

Boltzmann equation and H-theorem

Romain Chazotte

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Department of Physics
Heidelberg University
Germany
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Contents

1	Introduction	2
1.1	Many Body System	2
1.2	Liouville equation	2
1.3	History	3
2	BBGKY hierarchy	3
2.1	Equation for F_R	3
2.2	BBGKY hierarchy	5
3	Boltzmann equation	5
3.1	Boltzmann gas limit	5
3.2	Grad's derivation	5
3.3	Molecular chaos assumption	6
3.4	Boltzmann equation	6
4	Collision term	7
5	H-theorem	8
5.1	Deriving H-theorem	8
5.2	H-theorem and entropy	9
5.3	Solutions to H theorem	10
6	Quantum H-theorem	10
6.1	H-theorem in QIT	10
6.2	Quantum and Classical H-theorem	11
6.3	Examples	11
7	Recapping and Limitations	12
7.1	Recapping	12
7.2	Limitations	12

1 Introduction

This talk focused on the Boltzmann equation and the H-theorem. These were derived by Boltzmann in 1872 [1] in order to try to rigorously derive the second law of thermodynamics. While he didn't fully achieve his goal, the Boltzmann equation is still very relevant to this day, and the H-theorem was very influential in being one of the first motions of entropy in statistical physics. The Boltzmann equation is given by:

$$\frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{q}} + \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} = \frac{\partial f}{\partial t_{coll}} \quad (1)$$

it is a generally not solvable equation, and is in practice approximately numerically solved. The H-theorem states, that the measure H:

$$H = \int d\mathbf{q} d\mathbf{v} \ln(f) f \quad (2)$$

may decrease, but doesn't increase with time.

1.1 Many Body System

We are considering a system of many particles, with a particle number N . Each particle is described by position $\mathbf{q}_i$ and momentum $\mathbf{p}_i$, the equations of motion are given by the standard Hamiltonian equation $\dot{\mathbf{q}}_i = \frac{\partial H}{\partial \mathbf{p}_i}$ and $\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{q}_i}$.

For many particles, phase space gets densely filled, we go over to density distribution, $F_N(\mathbf{q}, \mathbf{p}, t) = F_N(\{\mathbf{q}_i\}, \{\mathbf{p}_i\}, t)$ being the probability of the system being in the exact micro state $\{\mathbf{q}_i\}, \{\mathbf{p}_i\}, t$, which I denote here as $\mathbf{q}, \mathbf{p}, t$. F_N is normalized, saying that the probability of the system to be in any state is one, symmetric under particle exchange, as we are only considering identical particles and vanishes for high $\mathbf{q}, \mathbf{p}$, as we are considering a system of finite size and energy.

1.2 Liouville equation

Important for the Boltzmann equation is the Liouville equation:

$$\frac{dF_N}{dt} = \frac{\partial F_N}{\partial t} + \frac{\partial F_N}{\partial \mathbf{q}} \dot{\mathbf{q}} + \frac{\partial F_N}{\partial \mathbf{p}} \dot{\mathbf{p}} = 0 \quad (3)$$

It is time reversible, so that if $F_N(\mathbf{q}(t), \mathbf{p}(t), t)$ is a solution, so is $F_N(\mathbf{q}(-t), \mathbf{p}(-t), -t)$.

1.3 History

After the publishing of Boltzmann's paper in 1872, a famous debate took place[2]. There was a lot of scepticism towards his theory, and a few very notable objections were formulated, which are relevant to this day. First, there was the Loschmidt, or time reversability objection, which brings up that arising from fully time reversible theories, it shouldn't be possible to derive not time reversible properties, as are the Boltzmann equation and the H-theorem. This happens in Boltzmann's theory due to the non time reversible Stosszahlansatz, which's merit can be debated to this day. Secondly, the Zermelo, or recurrence objection states, due to Poincaré recurrence, any system should after some arbitrarily long time be able to come back to its initial state. This directly contradicts H-theorem. Yet, they can be approximately reconciled, as for usual systems the recurrence time is infinitely long.

2 BBGKY hierarchy

We introduce the reduced distribution function F_R as

$$F_R(x_1, \dots, x_R, t) := \int dx_{R+1} \dots dx_N F_N \quad (4)$$

with x_i being the phase space volume of particle i .

