# Boltzmann equation and H-theorem

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## 1 Introduction

In 1872, Ludwig Boltzmann published a comprehensive paper in order to rigorously establish the second law of thermodynamics. This paper introduced two key findings: an integro-differential equation describing the time evolution of an ideal gas (known as the Boltzmann equation) and a mathematical proof demonstrating that this evolution would eventually reach the equilibrium state described by the Maxwell distribution. This second achievement, later known as the H-theorem, articulated the core of the second law of thermodynamics, which states that thermodynamic systems inevitably move towards a final state of equilibrium.

This discussion is focused on the Boltzmann equation and the H-theorem. Although he did not fully accomplish the goal of rigorously deriving the second law, the Boltzmann equation remains highly relevant today, and the H-theorem was groundbreaking as one of the earliest formalizations of entropy in statistical physics.

## 2 Probability density function

Consider an isolated system of $N$ equal particles, where each particle is described by its canonical coordinates $\mathbf{q}_i$ and conjugate momentum $\mathbf{p}_i$. In total, we have $6N$ variables and thus, a $6N$-dimensional phase space $\Gamma$. The dynamics of such a system are governed by the familiar Hamiltonian equations of motion:

$$\dot{\mathbf{q}}_\mathbf{i} = \frac{\partial H}{\partial \mathbf{p}_i}$$

$$\dot{\mathbf{p}}_\mathbf{i} = -\frac{\partial H}{\partial \mathbf{q}_i}$$

However, the particle count in a typical system is on the order of $10^{23}$, and the phase space is densely populated so solving these equations becomes impractical. This prompts a transition to a statistical framework in which we characterize the system's behavior through probabilistic distributions over phase space, as opposed to tracking the motion of individual particles. For this reason, we define a **probability density function**

$$F_N(\{\mathbf{q}\}, \{\mathbf{p}\}, t)$$

which describes the probability of finding the system in a particular microstate at time $t$. This function is normalized (i.e. the probability of the system being in any state is one), and symmetric under the particle exchange since we are considering classical indistinguishable particles.

## 3 The Liouville equation

We now want to determine how the probabilistic picture handles time changes in the system. Therefore, we examine the infinitesimal change $dF_N$ in the value of $F_N$, which gives:

$$dF_N = \frac{\partial F_N}{\partial t}dt + \sum_{i=1}^{N} \frac{\partial F_N}{\partial \mathbf{q}_i} \cdot d\mathbf{q}_i + \sum_{i=1}^{N} \frac{\partial F_N}{\partial \mathbf{p}_i} \cdot d\mathbf{p}_i$$

Dividing the expression above by $dt$ and keeping in mind that $\frac{d\mathbf{q}_i}{dt} = \dot{\mathbf{q}}_\mathbf{i}$ and $\frac{d\mathbf{p}_i}{dt} = \dot{\mathbf{p}}_\mathbf{i}$, we get **Liouville's equation:**

$$\frac{dF_N}{dt} = \frac{\partial F_N}{\partial t} + \sum_{i=1}^{N} \left[ \frac{\partial F_N}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{\partial F_N}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right] \tag{1}$$

Furthermore, **Liouville's theorem** asserts that the probability density function remains constant along the system's trajectories. To rephrase, as a system point traverses through phase space, the probability density near this point remains unchanging over time:

$$\frac{dF_N}{dt} = 0 \tag{2}$$

In statistical mechanics, this persistent density is termed the classical a priori probability.

## 4 Reduced distribution functions and BBGKY hierarchy of equations

Thus far, we observed that attempting to fully describe a system invariably presents a computational challenge due to the sheer number of degrees of freedom involved. One could argue that introducing the Liouville equation doesn't make things better since we still have derivatives with respect to individual positions and momenta, but we will now make the transition from a microscopic to a macroscopic picture.

