

0.0.1 Elementary derivation of Boltzmann's equation: streaming term

The Maxwell distribution ($\rightarrow??$) is the distribution of the velocity of a single particle. Therefore, Boltzmann wished to study the single-body distribution function $f(\mathbf{r}, \mathbf{v}, t)$, where $f(\mathbf{r}, \mathbf{v}, t)d\mathbf{r}d\mathbf{v}$ is the probability of finding a particle whose state specified by its position \mathbf{r} and velocity \mathbf{v} in a 6-dimensional volume element $d\mathbf{v}d\mathbf{r}$ centered at (\mathbf{r}, \mathbf{v}) . That is, f is the probability density on the μ -space.¹

If the particles do not interact with each other, then

$$\frac{\partial}{\partial t}f + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}}f = 0 \quad (0.0.1)$$

in the homogeneous space. The second term on the LHS describes the motion of the particle 'flowing with the stream with velocity \mathbf{v} ,' so it is called the *streaming term*.

Exercise 1. This describes a ballistic motion. Its solution with the initial condition $f(\mathbf{r}, \mathbf{v}, 0) = f_0(\mathbf{r}, \mathbf{v})$ reads $f(\mathbf{r}, \mathbf{v}, t) = f_0(\mathbf{r} - \mathbf{v}t, \mathbf{v})$. Check this statement. \square

Exercise 2. This is the Liouville equation ($\rightarrow??$) for a single body. \square

If the particle interact with other particles (if there are collisions), the above equation is not true and we must write

$$\frac{\partial}{\partial t}f + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}}f = \left(\frac{\partial f}{\partial t} \right)_{col}, \quad (0.0.2)$$

where the subscript *col* indicates the contribution of collisions. The reader should immediately realize that the streaming term does not contribute irreversibility at all.

0.0.2 Two-body collision term

To obtain the collision term, we assume the following:

- (1) There are only two-body collisions.
- (2) "Stosszahlansatz":² colliding particles are statistically uncorrelated.
- (3) f does not change as a function of spatial position within the range of the particle-particle interactions.

According to the assumption (2) the probability of collisions between the particles with velocity \mathbf{v} and velocity \mathbf{v}' around \mathbf{r} may be written as $n f(\mathbf{r}, \mathbf{v}) f(\mathbf{r}, \mathbf{v}') d\mathbf{v}d\mathbf{v}' d\mathbf{r}d\mathbf{r}$, where n is the number density of the particles.

Suppose the relative velocity of the two colliding particles (far before the collision) is \mathbf{g} , and the collision parameter is \mathbf{b} . The collision parameter is the distance vector between the two colliding particles projected to the subspace orthogonal to \mathbf{g} . More precisely, let us write the i th particle coordinates be $(\mathbf{r}_i, \mathbf{v}_i)$. Then,

$$\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1, \quad (0.0.3)$$

$$\mathbf{b} = (\mathbf{r}_2 - \mathbf{r}_1)(1 - \mathbf{g}\mathbf{g}^T/g^2), \quad (0.0.4)$$

where $g = |\mathbf{g}|$. The number of particles coming with the collision parameter \mathbf{b} per unit time can be written as

$$2\pi b db n f(\mathbf{r}_2, \mathbf{v}_2, t) g, \quad (0.0.5)$$

¹The 'true' μ -space is spanned by the position coordinates and the momentum coordinates instead of velocities.

²hypothesis of collision numbers

where $b = |\mathbf{b}|$. Therefore, the expected number of collisions with the particle with velocity \mathbf{v}_2 per unit time experienced by the particle with velocity \mathbf{v}_1 at \mathbf{r}_1 may be expected to be

$$2\pi b db n f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_1, \mathbf{v}_2, t) g d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{r}_1. \quad (0.0.6)$$

Here, we have used (3) to identify all the spatial coordinates in the density distribution functions.

