1, \mathbf{v}_1, t).$$

We introduce the peculiar velocity $\mathbf{v}_0 := \mathbf{v}_1 - \mathbf{u}$, this is the particle velocity w.r.t. the fluid flow velocity. The latter helps us define the temperature of the system as:

$$\frac{3}{2}RT = \xi = \frac{1}{2\rho} \int d\mathbf{v}_1 v_0^2 f(\mathbf{q}_1, \mathbf{v}_1, t). \quad (36)$$

and the pressure tensor:

$$\mathbf{P}_{ij} = \int d\mathbf{v}_1 v_{0,i} v_{0,j} f(\mathbf{q}_1, \mathbf{v}_1, t). \quad (37)$$

The hydrostatic pressure is given by:

$$p = \frac{1}{3} \int d\mathbf{v}_1 v_0^2 f(\mathbf{q}_1, \mathbf{v}_1, t) \quad (38)$$

because the diagonal components of \mathbf{P}_{ij} are equal.
We recover the equation of state of an ideal gas:

$$p = \frac{2}{3} \rho \xi = \rho RT. \quad (39)$$

We also introduce the heat flux in the system as:

$$\mathbf{Q} = \int d\mathbf{v}_1 \frac{v_0^2}{2} \mathbf{v}_0 f(\mathbf{q}_1, \mathbf{v}_1, t). \quad (40)$$

The hydrodynamic equations

Multiplying the Boltzmann equation successively by 1, \mathbf{v}_1 and $\frac{1}{2}v_1^2$ and integrating over \mathbf{v}_1 , because the collision term doesn't contribute to the result, we get:

$$\begin{aligned}\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{q}} \cdot (\rho \mathbf{u}) &= 0 \\ \frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial q_j}(\rho u_i u_j + P_{ji}) &= 0 \quad (41) \\ \frac{\partial}{\partial t}[\rho(\xi + \frac{1}{2}u^2)] + \frac{\partial}{\partial q_i}[\rho u_i(\xi + \frac{1}{2}u^2) + u_j P_{ji} + Q_i] &= 0.\end{aligned}$$

These are the hydrodynamic equations.

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Let us investigate how the system approaches equilibrium!

We introduce:

$$\begin{aligned} H[f] &= H(\mathbf{q}, t) := \int d\mathbf{v}_1 f_1 \ln f_1 \\ \bar{H}[f] &= \bar{H}(t) := \int d\mathbf{q} d\mathbf{v}_1 f_1 \ln f_1. \end{aligned} \tag{42}$$

First, consider spatially homogeneous system, that is, $f(\mathbf{q}, \mathbf{v}, t) = \rho f(\mathbf{v}, t)$. In equilibrium, we would have $\frac{\partial f}{\partial t} = 0$ and thus $\frac{\partial H}{\partial t} = 0$.

The H-Theorem states that the quantity H can only decrease with increasing time. We consider the time derivative of H :

$$\begin{aligned}\frac{\partial H}{\partial t} &= \frac{\partial}{\partial t} \int d\mathbf{v}_1 f_1 \ln f_1 = \int d\mathbf{v}_1 \frac{\partial f_1}{\partial t} \ln f_1 + \int d\mathbf{v}_1 f_1 \frac{1}{f_1} \frac{\partial f_1}{\partial t} \\ &= \int d\mathbf{v}_1 J(f) \ln f_1 + \int d\mathbf{v}_1 J(f) = \int d\mathbf{v}_1 J(f) \ln f_1.\end{aligned}\quad (43)$$

Using a previous result, we can rewrite the latter as:

$$\begin{aligned}\frac{\partial H}{\partial t} &= \frac{1}{4} \int d\mathbf{v}_1 J(f) [\ln f_1 + \ln f_2 - \ln \bar{f}_1 - \ln \bar{f}_2] \\ &= -\frac{1}{4} \int d\mathbf{v}_1 d\mathbf{v}_2 d\theta d\varphi B(\theta, V) [f_1 f_2 - \bar{f}_1 \bar{f}_2] \ln \frac{f_1 f_2}{\bar{f}_1 \bar{f}_2}\end{aligned}\quad (44)$$

so we can conclude that $\frac{\partial H}{\partial t} \leq 0$. The equality is obtained only if $f_1 f_2 = \bar{f}_1 \bar{f}_2$, which is equivalent to the statement that $\ln f$ should be a summational invariant.