In the following we will use $d\mathbf{X} := dx_{R+1} \dots dx_N$. We will for simplicity now assume a two particle potential proportional to $|\mathbf{r}_{ij}| = |\mathbf{q}_i - \mathbf{q}_j|$. We therefore have

$$\dot{\mathbf{p}}_i = \text{force} = - \sum_{j \neq i}^N \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i}$$

2.1 Equation for F_R

We will now use the Liouville equation:

$$\frac{dF_N}{dt} = \frac{\partial F_N}{\partial t} + \frac{\partial F_N}{\partial \mathbf{q}} \frac{\mathbf{p}}{m} + \frac{\partial F_N}{\partial \mathbf{p}} \dot{\mathbf{p}} = 0$$

to find relations for F_R . Integration of the first term gives:

$$\int d\mathbf{X} \partial_t F_N = \partial_t \int d\mathbf{X} F_N = \partial_t F_R$$

Integration of the second term gives:

$$\begin{aligned}
\int d\mathbf{X} \sum_i^N \frac{\partial F_N}{\partial \mathbf{q}_i} \frac{\mathbf{p}_i}{m} &= \sum_i^R \frac{\mathbf{p}_i}{m} \frac{\partial}{\partial \mathbf{q}_i} \int d\mathbf{X} F_N + \int d\mathbf{X} \sum_{R+1}^N \frac{\partial F_N}{\partial \mathbf{q}_i} \frac{\mathbf{p}_i}{m} \quad (5) \\
&= \sum_i^R \frac{\mathbf{p}_i}{m} \frac{\partial}{\partial \mathbf{q}_i} \int d\mathbf{X} F_N = \sum_i^R \frac{\mathbf{p}_i}{m} \frac{\partial F_R}{\partial \mathbf{q}_i}
\end{aligned}$$

where we can't pull the terms proportionate to variables being integrated over out of the integral. Yet we can see that the last term in eq.5 vanishes due to the boundary condition assumed at the beginning, namely F going to 0 at the boundary of our system.

Integration of the third term gives:

$$-\int d\mathbf{X} \sum_{i,j}^N \frac{\partial F_N}{\partial \mathbf{p}_i} \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} = -\sum_{i,j}^R \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} \frac{\partial}{\partial \mathbf{p}_i} \int d\mathbf{X} F_N \quad (6)$$

$$-\int d\mathbf{X} \sum_{i < R, R < j}^N \frac{\partial F_N}{\partial \mathbf{p}_i} \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} \quad (7)$$

$$-\int d\mathbf{X} \sum_{j, R < i}^N \frac{\partial F_N}{\partial \mathbf{p}_i} \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} \quad (8)$$

Where we split up the summation into three term, which show different properties due to integration.

The first term above gives:

$$-\sum_{i,j}^R \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} \frac{\partial}{\partial \mathbf{p}_i} \int d\mathbf{X} F_N = -\sum_{i,j}^R \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} \frac{\partial F_R}{\partial \mathbf{p}_i}$$

The second term above gives due to symmetry:

$$-\int d\mathbf{X} \sum_{i < R, R < j}^N \frac{\partial F_N}{\partial \mathbf{p}_i} \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} = -(N - R) \int dx_{R+1} \sum_i^R \frac{\partial F_{R+1}}{\partial \mathbf{p}_i} \frac{\partial \Phi_{i,R+1}}{\partial \mathbf{q}_i}$$

The third term above vanishes due to boundary conditions:

$$-\int d\mathbf{X} \sum_{j, R < i}^N \frac{\partial F_N}{\partial \mathbf{p}_i} \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} = 0$$

2.2 BBGKY hierarchy

Combining the above results we get:

$$\frac{\partial F_R}{\partial t} + \sum_i^R \frac{\mathbf{p}_i}{m} \frac{\partial F_R}{\partial \mathbf{q}_i} - \sum_{i,j}^R \frac{\partial \Phi_{ij}}{\partial \mathbf{q}_i} \frac{\partial F_R}{\partial \mathbf{p}_i} = (N - R) \int dx_{R+1} \sum_i^R \frac{\partial F_{R+1}}{\partial \mathbf{p}_i} \frac{\partial \Phi_{i,R+1}}{\partial \mathbf{q}_i} \quad (9)$$