0.0.3 Contribution of collisions to time evolution

The above collision process describes the collision $\{\mathbf{v}_1, \mathbf{v}_2\} \rightarrow \{\mathbf{v}'_1, \mathbf{v}'_2\}$, where the primed velocities after the collision are determined according to the energy and momentum conservation. Since mechanics is time reversal symmetric, there must be the collision process $\{\mathbf{v}'_1, \mathbf{v}'_2\} \rightarrow \{\mathbf{v}_1, \mathbf{v}_2\}$ as well.³ Therefore, the expectation value of the number of collisions that give velocity \mathbf{v}_1 after collision must be given by

$$2\pi b' db' n f(\mathbf{r}_1, \mathbf{v}'_1, t) f(\mathbf{r}_1, \mathbf{v}'_2, t) g' d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{r}_1. \quad (0.0.7)$$

Combining the above results, we may write

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_{col} d\mathbf{r}_1 d\mathbf{v}_1 &= n \int 2\pi b' db' f(\mathbf{r}_1, \mathbf{v}'_1, t) f(\mathbf{r}_1, \mathbf{v}'_2, t) g' d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{r}_1 \\ &\quad - n \int 2\pi b db f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_1, \mathbf{v}_2, t) g d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{r}_1. \end{aligned} \quad (0.0.8)$$

Now, we use the equality

$$b' db' g' d\mathbf{v}'_1 d\mathbf{v}'_2 d\mathbf{r}'_1 = b db g d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{r}_1 \quad (0.0.9)$$

that holds thanks to Liouville's theorem ($\rightarrow??$) applied to the two-body phase volume. Thus, we finally obtain

$$\left(\frac{\partial f}{\partial t}\right)_{col} = n \int 2\pi b db d\mathbf{v}_2 g [f(\mathbf{r}_1, \mathbf{v}'_1, t) f(\mathbf{r}_1, \mathbf{v}'_2, t) - f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_1, \mathbf{v}_2, t)]. \quad (0.0.10)$$

After the collision the relative velocity changes its direction to the direction specified by the azimuthal angle θ measured from the direction of $\mathbf{g} = \mathbf{v}_2 - \mathbf{v}_1$.

$$2\pi b db = \sigma(\theta) d\Omega, \quad (0.0.11)$$

where Ω is the solid angle of the annule between θ and $\theta + d\theta$, and $\sigma(\theta)$ is called the *differential scattering cross section*.¹ differential scattering cross section⁴

$$\left(\frac{\partial f}{\partial t}\right)_{col} = n \int \sigma d\Omega d\mathbf{v}_2 g [f(\mathbf{r}_1, \mathbf{v}'_1, t) f(\mathbf{r}_1, \mathbf{v}'_2, t) - f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_1, \mathbf{v}_2, t)]. \quad (0.0.12)$$

³Here, more precisely, we use the detailed balance ($\rightarrow??$).

⁴There are other definitions as well.

0.0.4 Boltzmann equation

Thus, we have arrived at the Boltzmann equation

$$\frac{\partial}{\partial t}f + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}}f = n \int \sigma d\Omega g [f(\mathbf{r}_1, \mathbf{v}'_1, t)f(\mathbf{r}_1, \mathbf{v}'_2, t) - f(\mathbf{r}_1, \mathbf{v}_1, t)f(\mathbf{r}_1, \mathbf{v}_2, t)]. \quad (0.0.13)$$

Here, $\mathbf{v}_1 + \mathbf{v}_2 = \mathbf{v}'_1 + \mathbf{v}'_2$ (and the energy conservation law) must be satisfied when the integration is performed.

Exercise 1. If there is an external force field \mathbf{F} , the streaming term (\rightarrow 0.0.1) must be modified. Give a necessary modification and write down the most general Boltzmann equation allowing spatial nonuniform equilibrium distributions. Of course, the external field must change spatially sufficiently gently to satisfy our assumption (3) in 0.0.2. \square .

A more careful (but still formal) derivation will be given later from the BBGKY hierarchy ($\rightarrow??$).