The transition from microscopic to macroscopic variables is obtained by integrating over a large number of particles. For that reason, we define the **reduced distribution function**:

$$F_R(\mathbf{x}_1,\ldots,\mathbf{x}_R,t) \equiv \int d\mathbf{x}_{R+1}\ldots d\mathbf{x}_N F_N(\mathbf{x}_1,\ldots,\mathbf{x}_R,\ldots,\mathbf{x}_N,t) \tag{3}$$

where $\mathbf{x}_i = (\mathbf{q}_i, \mathbf{p}_i)$ is a phase point at the time $t$.

The function $F_R$ is also called the $R$**-particle density function.** In analogy with $F_N$, we can say that $F_R$ is the probability distribution of the first $R$ particles, but regardless of the remaining $N-R$ because we integrated out the information about them. Furthermore, since we assumed that $F_N$ is symmetric, we can conclude that $F_R$ is symmetric in its $R$ arguments as well. Intuitively $F_1(\mathbf{x}_1,t)d\mathbf{x}_1$ is the probability of finding particle 1 in the state $d\mathbf{x}_1$ about $\mathbf{x}_1$.

We are interested in how $F_R$ evolve in time. Looking closely at (1), we can identify $\dot{\mathbf{q}}_\mathbf{i}$ and $\dot{\mathbf{p}}_\mathbf{i}$ as

$$\dot{\mathbf{q}}_\mathbf{i} = \frac{\mathbf{p}_i}{m}$$

$$\dot{\mathbf{p}}_\mathbf{i} = \mathbf{F}_i$$

where $\mathbf{F}_i$ is the total force on the $i$th particle. For simplicity, we assume that $\mathbf{F}_i$ is conservative and central, and only due to inter-particle forces. This means that the force on the $i$th particle exerted by the $j$th particle can be written as

$$\mathbf{F}_\mathbf{i} = -\sum_{j=1\neq i}^{N} \frac{\partial \phi_{ij}}{\partial \mathbf{q}_\mathbf{i}}$$

Substituting these expressions into (1) and taking (2) into account, we have:

$$\frac{\partial F_N}{\partial t} + \sum_{i=1}^{N} \frac{\mathbf{p}_\mathbf{i}}{m}\cdot\frac{\partial F_N}{\partial \mathbf{q}_i} + \sum_{i=1}^{N} \mathbf{F}_\mathbf{i}\cdot\frac{\partial F_N}{\partial \mathbf{p}_i} = 0$$

$$\frac{\partial F_N}{\partial t} + \sum_{i=1}^{N} \frac{\mathbf{p}_\mathbf{i}}{m}\cdot\frac{\partial F_N}{\partial \mathbf{q}_i} - \sum_{i,j=1}^{N} \frac{\partial \phi_{ij}}{\partial \mathbf{q}_\mathbf{i}}\cdot\frac{\partial F_N}{\partial \mathbf{p}_i} = 0 \tag{4}$$

To obtain an expression for $F_R$, we use the definition (3):

$$\int d\mathbf{x}_{R+1}\ldots d\mathbf{x}_N \frac{\partial F_N}{\partial t} + \int d\mathbf{x}_{R+1}\ldots d\mathbf{x}_N \sum_{i=1}^{N} \frac{\mathbf{p}_\mathbf{i}}{m}\cdot\frac{\partial F_N}{\partial \mathbf{q}_i} - \int d\mathbf{x}_{R+1}\ldots d\mathbf{x}_N \sum_{i,j=1}^{N} \frac{\partial \phi_{ij}}{\partial \mathbf{q}_\mathbf{i}}\cdot\frac{\partial F_N}{\partial \mathbf{p}_i} = 0 \tag{5}$$

This is a rather long expression, so we shall analyze it part by part.

For an arbitrary R we can take the Liouville equation and integrate over the coordinates and conjugate momenta of the last $N-R$ particles.