This equation is called the BBGKY (Bogoliubov–Born–Green–Kirkwood–Yvon) hierarchy, and lets us compute F_R for a given F_{R+1}

3 Boltzmann equation

3.1 Boltzmann gas limit

We now make some crucial assumptions about the structure of the gas

$$N \rightarrow \infty$$

$$m \rightarrow 0$$

$$\sigma \rightarrow 0$$

$$N\sigma^2 = \text{const}$$

$$Nm = \text{const}$$

Namely, we will only consider binary collisions, as third order collisions are proportionate to $N\sigma^3 \rightarrow 0$. We will also now consider a contact potential.

3.2 Grad's derivation

We now derive the Boltzmann equation according to Grad [3, 4] We introduce truncated distributions F_1^σ and F_2^σ such that:

$$F_1^\sigma := \int_{D_1} d\mathbf{q}_2 \dots d\mathbf{q}_N F_N$$

$$F_2^\sigma := \int_{D_2} d\mathbf{q}_3 \dots d\mathbf{q}_N F_N$$

D_1 being the space where $|\mathbf{q}_1 - \mathbf{q}_i| > \sigma$ for all $i > 1$ and D_2 defined accordingly.

In the Boltzmann gas limit (BGL) F_i^σ are equivalent to F_i

Deriving the BBGKY hierarchy for these now gives extra terms due to boundary conditions, given here for F_1^σ :

$$\frac{\partial F_1^\sigma}{\partial t} + \mathbf{v}_1 \frac{\partial F_1^\sigma}{\partial \mathbf{q}_1} + (N-1) \int_{S_2} d\mathbf{v}_2 dS_2 (\mathbf{v}_1 - \mathbf{v}_2) F_2^\sigma - (N-1) \frac{\partial}{\partial \mathbf{v}_1} \int_{|\mathbf{q}_1 - \mathbf{q}_2| > \sigma} d\mathbf{q}_2 \Phi'_{12} F_2^\sigma = 0 \quad (10)$$

The last term above is equal to 0, as the potential is 0 in outside of 1σ of a given point.

The second to last term can be reformulated to :

$$(N-1) \int d\mathbf{v}_2 d\omega \mathbf{V} [F_2^\sigma(\mathbf{q}_1, \mathbf{q}_2^+, t) - F_2^\sigma(\mathbf{q}_1, \mathbf{q}_2^-, t)] \quad (11)$$

with $\mathbf{V} = \mathbf{v}_1 - \mathbf{v}_2$. This is done by splitting up the integral into the part where the directed volume element gives a minus sign or a plus sign, and therefore reducing the integral to one on a half-sphere. Said half sphere can then be linearly mapped to one on a plane, leaving us with the given integral.

Crucially, we can identify one half sphere with particles going into a collision, as velocity and position difference of the two particles are aligned, while the opposite is true for the other half sphere, making it's interpretation be the particles going out of a collision.

Here, $F_2^\sigma(\mathbf{q}_1, \mathbf{q}_2^+, t)$ denotes particle going out of a collision, and $F_2^\sigma(\mathbf{q}_1, \mathbf{q}_2^-, t)$ particles going into a collision.

3.3 Molecular chaos assumption

We now need to make some assumptions to get the Boltzmann equation.

We first make the Molecular chaos assumption (Stosszahlansatz), stating two particles are uncorrelated:

$$F_1 F_1 = F_2$$

The $F_2^\sigma(\mathbf{q}_1, \mathbf{q}_2^+, t)$ distribution is considered to be after a collision. We associate it with the pre-collision uncorrelated function, which shouldn't change the outcome due to the Liouville theorem.

Lastly, we drop terms proportionate to σ .