The Boltzmann equation is an equation for a one-body distribution function. The actual system is an N ($\rightarrow \infty$) body system, so the justification of the Boltzmann equation is equivalent to justification of the reduction of N body description to the single body description. This has been accomplished by Lanford⁵ for the hard core gas case for a very short time ($\sim 1/4$ of the mean free time) in the so-called *Boltzmann-Grad limit* Boltzmann-Grad limit: $N \rightarrow \infty$, $Nd^2 \rightarrow 1$, where d is the hard core diameter). That is, the reliability of the Boltzmann equation has been demonstrated only for this microscopic time scale.

Remark. If the limit $N \rightarrow \infty$, $Nd^3 \rightarrow 1$ is considered, then the *Enskog equation* that replaces the collision term of the Boltzmann equation with the one that takes into account the spatial difference of the distribution at the scale of d is expected.^{6,7} \square

0.0.5 Collision invariants

Let φ be a function of single particle coordinates. Let us write φ_i be the quantity associated with particle i before the collision and φ'_i after the collision. Suppose particles 1 and 2 undergo a collision. If

$$\varphi_1 + \varphi_2 = \varphi'_1 + \varphi'_2, \quad (0.0.14)$$

we say φ is a *collision invariant*. collision invariant

The collision invariant, if continuous, must have the following form

$$\varphi = A + \mathbf{B} \cdot \mathbf{v} + C\mathbf{v}^2, \quad (0.0.15)$$

where A, C are constants and \mathbf{B} is a constant vector (actually, they can be functions of the position \mathbf{r}). This is not very trivial to show.⁸

⁵O E Lanford, III, "Time evolution of large classical systems," Lecture Notes in Physics **38**, 1-111 (1975).

⁶The Enskog equation is known to be a good model even for liquid. For example, see T. Scopigno, R. Di Leonardo, L. Comez, A. Q. R. Baron, D. Fioretto, and G. Ruocco, "Hard-Sphere-like Dynamics in a Non-Hard-Sphere Liquid," Phys. Rev. Lett., **94**, 155301 (2005).

⁷See a related paper: F Rezakhanlou, "A stochastic model associated with Enskog equation and its kinetic limit," Commun. Math. Phys. **232**, 327-375 (2003).

⁸A proof can be found in C Cercignani, *The Boltzmann Equation and Its Applications* (Springer-Verlag, New York, 1988), p74-78. If the reader accepts that there are only four additive constants of motion, the equation (0.0.15) looks trivial, but here, we are actually demonstrating that the additive invariants are only linear momenta and kinetic energy (in our case, we do not take into account of the angular momenta of the particles).

If φ is a collision invariant, then

$$I = \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g \varphi(\mathbf{v}_1) [f(\mathbf{r}_1, \mathbf{v}'_1, t) f(\mathbf{r}_1, \mathbf{v}'_2, t) - f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_1, \mathbf{v}_2, t)] = 0. \quad (0.0.16)$$

This follows from the following identity that is valid for any function of the single particle coordinates

$$I = \frac{1}{4} \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g (\varphi_1 + \varphi_2 - \varphi'_1 - \varphi'_2) [f(\mathbf{r}_1, \mathbf{v}'_1, t) f(\mathbf{r}_1, \mathbf{v}'_2, t) - f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_1, \mathbf{v}_2, t)]. \quad (0.0.17)$$

Here, an abbreviation $\varphi'_2 = \varphi(\mathbf{r}'_2, \mathbf{p}'_2)$, etc., is adopted.

