The Boltzmann Equation and H-Theorem

Julian Mayr

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Abstract

In statistical physics, it is usually easiest to describe the properties of a gas if it is either in equilibrium, through thermodynamics, or, if it can be described in a continuous way, through fluid dynamics. For gases not in equilibrium, a description on particle-level would be the best, but becomes too complex due to the high number of parameters. In this summary, an intermediate solution will be derived: The Boltzmann equation, which treats the gas as a mass density function in phase space, with evolution described by diffusion and collisions of particles. It is shown that, making the right assumptions, it can be derived from first principles, and it can be used to find the macroscopic Euler equations. Also, one finds that for a gas not in equilibrium, entropy will always increase, and the final maximum entropy equilibrium state is described by the Maxwell-Boltzmann Distribution.

1 Probability density functions

Assume a gas of N pointlike, identical, classical particles. The assumption of a classical particle, described completely by its six-dimensional phase space vector $\mathbf{x}_i = \begin{bmatrix} \mathbf{q}_i \\ \mathbf{p}_i \end{bmatrix}$, can be justified as a large-N-limit of quantum mechanics (it does obviously not hold for very low temperatures, where Fermi-Dirac and Bose-Einstein statistics take over). One can then

introduce a probability distribution

$$F_N(\{\mathbf{q}\}, \{\mathbf{p}\}, t) \prod_{i=1}^{N} d\mathbf{q}_i d\mathbf{p}_i \tag{1}$$

Where $F_N(\{\mathbf{q}\}, \{\mathbf{p}\}, t)$ is the probability of the system being in the phase space volume $\prod_{i=1}^{N} d\mathbf{q}_i d\mathbf{p}_i$ [1]. It is to be noted that, instead of trying to deterministically describe the time evolution of a gas, an a priori probability distribution is used from the beginning. This does not mean that the theory isn't an exact theory (indeed, it becomes exact in the right limit), but rather that it is a statistical one.

Since the exact phase space position of any particle isn't known, and the particles are indistinguishable, F is symmetric in all arguments $\mathbf{x}_i$. Still, this is a very microscopic theory: For a macroscopic gas, F is dependent on order of 6×10^{23} parameters

2   Liouville's Theorem

One important microscopic theorem that can be proven for these PDF is Liouville's Theorem

$$\frac{dF_N}{dt} = \frac{\partial F_N}{\partial t} + \sum_{i=1}^{N} \left[\frac{\partial F_N}{\partial \mathbf{q_i}} \cdot \dot{\mathbf{q_i}} + \frac{\partial F_N}{\partial \mathbf{p_i}} \cdot \dot{\mathbf{p_i}} \right] = 0 \tag{2}$$

it states that, on a particles path in phase space, the density of phase space points stays constant. It has been found first not by Liouville, but Gibbs [3], who in its derivation used an identity found by Liouville [2].

To prove it, choose an arbitrary volume V in phase space with $\eta_V = \eta \int_V F_N d\mathbf{x}$ particles in it. The number of particles inside of it changes as

$$\frac{\partial \eta_V}{\partial t} = \eta \int_V \frac{\partial F_N}{\partial t} d\mathbf{x} \tag{3}$$

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[1]To make equations more readable, we write $d\mathbf{p}_i = d^3 p$, $d\mathbf{q}_i = d^3 q$, $d\mathbf{x}_i = d^3 p d^3 q$, $\frac{\partial}{\partial \mathbf{q}_i} = \nabla_{q_i}$

It can of course also be described by incoming and outgoing particle flux into the Volume, using a surface integral.

$$\frac{d\eta_V}{dt} = -\eta \int_S dS(\hat{\mathbf{n}} \cdot \dot{\mathbf{x}}) F_N \tag{4}$$

Using Gauss Theorem, this is equal to

$$\frac{d\eta_V}{dt} = -\eta \int_V d\mathbf{x} \nabla_x \cdot (\dot{\mathbf{x}} F_N) \tag{5}$$

Subtracting both equations from each other

$$\frac{\partial F_N}{\partial t} + \nabla (\dot{\mathbf{x}} F_N) \tag{6}$$

$$= \frac{\partial F_N}{\partial t} + \sum_{i=1}^N \left(\frac{\partial F_N}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial F_N}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right) + \sum_{i=1}^N F_N \left(\frac{\partial \dot{\mathbf{p}}_i}{\partial \mathbf{p}_i} + \frac{\partial \dot{\mathbf{q}}_i}{\partial \mathbf{q}_i} \right) = 0 \tag{7}$$

The first two terms are the Liouville equation. The last term is zero, since

$$\frac{\partial \dot{\mathbf{p}}_i}{\partial \mathbf{p}_i} + \frac{\partial \dot{\mathbf{q}}_i}{\partial \mathbf{q}_i} = \frac{\partial H}{\partial \mathbf{q}_i \partial \mathbf{p}_i} - \frac{\partial H}{\partial \mathbf{p}_i \partial \mathbf{q}_i} = 0 \tag{8}$$

What is left is then Liouville's Theorem. It is the basis for deriving the Boltzmann equation.

3   Reduced Probability Density Functions

To convert this microscopic description of a gas into a macroscopic one, one needs to eliminate most degrees of freedom of F_N. One way of doing this would be integrating out all the unneeded variables

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

This naive way in this case is actually pretty efficient, since F_N is symmetric in its parameters. While one would intuitively describe $F_1 d\mathbf{x}_1$ as being the probability of finding particle 1 at

position $\mathbf{x}_1$ in phase space, due to symmetry, one can also describe it as the probability of any other particle at this position. This means F_1 is proportional to a particle density function. A function F_2 would then be a density function which also captures the impact that finding one particle at a position $\mathbf{x}_2$ would have on the a posteriori distribution of another particle $\mathbf{x}_1$. For example, assuming hard shell particles with some finite radius, $F_2(\mathbf{x}_1, \mathbf{x}_1, t) = 0$, since two hard shell particles cannot be in the same position.