The first term in (5) is the easiest one as we can interchange the partial derivative and integration:

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

Integrating the second term gives:

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

The third term is perhaps the most complicated:

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

The first term in the expression above is

$$-\sum_{i,j=1}^{R}\frac{\partial\phi_{ij}}{\partial\mathbf{q_i}}\cdot\frac{\partial}{\partial\mathbf{p}_i}\int d\mathbf{x}_{R+1}\dots d\mathbf{x}_N F_N=-\sum_{i,j=1}^{R}\frac{\partial\phi_{ij}}{\partial\mathbf{q_i}}\cdot\frac{\partial F_R}{\partial\mathbf{p}_i}$$

For the second term we can make use of the symmetry property of $F_N$ and rewrite it as

$$-\int d\mathbf{x}_{R+1}\dots d\mathbf{x}_N\sum_{\substack{1\le i\le R\\R+1\le j\le N}}^{N}\frac{\partial\phi_{ij}}{\partial\mathbf{q_i}}\cdot\frac{\partial F_N}{\partial\mathbf{p}_i}=-(N-R)\int d\mathbf{x}_{R+1}\sum_{i=1}^{R}\frac{\partial\phi_{iR+1}}{\partial\mathbf{q_i}}\cdot\frac{\partial F_{R+1}}{\partial\mathbf{p}_i}$$

The last term vanishes because of boundary conditions on $F_N$.

All in all, we have:

$$\frac{\partial F_R}{\partial t} + \sum_{i=1}^{R} \frac{\mathbf{p_i}}{m} \cdot \frac{\partial F_R}{\partial \mathbf{q}_i} - \sum_{i,j=1}^{R} \frac{\partial \phi_{ij}}{\partial \mathbf{q_i}} \cdot \frac{\partial F_R}{\partial \mathbf{p}_i} = (N-R) \int d\mathbf{x}_{R+1} \sum_{i=1}^{R} \frac{\partial \phi_{iR+1}}{\partial \mathbf{q_i}} \cdot \frac{\partial F_{R+1}}{\partial \mathbf{p}_i} \tag{6}$$

Equation (6) is called the **BBGKY hierarchy of equations**.

# 5 Boltzmann gas limit

To obtain the Boltzmann equation from the BBGKY equation we will follow the derivation by Grad. Before that, we need to impose some conditions on the system:

- The density is sufficiently low, so we only consider binary collisions between particles
- The spatial dependence of gas properties is sufficiently slow so we can consider the collisions to be localized
- The potential between particles is of short range so that the first statement remains valid

This set of conditions is called the **Boltzmann gas limit**, or BGL for short.

Before proceeding with the derivation, we need to describe the specific physical conditions or constraints under which we will be operating in mathematical language.
Firstly, since the number of particles $N$ is very large, we can take the limit $N \to \infty$. Secondly, the mass $m$ of each particle is taken to approach zero, but in a way that the mass of the whole system $mN$ remains constant. Thirdly, the range of interaction $\sigma$ approaches zero, but in a way that for $N$ particles the total area covered by these interactions $N\sigma^2$ is constant. Putting everything together, we have the following set of conditions:

$$\begin{aligned}
&N \to \infty \\
&m \to 0 \\
&\sigma \to 0 \\
&Nm = \text{const.} \\
&N\sigma^2 = \text{const.}
\end{aligned}$$

# 6 Boltzmann equation

For This section, we will follow the derivation by Grad [2], as presented in [1].
Let us consider $F_R$ as functions of phase points $\mathbf{y_R} = (\mathbf{q_r}, \mathbf{v_R})$, where $\mathbf{q_R}$ and $\mathbf{v_R}$ are spatial coordinate and velocity, respectively. Now we will introduce the truncated distribution functions $F_i^\sigma$ as distribution functions resulting from restricting the domain of reduced distribution functions. The first two truncated distributions are given by

$$F_1^\sigma \equiv \int_{D_1} d\mathbf{y_2} \dots d\mathbf{y_N} F_N \tag{7}$$

$$F_2^\sigma \equiv \int_{D_2} d\mathbf{y_3} \dots d\mathbf{y_N} F_N \tag{8}$$

where

$$\begin{aligned} D_1 &= \{\{\mathbf{q_2}, \dots, \mathbf{q_N}\} : |\mathbf{q_i} - \mathbf{q_1}| \geq \sigma,\ i = 2, \dots, N\} \\ D_2 &= \{\{\mathbf{q_3}, \dots, \mathbf{q_N}\} : |\mathbf{q_i} - \mathbf{q_1}| \geq \sigma,\ i = 3, \dots, N\} \end{aligned}$$