A demonstration follows:

$$I = \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g (f_{(1)} f_{(2)} - f_{(1')} f_{(2')}) \varphi_1, \quad (0.0.18)$$

$$= \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g (f_{(1)} f_{(2)} - f_{(1')} f_{(2')}) \varphi_2. \quad (0.0.19)$$

Here, we have used the abbreviation $f_{(1)} = f(\mathbf{r}_1, \mathbf{v}_1, t)$, etc. Now, we change the variable as $(\mathbf{v}_1, \mathbf{v}_2) \rightarrow (\mathbf{v}'_1, \mathbf{v}'_2)$ to obtain (with the aid of (0.0.9))

$$I = \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g (f_{(1')} f_{(2')} - f_{(1)} f_{(2)}) \varphi'_1, \quad (0.0.20)$$

$$= \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g (f_{(1')} f_{(2')} - f_{(1)} f_{(2)}) \varphi'_2. \quad (0.0.21)$$

Combining all of them, we reach the desired result.

0.0.6 Local equilibrium distribution

A density distribution function satisfying

$$\left(\frac{\partial f}{\partial t} \right)_{col} = 0 \quad (0.0.22)$$

is called a *local equilibrium distribution*. A local equilibrium distribution function must have the following form

$$\log f = A + \mathbf{B} \cdot \mathbf{v} + C \mathbf{v}^2, \quad (0.0.23)$$

where A, C are functions of spatial coordinates and \mathbf{B} is a vector dependent only on the spatial coordinates. Therefore, notice that a local equilibrium distribution is *not* generally a stationary distribution function (cf., ??).

To demonstrate this, we demonstrate the following fundamental inequality

$$J = \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g \log f(\mathbf{r}_1, \mathbf{v}_1, t) [f(\mathbf{r}_1, \mathbf{v}'_1, t) f(\mathbf{r}_1, \mathbf{v}'_2, t) - f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_1, \mathbf{v}_2, t)] \leq 0 \quad (0.0.24)$$

for any density distribution f . Thanks to (0.0.17) we obtain (for the abbreviations see above (0.0.20))

$$J = \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g \log \frac{f_{(1)} f_{(2)}}{f_{(1')} f_{(2')}} (f_{(1')} f_{(2')} - f_{(1)} f_{(2)}). \quad (0.0.25)$$

Let $\lambda = f_{(1)}f_{(2)}/f_{(1')}f_{(2')}$. Then, this can further be rewritten as

$$J = \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g (1 - \lambda) \log \lambda f_{(1')}f_{(2')}. \quad (0.0.26)$$

Since $(1 - \lambda) \log \lambda \leq 0$,⁹ we are done.

Thus, we have demonstrated that (0.0.22) implies that $\lambda = 1$. That is, $\log f$ must be an additive invariant of the collision. This concludes the demonstration of (0.0.23) (with the aid of 0.0.5). That is, for a spatially uniform case, the Maxwell distribution ($\rightarrow??$) is the unique invariant solution of the (spatially uniform) Boltzmann equation.

Remark. Often the Boltzmann equation is approximated with finitely many choices of velocity values instead of continuous velocities. If the Galileian invariance is violated as such cases, the equation is not generally compatible with thermodynamics. See Cercignani.¹⁰

0.0.7 H-theorem

We know that if there is no external force, the Maxwell distribution is the unique stationary solution of the Boltzmann equation as can be seen from 0.0.6). Boltzmann's original aim was to show not only that this is the unique stationary state but also that any initial condition would reach this state eventually.

To this end Boltzmann devised a Lyapunov function called *H-function*

$$H = \int f \log f d\mathbf{r}d\mathbf{v}. \quad (0.0.27)$$

Let us study its time evolution

$$\frac{dH}{dt} = \int (1 + \log f) \frac{\partial f}{\partial t} d\mathbf{r}d\mathbf{v} = \int \log f \frac{\partial f}{\partial t} d\mathbf{r}d\mathbf{v}. \quad (0.0.28)$$

The streaming term (\rightarrow 0.0.1) does not change H

$$\left(\frac{dH}{dt}\right)_{str} = \int \log f \left(\frac{\partial f}{\partial t}\right)_{str} d\mathbf{r}d\mathbf{v}, \quad (0.0.29)$$

$$= - \int \log f \mathbf{v} \frac{\partial}{\partial \mathbf{r}} f d\mathbf{r}d\mathbf{v} = 0. \quad (0.0.30)$$

