A.2 About Boltzmann equation

We review and summarize some of the properties of Boltzmann equation used in chapter 3, and present two of the historical paradoxes associated to the H-theorem to illustrate the complexity of the relaxation problem. For a more detailed presentation, see for instance [Pottier 2007].

A.2.1 Collisionless Boltzmann equation

We consider a dilute gas of N neutral atoms, which we assume to be described at time t by a distribution $f(\mathbf{r}, \mathbf{p}, t)$, not necessarily the equilibrium function. $f(\mathbf{r}, \mathbf{p}, t)\, d\mathbf{r}d\mathbf{p}$ gives the probability to find at time t a particle in volume $d\mathbf{r}$ around $\mathbf{r}$ with a momentum as close as $d\mathbf{p}$ from $\mathbf{p}$.

Liouville theorem states that the distribution function is constant along any trajectory in phase space. In absence of interactions between particles, it simply corresponds to particle conservations: the number of particles in the phase-space volume $d\mathbf{r}'d\mathbf{p}'$ around $(\mathbf{r}', \mathbf{p}')$ at time t' used to be in the phase-space volume $d\mathbf{r}d\mathbf{p}$ around $(\mathbf{r}, \mathbf{p})$ at time t, provided that

$$\partial_t \mathbf{r}(t) = \mathbf{p}(t)/m, \tag{A.16a}$$

$$\partial_t \mathbf{p}(t) = \mathbf{F}(\mathbf{r}(t)), \tag{A.16b}$$

where $\mathbf{F} = -\partial_{\mathbf{r}} U$ is the outer potential exerted on the atoms.

In terms of distribution function, Liouville theorem can be written as $f(\mathbf{r}', \mathbf{p}', t')\, d\mathbf{r}'d\mathbf{p}' = f(\mathbf{r}, \mathbf{p}, t)\, d\mathbf{r}d\mathbf{p}$, which we can express as

$$\left(\partial_t + \frac{\mathbf{p}}{m}\partial_{\mathbf{r}} + \mathbf{F}\partial_{\mathbf{p}}\right) f = 0, \tag{A.17}$$

and we introduce the Liouville operator $\mathcal{L}$ such that $\partial_t f = -\mathcal{L} f$:

$$\mathcal{L} = \frac{\mathbf{p}}{m}.\nabla_{\mathbf{r}} + \mathbf{F}.\nabla_{\mathbf{p}} \tag{A.18}$$

Equilibrium distribution

Starting from given initial conditions, it is almost impossible to predict from the previous equations the steady state that the system is going to reach. On the other hand, it is straightforward to verify that a Boltzmann distribution f_0 define as:

$$f_0(\mathbf{r}, \mathbf{p}) = \frac{N}{(2\pi\hbar)^3} \frac{\lambda_{dB}}{V_e} \exp\left(-\beta\left(\frac{p^2}{2m} + U(\mathbf{r})\right)\right), \tag{A.19}$$

where $V_e = \int d\mathbf{r} \exp\left(-\beta U(\mathbf{r})\right)$ is the effective volume occupied by the gas, is an stationary solution of the collisionless Boltzmann equation (A.17).

Considering a kinetic definition of the temperature as the standard deviation of the momentum distribution, we identify $\beta = (k_B T)^{-1}$ for the Boltzmann distribution (A.19). Remarkably, f_0 is completely defined by this single scalar parameter T, which implies that any physical quantity can be expressed as a function of the temperature. This is not the case for all solutions to the Boltzmann equation, and a steady state distribution can require more than one parameter.

The Boltzmann distribution plays a crucial role in the kinetic theory of gases and we introduce two properties of the Liouville operator that are useful to derive the results presented in this manuscript

- $\mathcal{L}[f_0] = 0$, since Boltzmann's distribution is a stationary solution of Boltzmann's equation.
- $\mathcal{L}$ is antisymmetric for the scalar product, ie $\langle \alpha | \mathcal{L}[\beta] \rangle = -\langle \mathcal{L}[\alpha] | \beta \rangle$ with

$$\langle \alpha | \beta \rangle = \int d\mathbf{r} d\mathbf{q} \, f_0 \alpha \beta \tag{A.20}$$

A.2.2 H theorem

General formulation of the Boltzmann equation

If interactions cannot be neglected between atoms, Liouville theorem still applies for the N particles distribution function. Several strategies can be considered to estimate the marginal single particle distribution. The BBGKY hierarchy treats the problem iteratively, expressing the single particle distribution as the solution of an equation involving the two-particles distribution and so on. The Vlasov equation corresponds to a mean field treatment of the second order of the BBGKY development and serves as framework for most of plasma physics.