4   The Boltzmann Gas Limit (BGL)

As for any other macroscopic statistical theory, the right assumptions are necessary for the Boltzmann equation to be valid. They are quite specific for the Boltzmann equation, since it assumes the existence of binary and no other collisions, with the binary collisions occurring on average every finite time interval τ.

First, assume a macroscopic gas, with particle number N going to infinity. Then, particle mass m and the characteristic force range σ need to be zero to avoid any macroscopic divergences. The important quantities are the constant multiplicatives of these constants. The easier one is

$$Nm = M = \text{const}$$

which just assumes a finite total mass. The less intuitive one is

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

The quantity $\frac{1}{N\sigma^2}$ is proportional to the average free path, which means this assumption results in a finite time between collisions. Had one chosen $N\sigma = const$, the free path would be infinite. The limit is then the one of a Knudsen Gas, a gas so dilute that particles do not collide. On the other hand, $N\sigma^3 = const$ would result in the free path being zero, and many particles constantly interacting, resulting in a very dense fluid. Both of these limits are not

described by the Boltzmann Equation, which can only be proven in the BGL limit.

5   Truncated Reduced PDF

The final piece for the derivation is to focus on binary collisions between particles. While integrating out variables, it is a good idea to define new, truncated reduced distribution functions

$$F_1^\sigma(\mathbf{x}_1, t) = \int_{D_1} d\mathbf{x}_2 \dots d\mathbf{x}_N F_N \tag{9}$$

$$F_2^\sigma(\mathbf{x}_1, \mathbf{x}_2, t) = \int_{D_2} d\mathbf{x}_3 \dots d\mathbf{x}_N F_N \tag{10}$$

with integration limits

$$D_1 = \{\{\mathbf{x}_2, \dots, \mathbf{x}_n\} : |\mathbf{x}_i - \mathbf{x}_1| \geq \sigma, i \in \{2, \dots, N\}\}\} \tag{11}$$

$$D_2 = \{\{\mathbf{x}_3, \dots, \mathbf{x}_n\} : |\mathbf{x}_i - \mathbf{x}_1| \geq \sigma, i \in \{3, \dots, N\}\}\} \tag{12}$$

This means that $F_1^\sigma(\mathbf{x}, t)$ is the probability of particle 1 being at position $\mathbf{x}$ in phase space, with no other particle being in range σ of it, and therefore without any particle interacting with it. F_2 only allows particle 2 being in range σ of particle 1, since they are both free variables.

In the BGL, the error from integrating over these new volumes instead of the original phase space is of order $\sigma \to 0$. Therefore, it doesn't matter which integration limits to choose for the derivation. However, the two truncated functions consider only binary collisions, which results in taking the correct limits naturally, instead of having to find them post derivation.

6 Reduction of the Liouville Equation

It is possible to derive the Boltzmann equation from the Liouville equation by integrating over all variables except $\mathbf{x_1}$, thereby reducing the microscopic probability density function to a macroscopic particle density function, and the microscopic Liouville equation to the kinetic Boltzmann equation.

$$\int_{D_1} d\mathbf{x}_2 \ldots d\mathbf{x}_N \left(\underbrace{\frac{\partial F_N}{\partial t}}_{\text{Part 1}} + \sum_{i=1}^{N} \left[\underbrace{\frac{\partial F_N}{\partial \mathbf{q_i}} \cdot \dot{\mathbf{q}}_{\mathbf{i}}}_{\text{Part 2}} + \underbrace{\frac{\partial F_N}{\partial \mathbf{p_i}} \cdot \dot{\mathbf{p}}_{\mathbf{i}}}_{\text{Part 3}} \right] \right) = 0 \tag{13}$$

Since this is a rather long calculation, we will calculate the integral over each of the 3 parts separately.

6.1 Part 1

This is the easiest part of the calculation, since the derivative $\frac{\partial}{\partial t}$ commutes with the integral

$$\int_{D_1} d\mathbf{x}_2 \ldots d\mathbf{x}_N \frac{\partial F_N}{\partial t} = \frac{\partial}{\partial t} \int_{D_1} d\mathbf{x}_2 \ldots d\mathbf{x}_N F_N \tag{14}$$

$$= \frac{\partial F_1^{\sigma}}{\partial t} \tag{15}$$

6.2 Part 2

The term

$$\int_{D_1} d\mathbf{x}_2 \ldots d\mathbf{x}_N \sum_{i=1}^{N} \left[\frac{\partial F_N}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right] \tag{16}$$

can be further separated into

$$\int_{D_1} d\mathbf{x}_2 \ldots d\mathbf{x}_N \sum_{i=2}^{N} \left[\frac{\partial F_N}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right] \tag{17}$$

$$+ \int_{D_1} d\mathbf{x}_2 \ldots d\mathbf{x}_N \left[\frac{\partial F_N}{\partial \mathbf{q}_1} \cdot \dot{\mathbf{q}}_1 \right] \tag{18}$$

These terms have to be treated differently, since $\mathbf{q}_1$ is not part of the integration, while $\mathbf{q}_2, \ldots, \mathbf{q}_N$ are.