The collision term does change H as we have just seen in (0.0.24)

$$\left(\frac{dH}{dt}\right)_{col} = \int \sigma d\Omega d\mathbf{v}_1 d\mathbf{v}_2 g \log f_{(1)} [f_{(1')}f_{(2')} - f_{(1)}f_{(2)}] \leq 0. \quad (0.0.31)$$

That is,

$$\frac{dH}{dt} \leq 0. \quad (0.0.32)$$

This vanishes if and only if $\log f$ is a sum of additive invariant as we have already seen in 0.0.6. That is, H is a Lyapunov function whose unique minimum is given by the Maxwell distribution.

Thus, Boltzmann concluded that his equation describes the irreversible process whose unique destination is the equilibrium state (for a mathematical statement see ??).

⁹ $f(\lambda) = (1 - \lambda) \log \lambda$ takes the unique maximum 0 at $\lambda = 1$; it is convex upward.

¹⁰ C. Cercignani, "Temperature, entropy, and kinetic theory," J. Stat. Phys. **87**, 1097-1109 (1997).

0.0.8 Boltzmann reaches $S \propto \log(\text{Komplexionszahl})$.

Thus, Boltzmann thought he demonstrated the second law purely mechanically. Almost immediately, his colleague Loschmidt¹¹ pointed out that without approximation time-reversal symmetric mechanics could not conclude such an irreversible equation.

Boltzmann realized the probabilistic element had been smuggled into his argument¹² and wrote a fully statistical paper:¹³ basically, he asserts that the mechanical content of the second law was that the macroscopic state evolves to the direction that increases the number of Komplexions = microscopic states compatible with the macroscopic state.

The most important conclusion is that the equilibrium state is the most probable macroscopic state allowed to the system, so it can be studied without explicit dynamical consideration. This way, the study of nonequilibrium states receded from the main stage of statistical mechanics.

Exercise 1. I wish you to trace Boltzmann's logic, answering the following questions.

Suppose there are N gas particles. Let w_n be the number of particles with the energy between $(n-1)\epsilon$ and $n\epsilon$ ($\epsilon > 0$).

(1) Obtain the number of Komplexions (ignoring the energy constraint), and (with the aid of Stirling's formula) show that its maximization condition is equivalent to the minimization condition of

$$M = \sum w_i \log w_i. \quad (0.0.33)$$

(2) Write $w_i = w(x)\epsilon$ and simultaneously take the $n \rightarrow \infty$ and $\epsilon \rightarrow 0$ limits, maintaining $x = n\epsilon$ finite. Show that minimizing M is equivalent to minimizing

$$M' = \int w(x) \log w(x) dx. \quad (0.0.34)$$

(3) We should not ignore the constraints that the total number of particles is N and the total energy is K . Under this condition, derive Maxwell's distribution in 3-space by minimizing M' . [In the original paper Boltzmann first reduced the problem to a single particle problem, and wrote $w(x)$ as $f(u, v, w)$, where u, v, w are three components of the velocity. Also Boltzmann understands w to be the probability density distribution function.]

(4) Now, Boltzmann realized that M' gives the entropy of the ideal gas. Show this. Based on this finding, he proposed

$$S \propto \log(\text{Number of Komplexions}). \quad (0.0.35)$$

At the end of this same paper he says, although the relation could be demonstrated rigorously (sic) with the aid of kinetic gas theory, he cannot do so for other phases. However, he also claims that the relation is likely. \square

¹¹About him and his relation to Boltzmann see the book by Lindley.

¹²This will be discussed when we rederive the Boltzmann equation from the BBGKY hierarchy ($\rightarrow??$).

¹³“Über der Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respective den Sätzen über des Wärmegleichgewicht,” Wiener Ber. **76**, 373-435 (1877) [On the relation between the second principle of mechanical heat theory and probability theory with respect to theorems of thermal equilibrium].