3.4 Boltzmann equation

We are now finally left with the famous Boltzmann equation:

$$\frac{\partial f}{\partial t} + \mathbf{v}_1 \frac{\partial f}{\partial \mathbf{q}_1} = \frac{1}{m} \int d\mathbf{v}_2 d\omega \mathbf{V} [f(\mathbf{q}_1, \bar{\mathbf{v}}_1, t) f(\mathbf{q}_1, \bar{\mathbf{v}}_2, t) - f(\mathbf{q}_1, \mathbf{v}_1, t) f(\mathbf{q}_1, \mathbf{v}_2, t)] \quad (12)$$

$\bar{\mathbf{v}}_1$ and $\bar{\mathbf{v}}_2$ are pre-collision velocities that become $\mathbf{v}_1$ and $\mathbf{v}_2$ after the collision. Here one can also see how to heuristically derive this formula. the total change of the one particle distribution is proportionate to the integral over all possible angles a particle could come from times all possible velocities it could have times the probability of the two particles colliding, with the first term accounting for particles colliding into the desired state, and the subtracted term being particles leaving said state. The last term above is more generally called the collision term $J(f)$, easing the notation

4 Collision term

A systems parameters can be determined by integrating over some Measure $A(\mathbf{v})$:

$$\langle A \rangle = \int d\mathbf{v} A f$$

Accordingly, we are now interested in the same integral over the collision term J , or to say the change of said measure over time due to collisions:

$$\int d\mathbf{v}_1 J(f) A$$

We rewrite $\bar{f}_i := f(\mathbf{q}_1, \bar{\mathbf{v}}_i, t)$ and $f_i := f(\mathbf{q}_1, \mathbf{v}_i, t)$ to have:

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

We now look for symmetries in order to find A such that the formula above vanishes.

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

The equation is symmetric under exchange of $\mathbf{v}_i$ and $\mathbf{v}_j$, as well as anti-symmetric under exchange of $\bar{\mathbf{v}}_i$ and $\mathbf{v}_i$. We can therefore reformulate to:

$$\begin{aligned} \int d\mathbf{v}_1 J(f) A &= \frac{1}{m} \int d\mathbf{v}_2 d\mathbf{v}_1 d\omega \mathbf{V}[\bar{f}_1 \bar{f}_2 - f_1 f_2] A(\mathbf{v}_2) \\ \int d\mathbf{v}_1 J(f) A &= -\frac{1}{m} \int d\mathbf{v}_2 d\mathbf{v}_1 d\omega \mathbf{V}[\bar{f}_1 \bar{f}_2 - f_1 f_2] A(\bar{\mathbf{v}}_1) \\ \int d\mathbf{v}_1 J(f) A &= -\frac{1}{m} \int d\mathbf{v}_2 d\mathbf{v}_1 d\omega \mathbf{V}[\bar{f}_1 \bar{f}_2 - f_1 f_2] A(\bar{\mathbf{v}}_2) \end{aligned}$$

Adding all 4 of them up and dividing by 4 now gives us a new expression for $\int d\mathbf{v}_1 J(f)A$:

$$4 \int d\mathbf{v}_1 J(f)A = \frac{1}{m} \int d\mathbf{v}_2 d\mathbf{v}_1 d\omega \mathbf{V}[\bar{f}_1 \bar{f}_2 - f_1 f_2][A(\mathbf{v}_1) + A(\mathbf{v}_2) - A(\bar{\mathbf{v}}_1) - A(\bar{\mathbf{v}}_2)]$$

$$\int d\mathbf{v}_1 J(f)A = \frac{1}{4} \frac{1}{m} \int d\mathbf{v}_2 d\mathbf{v}_1 d\omega \mathbf{V}[\bar{f}_1 \bar{f}_2 - f_1 f_2][A(\mathbf{v}_1) + A(\mathbf{v}_2) - A(\bar{\mathbf{v}}_1) - A(\bar{\mathbf{v}}_2)] \quad (13)$$

In order to find A such that eq.13 vanishes, we now only need to find solutions of:

$$[A(\mathbf{v}_1) + A(\mathbf{v}_2) - A(\bar{\mathbf{v}}_1) - A(\bar{\mathbf{v}}_2)] = 0 \quad (14)$$

This is solved for A = Constant, $\mathbf{v}$, $\mathbf{v}^2$:

$$C + C - C - C = 0$$

$$\mathbf{v}_1 + \mathbf{v}_2 - \bar{\mathbf{v}}_1 - \bar{\mathbf{v}}_2 = 0$$

$$\mathbf{v}_1^2 + \mathbf{v}_2^2 - \bar{\mathbf{v}}_1^2 - \bar{\mathbf{v}}_2^2 = 0$$

with the last two being due to conservation laws. Why we want this will become clear later.