The first part can be solved by partial integration for each element of the sum over $\mathbf{q}_i$.

$$\int_{D_1} d\mathbf{x}_2 \ldots d\mathbf{x}_N \sum_{i=2}^{N} \left[\frac{\partial F_N}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right] \tag{19}$$

$$= - \int_{D_1} d\mathbf{x}_2 \ldots d\mathbf{x}_N \sum_{i=2}^{N} \mathbf{q}_i F_N \dot{\mathbf{q}}_i + \left[\sum_{i=2}^{N} \int_{D_1} d\mathbf{x}_2 \ldots d\bar{\mathbf{x}}_i \ldots d\mathbf{x}_N F_N \dot{\mathbf{q}}_i \right]_{\mathbf{x}_i(D_1)} \tag{20}$$

with $\bar{\mathbf{x}}_i$ not being integrated over. By analyzing boundary behavior, it can be seen that the first term vanishes: The probability of infinite momenta is zero, so F_N vanishes at that boundary. Considering a system confined in a box large enough that boundary terms do not play a role, but not infinitely large, F_N will also vanish at infinite $\mathbf{q}_i$. Terms on the other integration boundary, the sphere around $\mathbf{q}_1$ are proportional to its size $\sigma \to 0$.

The second term can be reduced due to the indistinguishability of particles

$$\left[\sum_{i=2}^{N} \int_{D_1} d\mathbf{x}_2 \ldots d\bar{\mathbf{x}}_i \ldots d\mathbf{x}_N F_N \dot{\mathbf{q}}_i \right]_{\mathbf{x}_i(D_1)} = (N-1) \left[\int_{D_2} d\mathbf{x}_3 \ldots d\mathbf{x}_N F_N \dot{\mathbf{q}}_2 \right]_{\mathbf{x}_2(D_1)} \tag{21}$$

Since F_N vanishes at infinity, evaluation of $\mathbf{x}_2$ on D_1 yields only a surface integral over the sphere S_2 around $\mathbf{q}_1$.

$$(N-1) \left[\int_{D_2} d\mathbf{x}_3 \ldots d\mathbf{x}_N F_N \dot{\mathbf{q}}_2 \right]_{\mathbf{x}_2(D_1)} = -(N-1) \left[\int dS_2 d\mathbf{p}_2 \int_{D_2} d\mathbf{x}_3 \ldots d\mathbf{x}_N F_N \dot{\mathbf{q}}_2 \right] \tag{22}$$

$$= -(N-1) \int dS_2 d\mathbf{v}_2 \mathbf{v}_2 F_2^{\sigma}(\mathbf{x}_1, \mathbf{x}_2, t) \tag{23}$$

This is the first boundary term resulting from the truncated phase space.

In equation 18, one cannot simply pull out the derivative from the integral, since, due to the truncated phase space, the other coordinates x_i are actually dependent on x_1. This is easier seen rewriting the integration as

$$\int_{D_1} d\mathbf{x}_2 \dots d\mathbf{x}_N \left[\frac{\partial F_N}{\partial \mathbf{q}_1} \cdot \dot{\mathbf{q}}_1 \right] = \int d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{i=2}^{N} \left[\Theta(|\mathbf{q}_i - \mathbf{q}_1| - \sigma) \right] \frac{\partial F_N}{\partial \mathbf{q}_1} \cdot \dot{\mathbf{q}}_1 \qquad (24)$$

rewriting the truncation of the phase space using Heaviside step functions Θ. Pulling out the derivative, derivatives of the Θ resulting from the product rule need to be subtracted.

$$\int d\mathbf{x}_2 \dots d\mathbf{x}_N \prod_{i=2}^{N} \left[\Theta(|\mathbf{q}_i - \mathbf{q}_1| - \sigma) \right] \frac{\partial F_N}{\partial \mathbf{q}_1} \cdot \dot{\mathbf{q}}_1 \qquad (25)$$

$$= \dot{\mathbf{q}}_1 \frac{\partial}{\partial \mathbf{q}_1} \int d\mathbf{x}_2 \dots d\mathbf{x}_N \prod_{i=2}^{N} \left[\Theta(|\mathbf{q}_i - \dot{\mathbf{q}}_1| - \sigma) \right] F_N \qquad (26)$$

$$- \dot{\mathbf{q}}_1 \int d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{i=2}^{N} \left[\frac{\partial \Theta(|\mathbf{q}_i - \mathbf{q}_1| - \sigma)}{\partial \mathbf{q}_1} \prod_{j=2 \neq i}^{N} \Theta(|\mathbf{q}_j - \mathbf{q}_1| - \sigma) \right] F_N \qquad (27)$$

$$= \dot{\mathbf{q}}_1 \frac{\partial F_1^\sigma}{\partial \mathbf{q}_1} - \dot{\mathbf{q}}_1 (N-1) \int d\mathbf{x}_2 \dots d\mathbf{x}_N \delta(|\mathbf{q}_2 - \mathbf{q}_1| - \sigma) \prod_{i=3}^{N} \Theta(|\mathbf{q}_i - \mathbf{q}_1| - \sigma) F_N \qquad (28)$$

$$= \dot{\mathbf{q}}_1 \frac{\partial F_1^\sigma}{\partial \mathbf{q}_1} + \dot{\mathbf{q}}_1 \int dS_2 d\mathbf{p}_2 \int_{D_2} d\mathbf{x}_3 \dots d\mathbf{x}_N F_N \qquad (29)$$