Does the equilibrium have to be reached? The quantity H is bound from below! The energy of the system must be finite, so:

$$\int d\mathbf{v}_1 f_1 v_1^2 < \infty. \quad (45)$$

Now, if H would diverge, $-\ln f_1 \rightarrow \infty$ faster than $v_1^2 \rightarrow \infty$, so $f_1 \rightarrow 0$ faster than $e^{-v_1^2} \rightarrow 0$. But if this is the case, $H < \infty$, since $\lim_{x \rightarrow 0} e^{-x^2} x^n = 0 \forall n$. So we have contradiction and H must converge.

This means, together with $\frac{\partial H}{\partial t} \leq 0$ that an equilibrium state has to be reached.

Maxwell distribution

As we saw at last, $\ln f$ should be a summational invariant in equilibrium, so we can write it as:

$$\ln f_M(\mathbf{v}_1) = A + \mathbf{B} \cdot \mathbf{v}_1 + C v_1^2. \quad (46)$$

The constants are not arbitrary, but depend on the macroscopic properties of the system. So one gets for f precisely the Maxwell distribution:

$$f_M(\mathbf{v}_1) = \frac{\rho}{(2\pi RT)^{\frac{3}{2}}} e^{-\frac{(v_1-u)^2}{2RT}}. \quad (47)$$

This is referred to as absolute Maxwellian distribution, because of the spatial homogeneity.

Nonuniform system

We briefly mention the results for a spatially inhomogeneous system without derivations.

In that case, the H-Theorem states that the quantity \bar{H} should fulfill $\frac{\partial \bar{H}}{\partial t} \leq 0$. The equilibrium is, as before, at $\frac{\partial \bar{H}}{\partial t} = 0$ and the distribution functions takes a local Maxwellian form:

$$\ln f_{LM}(\mathbf{q}, \mathbf{v}_1, t) = A(\mathbf{q}, t) + \mathbf{B}(\mathbf{q}, t) \cdot \mathbf{v}_1 + C(\mathbf{q}, t)v_1^2. \quad (48)$$

Here, the coefficients as functions of (\mathbf{q}, t) are constrained by the Boltzmann equation:

$$\frac{\partial f_{LM}}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f_{LM}}{\partial \mathbf{q}} = J(f_{LM}) = 0. \quad (49)$$

Conclusion

Boltzmann equation:

$$\begin{aligned} & \frac{\partial f}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f}{\partial \mathbf{q}_1} \\ &= \frac{1}{m} \int d\omega d\mathbf{v}_2 V[f(\mathbf{q}_1, \bar{\mathbf{v}}_1, t)f(\mathbf{q}_1, \bar{\mathbf{v}}_2, t) - f(\mathbf{q}_1, \mathbf{v}_1, t)f(\mathbf{q}_1, \mathbf{v}_2, t)], \end{aligned}$$

- ▶ is suitable for describing systems in nonequilibrium.
- ▶ is in accordance with macroscopic results (e.g. hydrodynamic equations etc.)

H-Theorem: $\frac{\partial H}{\partial t} \leq 0$ describes how the system approaches equilibrium.

Further questions:

- ▶ Boltzmann eq. in (noneq.) QFT?[Ber15]
- ▶ Quantum H-Theorem?[al12]

References



Lesovik GB et al. "H-theorem in quantum physics". In: *Scientific Reports* 6 32815 (2016 Sep 12).



J. Berges. *Nonequilibrium Quantum Fields: From Cold Atoms to Cosmology*. 2015. arXiv: 1503.02907 [hep-ph].



M. Born und H.S. Green. *A General Kinetic Theory of Liquids*. Cambridge, England: Cambridge University Press, 1949.



N.N. Bogoliubov. *Studies in statistical mechanics*. Hrsg. von J. de Boehr und G.E. Uhlenbeck. Eds. New York: Wiley, 1962, vol 1.



L. Boltzmann. *Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen*. Sitzber. Akademie, 1872, S. 66, 275.



H. Grad. "Principles of the Kinetic Theory of Gases". In: *Flügge S. (eds) Thermodynamik der Gase / Thermodynamics of Gases. Handbuch der Physik / Encyclopedia of Physics*. Springer, Berlin, Heidelberg, 1958, vol 3/ 12.



Stewart Harris. *An introduction to the theory of the Boltzmann equation*. New York: Holt, Rinehart, und Winston, 1971.



J.G. Kirkwood. "The Statistical Mechanical Theory of Transport Processes I. General Theory". In: *J. Chem. Phys.* 15 (1947), S. 72.



J. Yvon. *La Theorie Statistique des Fluides et l'Equation d'Etat*. Paris: Hermann, 1935.