5 H-theorem

We now come to the H theorem. It states that the measure H,

$$H = \int d\mathbf{q} d\mathbf{v} \ln(f) f$$

may decrease, but doesn't increase over time

5.1 Deriving H-theorem

In order to derive the H-theorem, we take the derivative of H to t, in order to look at how H changes over time

$$\begin{aligned} \frac{\partial H}{\partial t} &= \int d\mathbf{q} d\mathbf{v} (\ln(f) \partial_t f + f \partial_t \ln(f)) \\ &= \int d\mathbf{q} d\mathbf{v} (\ln(f) \partial_t f + \frac{f}{f} \partial_t f) = \int d\mathbf{q} d\mathbf{v} (\ln(f) \partial_t f + \partial_t f) \end{aligned}$$

For a uniform gas $\partial_{\mathbf{q}}f = 0$, so we get from the Boltzmann equation 12: $\frac{\partial f}{\partial t} = J$.

Therefore:

$$\frac{\partial H}{\partial t} = \int d\mathbf{q}d\mathbf{v} \ln(f)J + \int d\mathbf{q}d\mathbf{v} J = \int d\mathbf{q}d\mathbf{v} \ln(f)J \quad (15)$$

This leads to

$$\begin{aligned} \frac{\partial H}{\partial t} &= \frac{1}{4} \frac{1}{m} \int d\mathbf{v}_2 d\mathbf{v}_1 d\omega \mathbf{V}[\bar{f}_1 \bar{f}_2 - f_1 f_2][\ln(f_1) + \ln(f_2) - \ln(\bar{f}_1) - \ln(\bar{f}_2)] \quad (16) \\ &= \frac{1}{4} \frac{1}{m} \int d\mathbf{v}_2 d\mathbf{v}_1 d\omega \mathbf{V}[\bar{f}_1 \bar{f}_2 - f_1 f_2][\ln(\frac{f_1 f_2}{\bar{f}_1 \bar{f}_2})] \leq 0 \end{aligned}$$

as the $\ln$ will become negative exactly then, when the term in front of it is positive. In particular, one can also see that H will only stay constant for unchanging distributions.

5.2 H-theorem and entropy

We have now finally proven that the measure H :

$$H = \int d\mathbf{q}d\mathbf{v} \ln(f)f$$

will decrease over time, and only stay constant for a non changing distribution.

This is closely related to entropy, given by:

$$S = -k_b \int d\mathbf{q}d\mathbf{v} \ln(\mathbf{p})\mathbf{p}$$

k_b being the Boltzmann constant.

An alternative, more intuitive definition is given by:

$$S = -k_b \ln(\Omega)$$

stating that the entropy is proportionate to how much we know about the systems exact microstate if given full knowlege of its macrostate

5.3 Solutions to H theorem

We now want to find solutions of

$$\frac{\partial H}{\partial t} = \int d\mathbf{q} d\mathbf{v} \ln(f) J = 0$$

in order to find the stable state of minimum H.

We found stable solutions of A to be Constant, $\mathbf{v}$ and v^2 , therefore:

$$\ln(f) = a + b\mathbf{v} + c\mathbf{v}^2$$

This, with some further considerations, then leads to the Maxwell Boltzmann distribution at equilibrium.

6 Quantum H-theorem

6.1 H-theorem in QIT

We will now look at a newer publication of 2016 about the H theorem in quantum physics [5]

We first define a quantum channel $\Phi(\hat{\rho})$, $\hat{\rho}$ being the density matrix operator of the system, loosely, it is any possible change the system can go through.

Generally, $\Phi(\hat{\rho})$ is trace preserving, as the trace of $\hat{\rho}$ is constant and equal to one, as well as $\Phi(\hat{\rho})$ being positive, as $\hat{\rho}$ is positive definite.