$$= \dot{\mathbf{q}}_1 \frac{\partial F_1^\sigma}{\partial \mathbf{q}_1} + \dot{\mathbf{q}}_1 \int dS_2 d\mathbf{p}_2 F_2^\sigma \qquad (30)$$

where again, the parameter symmetry of F_N was used to convert $\mathbf{x}_1, \mathbf{x}_2$ into the only free variables. The δ-function fixes one degree of freedom in the $\mathbf{x}_2$ integration and only leaves the momentum and sphere integral. Putting the terms together, and replacing momentum $\mathbf{p}$ with velocity $\mathbf{v} = \dot{\mathbf{q}}$

$$\int_{D_1} d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{i=1}^{N} \left[\frac{\partial F_N}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right] = \dot{\mathbf{v}}_1 \frac{\partial F_1^\sigma}{\partial \mathbf{q}_1} + \int dS_2 d\mathbf{v}_2 (\mathbf{v}_1 - \mathbf{v}_2) F_2^\sigma \qquad (31)$$

It is interesting to see how the boundary terms end up summing up symmetrically in this way.

6.3 Part 3

In Part 3

$$\int_{D_1} d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{i=2}^{N} \left[\frac{\partial F_N}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i \right] \tag{32}$$

the term $\dot{\mathbf{p}}_i$ is a force. Disregarding external fields, all forces acting onto particle i stem from the potentials of the other particles. Therefore, $\dot{\mathbf{p}}_i$ can be rewritten as a sum over potentials ϕ_{ij}

$$\dot{\mathbf{p}}_i = \sum_{j=1 \neq i}^{N} \frac{\partial \phi_{ij}}{\partial \mathbf{q}_j} \tag{33}$$

and the integral as

$$\int_{D_1} d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{i,j=1}^{N} \left[\frac{\partial F_N}{\partial \mathbf{p}_i} \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \right] \tag{34}$$

with $\phi_{ii} = 0$, which separates into

$$\int_{D_1} d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{i=2,j=1}^{N} \left[\frac{\partial F_N}{\partial \mathbf{p}_i} \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \right] + \int_{D_1} d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{j=2}^{N} \left[\frac{\partial F_N}{\partial \mathbf{p}_1} \frac{\partial \phi_{1j}}{\partial \mathbf{q}_1} \right] \tag{35}$$

After partial integration, the first term vanishes similar to eq. 20, but without boundary terms. In D_1, every particle is at least σ away from the first one, and therefore out of its potential. Therefore, all ϕ_{1j} and their derivatives disappear in the integration limits. Therefore

$$\int_{D_1} d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{i=2}^{N} \left[\frac{\partial F_N}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i \right] = 0 \tag{36}$$
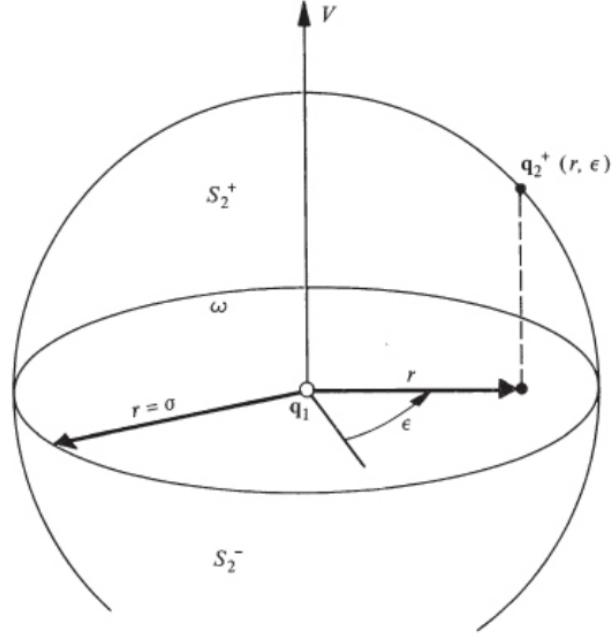
Figure 1: The double cover projection from the disk of a sphere onto its surface. Adapted from Steward Harris - An introduction to the history of the Boltzmann equation (2012)

7 The Boltzmann equation

Putting all the parts together

$$\frac{\partial F_1^\sigma}{\partial t} + \dot{\mathbf{q}}_1 \frac{\partial F_1^\sigma}{\partial \mathbf{q}_1} = (N-1) \int dS_2 d\mathbf{v}_2 (\mathbf{v}_2 - \mathbf{v}_1) F_2^\sigma \tag{37}$$

The left hand side looks very much like the Boltzmann equation's diffusion term already. To transform the right hand side into the collision term, first, the sphere integral is converted into a disk integral. This is done by realizing the sphere is a double cover of the disk (See Fig 1), projecting onto coordinates $\mathbf{x}^+$ (top half of the sphere) and $\mathbf{x}^-$ (bottom half of the sphere), to rewrite the integral term as

$$\int dS_2 d\mathbf{v}_2 (\mathbf{v}_2 - \mathbf{v}_1) F_2^\sigma = (N-1) \int d\omega d v_2 |\mathbf{v}_2 - \mathbf{v}_1| \left[F_2^\sigma(\mathbf{x}_1, \mathbf{x}_2^+, t) - F_2^\sigma(\mathbf{x}_1, \mathbf{x}_2^-, t) \right] \tag{38}$$

with $d\omega$ being the disk area element. Now, some assumptions need to be made to transform the RHS. First, drop the index σ, which is allowed in the BGL, as explained earlier.