To put it in words, $D_i$ is part of the physical space where $|\mathbf{q_j} - \mathbf{q_1}| \geq \sigma$ for $j = i+1, \dots, N$ is fulfilled. As we have mentioned before, we can think of $\sigma$ as the diameter of the particle, so the center of $i$th particle can not lie within the volume $|\mathbf{q_j} - \mathbf{q_1}| < \sigma$.

Since truncated functions become equal to reduced functions in the BGL (we will not prove this), they also satisfy Liouville's equation. Integrating Liouville's equation over $D_1$ gives the BBGKY equation for $F_1^\sigma$:

$$\frac{\partial F_1^\sigma}{\partial t} + \mathbf{v_1} \cdot \frac{\partial F_1^\sigma}{\partial \mathbf{q_1}} + (N-1) \oint_{S_2} d\mathbf{v_2} d\mathbf{S_2} \cdot (\mathbf{v_1} - \mathbf{v_2}) F_2^\sigma - (N-1) \frac{\partial}{\partial \mathbf{v_1}} \cdot \int_{|\mathbf{q_1} - \mathbf{q_2}| > \sigma} d\mathbf{y_2} \phi'_{12} F_2^\sigma = 0 \tag{9}$$

where $S_i$ is the surface of the sphere $|\mathbf{q}_i - \mathbf{q}_1| = \sigma$. The last term in (9) is zero because $\phi_{12} = \phi'_{12} = 0$ in physical space where $|\mathbf{q_1} - \mathbf{q_2} > 0$. The surface integral contains contributions from particles completing a collision $(\mathbf{v_2} - \mathbf{v_1}) \cdot d\mathbf{S_2} > 0$, and initiating a collision $(\mathbf{v_2} - \mathbf{v_1}) \cdot d\mathbf{S_2} < 0$.

Now we introduce a coordinate system in the plane perpendicular to the vector $\mathbf{V} = \mathbf{v_2} - \mathbf{v_1}$ with origin at $\mathbf{q_1}$, and define the polar coordinate system $r, \varphi$.
Each point on $S_2$ corresponds to a point on the disk $0 \leq r \leq \sigma$ and $0 < \varphi \leq 2\pi$. The disk is covered twice: once by projecting $S_2^+$ where $\mathbf{V} \cdot d\mathbf{S_2} > 0$ and once by projecting $S_2^-$ where $\mathbf{V} \cdot d\mathbf{S_2} < 0$. The infinitesimal disk area is given by $d\omega = r dr d\varphi$.

Integrating over the disk area gives

$$\frac{\partial F_1^\sigma}{\partial t} + \mathbf{v_i} \cdot \frac{\partial F_1^\sigma}{\partial \mathbf{q_1}} = (N-1) \int d\omega d\mathbf{v_2} V [F_2^\sigma(\mathbf{y_1}, \mathbf{y_2^+}, \mathbf{t}) - F_2^\sigma(\mathbf{y_1}, \mathbf{y_2^-}, \mathbf{t})]$$