In quantum information theory we define the entropy as

$$S(\hat{\rho}) = -k_b \text{tr}(\hat{\rho} \log(\hat{\rho})) \quad (17)$$

The entropy gain through a channel $\Phi(\hat{\rho})$ is then given as

$$S(\Phi(\hat{\rho})) - S(\hat{\rho}) \geq -k_b \text{tr}(\Phi(\hat{\rho}) \log(\Phi(\hat{1}))) \quad (18)$$

We define a Unital channel as a channel for which $\Phi(\hat{1}) = \hat{1}$. For such a channel the entropy gain is non-negative, as inserting it above leads to $\Delta S \geq \log(1) = 0$

One can therefore state a quantum H-theorem: for a system evolving with a Unital channel, the entropy change is non-negative.

For an N-dimensional Hilbert space, this condition becomes necessary.

We prove this by assuming ΔS to be non-negative.

System of maximal entropy $\frac{1}{N}\hat{1} \rightarrow S(\Phi(\hat{\rho})) = S(\hat{\rho}) \rightarrow \Phi(\hat{\rho}) = \hat{\rho} \rightarrow \Phi(\hat{1}) = \hat{1}$

Where we assumed there to only be one state of maximum entropy, which is proportionate to $\hat{1}$. While for a infinite dimensional space entropy is not continuous, for a finite dimensional one this proves that for a channel with non-diminishing entropy, the channel is Unital.

6.2 Quantum and Classical H-theorem

While in classical physics entropy change is non-negative for isolated systems, quantum entropy doesn't change for isolated systems. Therefore we will look for some kind of notion of a quasi isolated system

This quasi isolation should be without energy exchange, as if entangled to some system with energy exchange, non-negativeness gets broken, for example if prepared in state of maximum entropy $\frac{1}{N} \sum^N |E_n\rangle\langle E_n|$ entropy will decrease with decreasing energy.

We now choose a system that for the given time will be entangled to another system, while having a negligible energy exchange. An example are nuclear spins with degenerate ground states.

We introduce the evolution operator $\hat{U}$ of a grand system comprised of a system and a reservoir. We write this as

$$\hat{U} = \sum |\psi_{j,E}\rangle\langle\psi_{i,E}| s_{ji,E} \hat{F}_{ji,E} \quad (19)$$

$s_{ji,E}$ being the systems transition amplitudes, $\hat{F}_{ji,E}$ being operators acting on the reservoir.

Checking for unitality one finds

$$\Phi_{j,j'}(\hat{1}) - \hat{1}_{j,j'} = \sum_i s_{ji,E} s_{j'i,E}^* \langle [\hat{F}_{j'i}^\dagger \hat{F}_{ji}] \rangle$$

We now restate the quantum H-theorem: Let a quantum system be initially disentangled from a reservoir and it be energy isolated during the evolution. Then for $\sum_i s_{ji,E} s_{j'i,E}^* \langle [\hat{F}_{j'i}^\dagger \hat{F}_{ji}] \rangle = 0$ the resulting quantum channel is unital and the entropy change is non-negative.

6.3 Examples

For above to hold we need either $[\hat{F}_{j'i}^\dagger, \hat{F}_{ji}]$ or more generally $\langle [\hat{F}_{j'i}^\dagger, \hat{F}_{ji}] \rangle$ to be zero

An example of the first case would be quasi elastic scattering of an electron on a phonon bath, an example of the second case is an electron interacting with 3D nuclear spins, with the commutator vanishing on average

7 Recapping and Limitations

7.1 Recapping

The Boltzmann equation is given by:

$$\frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{q}} + \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} = \frac{\partial f}{\partial t_{coll}} \quad (20)$$

and describes the evolution of the 1 particle distribution. The H-theorem states, that the measure H:

$$H = \int d\mathbf{q} d\mathbf{v} \ln(f) f \quad (21)$$

decreases, but doesn't increase with time. For both, the highly debated molecular chaos assumption, or Stosszahlansatz, is made.

Newer applications are considered to this day, as in the quantum H-theorem.

7.2 Limitations

In Boltzmann's theory particles are assumed to be point-like. This is obviously only an approximation, yet one can also derive a similar equation that considers non point-like ones. Also, inelastic collisions might arise due to internal degrees of freedom of the particles.

Lastly, assuming only binary collisions isn't a good approximation for many real world fluids or dense gases.

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