$$\int dS_2 d\mathbf{v}_2 (\mathbf{v}_2 - \mathbf{v}_1) F_2 = (N-1) \int d\omega dv_2 |\mathbf{v}_2 - \mathbf{v}_1| \left[F_2(\mathbf{x}_1, \mathbf{x}_2^+, t) - F_2(\mathbf{x}_1, \mathbf{x}_2^-, t) \right] \quad (39)$$

Next, particles $\mathbf{x}_1$ and $\mathbf{x}_2^+$ should be uncorrelated. Since $\mathbf{x}_1$, $\mathbf{x}_2^+$ describe post collision particles, they needs to be replaced by their most recent pre-collision phases $\mathbf{X}_1$, $\mathbf{X}_2$ at time $t - \tau$

$$F_2(\mathbf{x}_1, \mathbf{x}_2^+, t) \approx F_2(\mathbf{X}_1, \mathbf{X}_2, t - \tau) \quad (40)$$

This is justified by considering that, in the small time τ particles 1 and 2 only interact with each other. The two particle Liouville equation is therefore a good approximation on this interval, and its solution is just $F_2 = const$.

Now, the famous *Stosszahlansatz* is used.

$$F_2(\mathbf{x}_1, \mathbf{x}_2^-, t) = F_1(\mathbf{x}_1, t) F_1(\mathbf{x}_2^-, t) \quad (41)$$

$$F_2(\mathbf{X}_1, \mathbf{X}_2, t - \tau) = F_1(\mathbf{X}_1, t - \tau) F_1(\mathbf{X}_2, t - \tau) \quad (42)$$

It states that the phase of particle 1 and 2 is uncorrelated, since they haven't collided before. This is exact in the BGL, where the error is of order $1/N = 0$, and assuming particles collide with random other particles. In reality, particles will "forget" about each other after a few collisions, and will lose their explicit phase dependence.

Finally, the approximations

$$N - 1 \approx N \quad (43)$$

$$\tau \propto \sigma = 0 \quad (44)$$

$$\mathbf{X}_1 = \mathbf{X}_2 = \mathbf{x}_2 = \mathbf{x}_1 \text{ with error} \propto \sigma \quad (45)$$

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are made, relative velocity $V = |\mathbf{v}_2 - \mathbf{v}_1|$ and mass density function $f(\mathbf{x}, t) = NmF(\mathbf{x}, t)$ are introduced. The Boltzmann equation is then found as

$$\frac{\partial f}{\partial t} + \mathbf{v}_1 \frac{\partial f}{\partial \mathbf{q}} = \frac{1}{m} \int d\omega d\mathbf{v}_2 V \left[f(\mathbf{q}, \bar{\mathbf{v}}_1, t) f(\mathbf{q}, \bar{\mathbf{v}}_2, t) - f(\mathbf{q}, \mathbf{v}_1, t) f(\mathbf{q}, \mathbf{v}_2, t) \right] \qquad (46)$$

The LHS is called the diffusion term, and corresponds to the movement of free, non colliding particles. The RHS, from now on called $J(f)$, is the collision term, and describes particles with velocities $\mathbf{v}_1 . \mathbf{v}_2$ at location q colliding into new post collision velocities $\bar{\mathbf{v}}_1, \bar{\mathbf{v}}_2$. This point of view was what Boltzmann used to derive his equation heuristically, instead of formally from the Liouville equation as done here. Through analysis of two particle collisions, one often sees the disk integral replaced by a cross section term $B(\theta, \phi)$

$$J(f) = \frac{1}{m} \int dr d\phi d\mathbf{v}_2 V \left[f(\mathbf{q}, \bar{\mathbf{v}}_1, t) f(\mathbf{q}, \bar{\mathbf{v}}_2, t) - f(\mathbf{q}, \mathbf{v}_1, t) f(\mathbf{q}, \mathbf{v}_2, t) \right] \qquad (47)$$

$$= \frac{1}{m} \int \frac{\partial r(\theta, \phi)}{\partial \theta} d\theta d\phi d\mathbf{v}_2 V \left[f(\mathbf{q}, \bar{\mathbf{v}}_1, t) f(\mathbf{q}, \bar{\mathbf{v}}_2, t) - f(\mathbf{q}, \mathbf{v}_1, t) f(\mathbf{q}, \mathbf{v}_2, t) \right] \qquad (48)$$

$$= \frac{1}{m} \int B(\theta, \phi) d\theta d\phi d\mathbf{v}_2 \left[f(\mathbf{q}, \bar{\mathbf{v}}_1, t) f(\mathbf{q}, \bar{\mathbf{v}}_2, t) - f(\mathbf{q}, \mathbf{v}_1, t) f(\mathbf{q}, \mathbf{v}_2, t) \right] \qquad (49)$$

Where the deflection angle during a collision is quantified by $\pi - 2\theta$.

On the left hand side, a force term, corresponding to an external field, is added. This could have been derived in eq. 33, by adding the external field to the binary force terms. It however doesn't add anything interesting in this summary, so it is omitted.