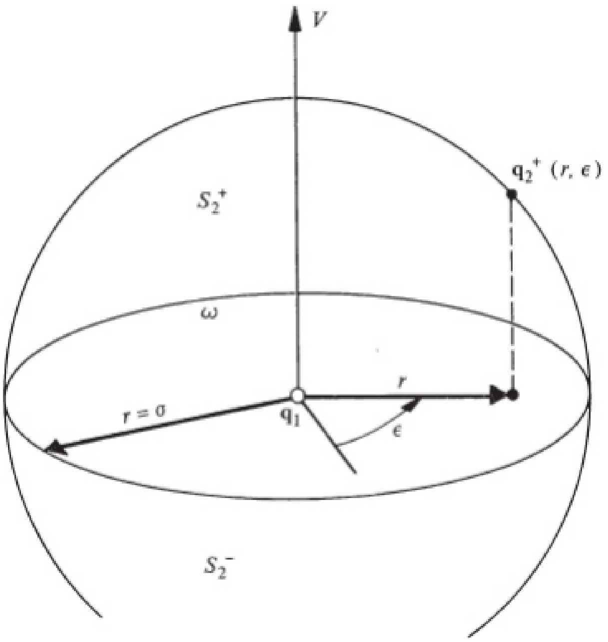

Figure 1: Image adapted from [1]

where $\mathbf{y_2^\pm} = (\mathbf{q_2^\pm}, \mathbf{v_2})$. In BGL we can approximate $(N-1) \approx N$, which leads us to

$$\frac{\partial F_1^\sigma}{\partial t} + \mathbf{v_1} \cdot \frac{\partial F_1^\sigma}{\partial \mathbf{q_1}} = N \int d\omega d\mathbf{v_2} V[F_2^\sigma(\mathbf{y_1}, \mathbf{y_2^+}, \mathbf{t}) - F_2^\sigma(\mathbf{y_1}, \mathbf{y_2^-}, \mathbf{t})] \tag{10}$$

Finally, we define a mass density function $f = NmF$ and use the collision number assumption, or **Stosszahlansatz**, which is that the two-particle density function factorizes in its arguments,

$$F_2(\mathbf{y_1}, \mathbf{y_2}, t) = F_1(\mathbf{y_1}, t)F_2(\mathbf{y_2}, t)$$

We can also approximate the equation further by letting $\mathbf{q_2} \to \mathbf{q_1}$. This leads to the famous Boltzmann equation:

$$\frac{\partial f}{\partial t} + \mathbf{v_1} \cdot \frac{\partial f}{\partial \mathbf{q_1}} = \frac{1}{m} \int d\omega d\mathbf{v_2} V[f(\mathbf{q_1}, \mathbf{v_1'}, t)f(\mathbf{q_1}, \mathbf{v_2'}, t) - f(\mathbf{q_1}, \mathbf{v_1}, t)f(\mathbf{q_1}, \mathbf{v_2}, t)] \tag{11}$$

where $\mathbf{v_1'}$ and $\mathbf{v_2'}$ are velocities after the collision. The term on the RHS of (11) is called **the collision term**,

$$J(f) = \frac{1}{m} \int d\omega d\mathbf{v_2} V(f_1' f_2' - f_1 f_2)$$

and describes particles with velocities $\mathbf{v_1}$ and $\mathbf{v_2}$ at location $\mathbf{q}$ colliding into new post-collision velocities $\mathbf{v_1'}$ and $\mathbf{v_2'}$, whereas the LHS is called **the diffusion term,** and corresponds to the movement of free, non-colliding particles. Moreover, since we are analyzing two-particle collisions, the disk integral is often replaced by a cross-section term $B(\theta, \phi)$, so the collision term becomes

$$J(f) = \frac{1}{m}\int B(\theta,\phi)d\theta d\phi d\mathbf{v_2}(f_1'f_2' - f_1f_2) \tag{12}$$

# 7 Symmetry properties of the collision term

In this section, we will briefly discuss some symmetry properties of the collision term. For that purpose, we introduce an arbitrary function of $\mathbf{v_1}$; $\psi$, and integrate the collision term (12) as follows:

$$\int d\mathbf{v_1}J(f)\psi(\mathbf{v_1}) = \frac{1}{m}\int d\theta d\phi d\mathbf{v_1}d\mathbf{v_2}B(\theta,\phi)(f_1'f_2' - f_1f_2)\psi(\mathbf{v_1}) \tag{13}$$