7.1 Symmetries

For further calculations, the symmetries of the collision term are important. Integrating over $\int d\mathbf{v}_1 J(f(\mathbf{x}_1, t)) \psi(\mathbf{v}_1)$, with ψ being any function of v_1, the term becomes

$$\int d\mathbf{v}_1 J(f(\mathbf{x}_1, t)) \psi(\mathbf{v}_1) = \int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f(\mathbf{q}, \bar{\mathbf{v}}_1, t) f(\mathbf{q}, \bar{\mathbf{v}}_2, t) - f(\mathbf{q}, \mathbf{v}_1, t) f(\mathbf{q}, \mathbf{v}_2, t) \right] \psi(\mathbf{v}_1)$$

$$(50)$$

Introducing the new notation

$$f_1' = f(\mathbf{q}, \bar{\mathbf{v}}_1, t) \tag{51}$$

$$f_2' = f(\mathbf{q}, \bar{\mathbf{v}}_2, t) \tag{52}$$

$$f_1 = f(\mathbf{q}, \mathbf{v}_1, t) \tag{53}$$

$$f_2 = f(\mathbf{q}, \mathbf{v}_2, t) \tag{54}$$

the integral is symmetric in $\mathbf{v}_1$ and $\mathbf{v}_2$ and therefore, one can exchange

$$\int d\mathbf{v}_1 J(f_1)\psi(\mathbf{v}_1) = \int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1' f_2' - f_1 f_2\right] \psi(\mathbf{v}_1) \tag{55}$$

$$= \int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1' f_2' - f_1 f_2\right] \psi(\mathbf{v}_2) \tag{56}$$

Through variable substitution, one can also find

$$\int d\mathbf{v}_1 J(f_1)\psi(\mathbf{v}_1) = \int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1' f_2' - f_1 f_2\right] \psi(\mathbf{v}_1) \tag{57}$$

$$= -\int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1' f_2' - f_1 f_2\right] \psi(\bar{\mathbf{v}}_1) \tag{58}$$

$$= -\int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1' f_2' - f_1 f_2\right] \psi(\bar{\mathbf{v}}_2) \tag{59}$$

Putting everything together, the final symmetry is

$$\int d\mathbf{v}_1 J(f_1)\psi(\mathbf{v}_1) = \frac{1}{4} \int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1' f_2' - f_1 f_2\right] \left(\psi(\mathbf{v}_1) + \psi(\mathbf{v}_2) - \psi(\bar{\mathbf{v}}_1) - \psi(\bar{\mathbf{v}}_2)\right) \tag{60}$$

This symmetry produces some obvious invariants of the collision term integral setting $\psi(\mathbf{v}_1) = 1$, one finds

$$\int d\mathbf{v}_1 J(f_1) = \frac{1}{4} \int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1' f_2' - f_1 f_2\right] (1 + 1 - 1 - 1) = 0 \tag{61}$$

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Plugging in $\psi(\mathbf{v}_1) = \mathbf{v}_1$ or $\psi(\mathbf{v}_1) = \mathbf{v}_1^2$, one also finds

$$\int d\mathbf{v}_1 J(f_1)\mathbf{v}_1 = \frac{1}{4}\int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1'f_2' - f_1 f_2\right](\mathbf{v}_1 + \mathbf{v}_2 - \bar{\mathbf{v}}_1 - \bar{\mathbf{v}}_2) = 0 \qquad (62)$$

$$\int d\mathbf{v}_1 J(f_1)\mathbf{v}_1^2 = \frac{1}{4}\int d\theta d\phi d\mathbf{v}_1 d\mathbf{v}_2 \left[f_1'f_2' - f_1 f_2\right]\left(\mathbf{v}_1^2 + \mathbf{v}_2^2 - \bar{\mathbf{v}}_1^2 - \bar{\mathbf{v}}_2^2\right) = 0 \qquad (63)$$

$$(64)$$

due to momentum and energy conservation (assuming all identical mass particles, as before). These are not only some obvious eigenvalue zero eigenfunctions of the operator $\int d\mathbf{v}_1 J(\mathbf{v}_1)$, but one can also show (see [5]) that these are the *only* eigenfunctions with eigenvalue zero.

8   The H-Theorem and the Maxwell Distribution

The Boltzmann equation is a monstrously complex equation: It is partial differential in two variables and integral in another two. Indeed, only 50 years after its first publication by Boltzmann, a first approximate solution was found. However, even without being solved, it provides a lot of information about the time evolution of gases. One of the most prominent ones is the H-Theorem, which states that the entropy of any Boltzmann gas will increase with time and the gas will reach the maximum entropy state, which is described by the Maxwell-Boltzmann distribution.

The quantity H is defined as

$$H = \int d\mathbf{v}_1 f \ln f \qquad (65)$$

It is directly proportional to the negative entropy of a gas. The second law of thermodynamics can easily be proven for a uniform gas $f(\mathbf{q}, \mathbf{v}, t) = \rho f(\mathbf{v}, t)$. It is also possible for a non-uniform gas, but this prove is out of scope for this summary. Calculating the time derivative

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of H, one finds

$$\frac{\partial H}{\partial t} = \int d\mathbf{v}_1 \left[\frac{\partial f_1}{\partial t} \ln f_1 + \frac{\partial f_1}{\partial t} \frac{f_1}{f_1} \right] \tag{66}$$

$$= \int d\mathbf{v}_1 J(f) \ln f_1 \tag{67}$$

The term $\frac{\partial f}{\partial t}$ is equal to $J(f_1)$ since the other LHS term in the Boltzmann equation vanishes for a uniform gas. The term $\int d\mathbf{v}_1 \frac{\partial f}{\partial t} = \int d\mathbf{v}_1 J(f_1) = 0$ as seen in eq 61. Using the symmetry from eq. 60, this transforms to

$$\frac{\partial H}{\partial t} = \int d\mathbf{v}_1 d\mathbf{v}_2 d\theta d\phi \left[f_1' f_2' - f_1 f_2 \right] (\ln f_1 + \ln f_2 - \ln f_1' - \ln f_2') \tag{68}$$

$$= -\int d\mathbf{v}_1 d\mathbf{v}_2 d\theta d\phi \left[f_1 f_2 - f_1' f_2' \right] \ln \frac{f_1 f_2}{f_1' f_2'} \leq 0 \tag{69}$$

since the sign of the term in brackets is always the same as the sign of the logarithm. This means H is always decreasing (and therefore, entropy is always increasing). H cannot diverge to negative infinity, as it is bounded from below (See Fig 2). This means H must eventually arrive at an equlibrium state where $\frac{\partial H}{\partial t} = 0$. At equilibrium

$$\int d\mathbf{v}_2 J(f) \ln f_1 = 0 \tag{70}$$

As stated before, this integral has only three functions for which it vanishes, 1, $\mathbf{v}_1$ and $\mathbf{v}^2$. Therefore, $\ln f_1$ must be a linear combination

$$\ln f_1 = A + \mathbf{B}\mathbf{v} + C\mathbf{v}^2 \tag{71}$$

These parameters A, B, C are not arbitrary, but determined by the macroscopic invariants density $\rho = \int d\mathbf{v} f(\mathbf{q}, \mathbf{v}, t)$, average momentum $u = \int d\mathbf{v}\mathbf{v} f(\mathbf{q}, \mathbf{v}, t)$ and energy density $E = \int d\mathbf{v}\mathbf{v}^2 f(\mathbf{q}, \mathbf{v}, t)$. For a uniform gas, u will not be position dependent and is therefore 0 in a
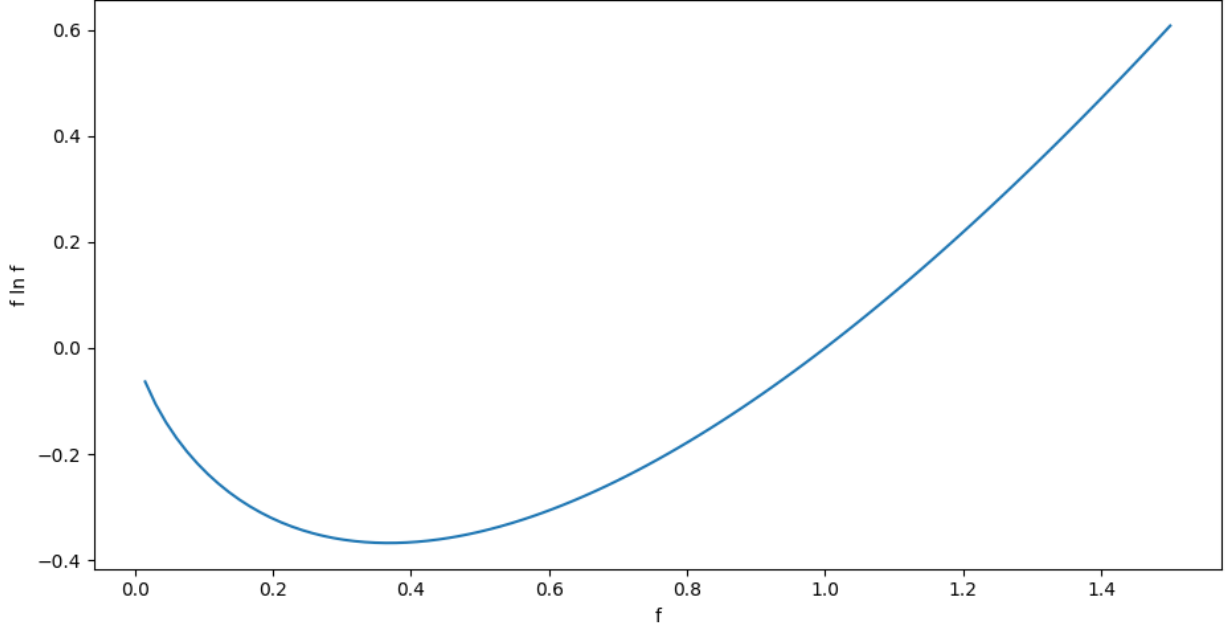
Figure 2: The function H cannot diverge to negative infinity, since $f \ln f$ is bounded from below, and becomes 0 at $f = 0$, which is the boundary condition

center of mass frame. In this frame, one can then write

$$f = A' \exp\left(C\mathbf{v}^2\right) \tag{72}$$

This just leaves C as a free parameter, which then determines normalization factor A'. Knowing the root mean squared velocity $v_{RMS} = \sqrt{\frac{kT}{m}}$ with Boltzmann constant k, Temperature T, which can be derived from the equipartition theorem, one can then plug this into eq. 72 as the variance of the Gaussian, normalize and find

$$f_M(\mathbf{v})d\mathbf{v} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{\mathbf{v}^2 m}{2kT}\right) d\mathbf{v} \tag{73}$$

This is the famous Maxwell-Boltzmann distribution for three dimensions (for a d-dimensional gas, the exponent of the normalization factor changes to $d/2$). It describes the equilibrium probability density for the velocity of a gas of classical particles. Of course, it is known today that, especially for low temperatures, this distribution ceases to be accurate due to

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quantum effects and has to be replaced by the Bose-Einstein distribution for bosons, or the Fermi-Dirac distribution for fermions. Nevertheless, at room temperature, the Maxwell distribution describes gases very accurately.