We can interchange the dummy variables $\mathbf{v_1}$ and $\mathbf{v_2}$ on the RHS of (13) (since the integral is symmetric in $\mathbf{v_1}$ and $\mathbf{v_2}$) to obtain:

$$\int d\mathbf{v_1}J(f)\psi(\mathbf{v_1}) = \frac{1}{m}\int d\theta d\phi d\mathbf{v_1}d\mathbf{v_2}B(\theta,\phi)(f_1'f_2' - f_1f_2)\psi(\mathbf{v_2}) \tag{14}$$

Furthermore, replacing $\mathbf{v_1}$ and $\mathbf{v_2}$ by $\mathbf{v_1'}$ and $\mathbf{v_2'}$ gives:

$$\int d\mathbf{v_1}J(f)\psi(\mathbf{v_1}) = -\frac{1}{m}\int d\theta d\phi d\mathbf{v_1}d\mathbf{v_2}B(\theta,\phi)(f_1'f_2' - f_1f_2)\psi(\mathbf{v_1'}) \tag{15}$$

$$\int d\mathbf{v_1}J(f)\psi(\mathbf{v_1}) = -\frac{1}{m}\int d\theta d\phi d\mathbf{v_1}d\mathbf{v_2}B(\theta,\phi)(f_1'f_2' - f_1f_2)\psi(\mathbf{v_2'}) \tag{16}$$

where the negative sign comes from momentum conservation $\mathbf{v_1} + \mathbf{v_2} = \mathbf{v_1'} + \mathbf{v_2'}$.

Combining (13) – (16) expresses the basic symmetry property of $J(f)$:

$$\begin{aligned}\int d\mathbf{v_1}J(f)\psi(\mathbf{v_1}) &= \frac{1}{4m}\int d\theta d\phi d\mathbf{v_1}d\mathbf{v_2}B(\theta,\phi)[f_1'f_2' - f_1f_2]\cdot[\psi(\mathbf{v_1}) + \psi(\mathbf{v_2}) - \psi(\mathbf{v_1'}) - \psi(\mathbf{v_2'})] \\ &= \frac{1}{4}\int d\mathbf{v_1}J(f)\cdot[\psi(\mathbf{v_1}) + \psi(\mathbf{v_2}) - \psi(\mathbf{v_1'}) - \psi(\mathbf{v_2'})] \qquad (17)\end{aligned}$$

This symmetry produces the so-called **summational invariants**, which are molecular properties for which there is no net change due to a collision, i.e. the expression in (17) is zero. In this case, we have 3 summational invariants:

- the number of particles, $\psi(\mathbf{v_1}) = 1$

$$\int d\mathbf{v_1}J(f) = \frac{1}{4}\int d\mathbf{v_1}J(f)\cdot[1 + 1 - 1 - 1] = 0$$

- the linear momentum $\psi(\mathbf{v_1}) = m\mathbf{v_1}$

$$\int d\mathbf{v_1}J(f) = \frac{1}{4}\int d\mathbf{v_1}J(f)\cdot[m\mathbf{v_1} + m\mathbf{v_2} - m\mathbf{v_1'} - m\mathbf{v_2'}] = 0$$

- total energy $\psi(\mathbf{v_1}) = \frac{v_1^2}{2m}$

$$\int d\mathbf{v_1} J(f) = \frac{1}{4}\int d\mathbf{v_1} J(f) \cdot \left[\frac{v_1^2}{2m} + \frac{v_2^2}{2m} - \frac{v_1'^2}{2m} - \frac{v_2'^2}{2m}\right] = 0$$

# 8 H-theorem

As we have seen, the Boltzmann equation is an extremely complex one; it is differential in two variables and integral in the other two. It comes as no surprise that it took almost fifty years after Boltzmann derived it to obtain an approximate solution. Nevertheless, even without solving the equation, it offers significant insights into the time evolution of gases. One of the most notable is the H-Theorem, which asserts that the entropy of any Boltzmann gas will increase over time, eventually reaching a state of maximum entropy described by the Maxwell-Boltzmann distribution.