9   Hydrodynamic equations

The zero-value eigenfunctions of the collision integral also allow integrating over both sides of the Boltzmann equation, letting the collision term vanish, and getting a new, differential and not integral, equation for each function. The easiest one to find is the integral over $\int d\mathbf{v}m$. One finds

$$\int d\mathbf{v}m \left[\frac{\partial f(\mathbf{q}, \mathbf{v}, t)}{\partial t} + \mathbf{v} \frac{\partial f(\mathbf{q}, \mathbf{v}, t)}{\partial \mathbf{q}} \right] = \frac{\partial \rho}{\partial t} + \frac{\partial (\rho \mathbf{u})}{\partial \mathbf{q}} = 0 \tag{74}$$

where after partial integration over the second term, this is the continuity equation for a fluid with average velocity $\mathbf{u}(\mathbf{q})$. A more advanced integration, which will not be explicitly done, yields results for the $\int d\mathbf{v}m\mathbf{v}$ and $\int d\mathbf{v}m\mathbf{v}^2$ integrals.

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = \mathbf{g} - \frac{1}{\rho}\nabla P + \frac{1}{\rho}\nabla \cdot \pi \tag{75}$$

$$\frac{\partial \epsilon}{\partial t} + \mathbf{u} \cdot \nabla \epsilon = -\frac{P}{\rho}\nabla \cdot \mathbf{u} - \frac{1}{\rho}\nabla \cdot \mathbf{F} + \frac{1}{\rho}\Psi \tag{76}$$

with $\mathbf{u}$ mean fluid velocity, ω particle random velocity, ρ density, $P = \frac{1}{3}\rho\langle|w|^2\rangle$ pressure, $\pi_{ij} = P\delta_{ij} - \rho\langle\omega_i\omega_j\rangle$ stress tensor, $\epsilon = \frac{1}{2}\rho\langle|\omega|^2\rangle$ specific internal energy, $\mathbf{F} = \frac{1}{2}\rho\langle\omega|\omega|^2\rangle$ conduction heat flux, $\Psi = \sum_{i,j} \pi_{ij}\frac{\partial u_i}{\partial x_j}$ viscous dissipation rate. These are sometimes called the "Navier-Stokes-equations", although they do not resemble the Navier-Stokes-equation exactly and its derivation from these is rather cumbersome. Since these are 5 equations with a total of 13 degrees of freedom, the derivation of hydrodynamic equations will always involve the fixing of some terms to transform these into a complete description of a fluid. An

easy example are the Euler equations, which can be derived by dropping the diffuse terms

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{77}$$

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = \mathbf{g} - \frac{1}{\rho}\nabla P \tag{78}$$

$$\frac{\partial \epsilon}{\partial t} + \mathbf{u} \cdot \nabla \epsilon = -\frac{P}{\rho}\nabla \cdot \mathbf{u} \tag{79}$$

These equations describe adiabatic, non-viscous flow. We have now gone from a microscopic description through the Liouville and Hamiltonian equations, to a kinetic Boltzmann equation, which treats the particle density function with a diffusion and a gain and loss collision term, to a final, macroscopic description, treating the particle density as a continuous Newtonian fluid. Each step, one makes approximations and loses information, but gains easier solvability.

10 Quantum analogues

The Boltzmann equation was explicitly derived for a gas of classically behaving particles. Quantum versions (mostly semiclassical, adding a Pauli blocking or density of states term) of the equation exist, and have been shown to describe heavy-ion-collisions [1] and semiconductors [7]. A quantum H-Theorem is more difficult to propose. One might make the semiclassical approach by modifying the derivation of the Maxwell-Distribution, to find the Fermi-Dirac or Bose-Einstein distribution instead [4]. For a general quantum system, these methods will not work. Instead, for a fully quantum version, one needs to introduce the density matrix

$$\rho = |\psi\rangle\langle\psi| \tag{80}$$

for a pure quantum state psi. The density matrix formalism the advantage of being able to describe probability distributions over quantum states and separating them from superpositions, by introducing impure states, with the purity defined by the off-diagonal *coherences*,

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and the measurement probabilities described by the diagonal elements. Entropy for these states is defined by the von-Neumann entropy

$$S = -\operatorname{tr}\rho\ln\rho \tag{81}$$

For a completely decoherent state, the density matrix becomes diagonal and one recovers the classical definition of entropy

$$H = -\sum_i p_i \log p_i \tag{82}$$

For a pure state, the entropy is always zero. When looking for an H-Theorem, one runs into the problem that, under standard unitary time evolution

$$S(U\rho U^\dagger) = S(U) \tag{83}$$

This can be solved by looking at a subsystem S interacting with an environment E. The density matrix of the system ρ_S is then defined by the partial trace

$$\rho_S = \operatorname{tr}_E \rho \tag{84}$$

where ρ is the full density matrix. The evolution of the system density matrix is then not unitary, but described by *quantum channels*, completely positive trace preserving maps between density matrices.

For a general environment, the H-Theorem can obviously not hold, since a warm system inside a cold environment would decrease in entropy. One has to make the assumption of negligible total energy exchange, such that only entanglement with the environment changes the systems state.

A special kind of quantum channel are unital channels ϕ for which $\phi(\mathbb{1}) = \mathbb{1}$. The state $\mathbb{1}$,

the identity matrix, is the maximum chaotic, and completely decoherent quantum state.

An H-Theorem can then be formulated as follows: *The entropy gain during evolution is nonnegative if the system evolution can be described by the unital channel* [6].

A problem with this definition is that it is in some way circular: A map with a fixed point $\mathbb{1}$ will in most cases converge to this fixed point. However, it is a practical definition: A lot of real-life quantum channels, such as dephasing and bit flips, leave the identity invariant. This formulation of the H-Theorem therefore, in most cases, does describe the thermalization of open quantum systems.

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