The quantity $H$ is defined as

$$H = \int d\mathbf{v_1} f_1 \ln(f_1) \tag{18}$$

In this section, we will consider a homogenous system, where the density function does not depend on the spatial coordinates $f(\mathbf{q}, \mathbf{v}, t) = \rho f(\mathbf{v}, t)$, where $\rho$ is constant in the system. This implies that the density function is stationary in an equilibrium state, $\frac{\partial f}{\partial t} = 0$, and thus $\frac{\partial H}{\partial t} = 0$. In other words, the equilibrium state is when the partial time derivative of $H$ equals zero.

Let us now formally take the time derivative of $H$:

$$\begin{aligned}
\frac{\partial H}{\partial t} &= \frac{\partial}{\partial t}\int d\mathbf{v_1} f_1 \ln(f_1) \\
&= \int d\mathbf{v_1} \frac{\partial f_1}{\partial t} \ln(f_1) + \int d\mathbf{v_1} f_1 \frac{1}{f_1}\frac{\partial f_1}{\partial t} \\
&= \int d\mathbf{v_1} J(f_1) \ln(f_1) + \int d\mathbf{v_1} J(f_1) \\
&= \int d\mathbf{v_1} J(f_1) \ln(f_1)
\end{aligned}$$

Plugging (17) into the expression above, we have:

$$\begin{aligned}
\frac{\partial H}{\partial t} &= \frac{1}{4}\int d\mathbf{v_1} J(f_1)[\ln(f_1) + \ln(f_2) - \ln(f_1') - \ln(f_2')] \\
&= -\frac{1}{4}\int d\mathbf{v_1} d\mathbf{v_2} d\theta d\phi B(\theta, \phi)[f_1 f_2 - f_1' f_2'] \ln\left(\frac{f_1 f_2}{f_1' f_2'}\right)
\end{aligned} \tag{19}$$

Since the cross-section $B(\theta, \phi)$ is positive for all values of its arguments, the sign of the integral is determined by the product $[f_1 f_2 - f_1' f_2'] \ln\left(\frac{f_1 f_2}{f_1' f_2'}\right)$. These two terms always have the same sign, so the integral is positive and

$$\frac{\partial H}{\partial t} \leq 0 \tag{20}$$

which is the statement of the H-theorem. Of course, the equality is achieved only in equilibrium, where $f_1 f_2 = f_1' f_2'$. This implies that $\ln(f_1)$ is also a summational invariant of the collision term and so it must be a linear combination

$$\ln(f_M) = A + B\mathbf{v_1} + C\mathbf{v_1^2}$$

for some constants $A$, $B$, and $C$. These constants are not arbitrary but depend on the macroscopic properties of the system. The value of $f$ obtained for the equilibrium state is

$$f_M(\mathbf{v_1}) = \frac{\rho}{(2\pi RT)^{\frac{3}{2}}}\, e^{-\frac{(v_1-u)^2}{2RT}}$$

which is the Maxwell distribution.

# 9 Conclusion

To summarize, the Boltzmann equation is a kinetic equation derived from the BBGKY hierarchy after truncation, which is considered exact in the BGL. Although we did not find its general solution, we were still able to extract some significant results from it. The equation allows us to describe systems that are not in equilibrium, which is crucial for establishing the conditions under which a system moves towards equilibrium, known as the H-Theorem. This theorem essentially generalizes the second law of thermodynamics for non-equilibrium situations, where entropy cannot be clearly defined. However, in equilibrium, the specific quantity of interest in the H-Theorem, H, is exactly the negative of entropy. Furthermore, in equilibrium, it was demonstrated that the distribution function assumes a Maxwellian form.

# References

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

[2] 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