Boltzmann approach relies on a series of simplifications:

- Only binary collisions are taken into account. This supposes that the gas is dilute enough for three-body events to be extremely rare.
- All collisions are considered as elastic and no internal degrees of freedom are changed. Most of the time, the interactions are treated as independent of the energy of the particles.
- All collisions are micro-reversible: the probability for two colliding atoms with momentum $\mathbf{p}_1$ and $\mathbf{p}_2$ to emerge from the collision with momentum $\mathbf{p}_1'$ and $\mathbf{p}_2'$ is the same as the probability of the reverse process.

- The *Stosszahlansatz*, or pre-collisional chaos, is probably the strongest hypothesis as it supposes that, before their interaction, the two particles are completely uncorrelated.

Under those conditions, the time evolution of the distribution function can be expressed as

$$\left(\partial_t + \frac{\mathbf{p}}{m}\partial_{\mathbf{r}} + \mathbf{F}\partial_{\mathbf{p}}\right) f = \left(\frac{\partial f}{\partial t}\right)_{\text{collisions}}, \tag{A.21}$$

where the collision term takes the form

$$\left(\frac{\partial f}{\partial t}\right)_{\text{collisions}} = \int d\mathbf{q} \int d\Omega\, \sigma\left(\mathbf{p}, \mathbf{q}, \Omega\right) \left|\frac{\mathbf{p}}{m} - \frac{\mathbf{q}}{m}\right| \left(f_{\mathbf{p}'} f_{\mathbf{q}'} - f_{\mathbf{p}} f_{\mathbf{q}}\right). \tag{A.22}$$

In the integral, $\mathbf{p}'$ has the same modulus as $\mathbf{p}$ but is oriented in the Ω direction and $\mathbf{q}'$ is fixed by the energy and momentum conservation. The cross-section $\sigma(\Omega)$ corresponds to the probability for particles to deviate from their initial trajectories by a solid angle Ω. The value of the cross section depends on the nature of the interactions, as detailed in annex A.4.

H theorem

It is often assumed that, in presence of collisions, the distribution function will eventually relax towards f_0 (even though particles in a harmonic potential provide a good counter example through the undamped oscillations of both the center-of-mass motion (see Kohn theorem below) and the monopole breathing mode [Lobser *et al.* 2015]). The qualitative idea relies on the *H* theorem, that plays a key-role in Boltzmann theory and has been a bone of contention since its formulation [Vilani 2010].

Boltzmann introduced the quantity H define as

$$H(t) = \int d\mathbf{r}d\mathbf{p}\, f\left(\mathbf{r}, \mathbf{p}, t\right) \log f((\mathbf{r}, \mathbf{p}, t) \tag{A.23}$$

which can easily be related to the more familiar entropy $S(t) = -k_B H(t)$.

The H-theorem states that this quantity can only decrease during the time evolution of the system

$$\frac{d}{dt} H(t) \leq 0 \tag{A.24}$$

or equivalently, the entropy of the isolated system can only increase.

The demonstration relies on the integration of eq.(A.21) and the inequality saturates for distributions such that the collision term vanishes. In the interacting case, the only distributions verifying this condition are the local Maxwellians defined as

$$f\left(\mathbf{r}, \mathbf{p}, t\right) = n(\mathbf{r}, t) \left(\frac{1}{2\pi m k_B T(\mathbf{r}, t)}\right)^{3/2} \exp\left(-\frac{(\mathbf{p} - m\mathbf{u}(\mathbf{r}, t))^2}{2mk_B T(\mathbf{r}, t)}\right), \tag{A.25}$$

where the density n, temperature T and velocity $\mathbf{u}$ fields are free parameters. Note that such a distribution may not be a steady state of Boltzmann equation (ie $\mathcal{L}[f] \neq 0$). The non-interacting case, considered in chapter 3 and 4, provides an additional situation of evolution with constant entropy.

Classical paradoxes

- Loschmidt's reversibility paradox [Loschmidt 1876]

> Starting from a given initial condition, H decreases during the evolution of the system. At time t, H has reached a value $H(t) < H_0$ and we reverse the speed of all particles. Since collisions are micro-reversible, the system will resume its initial configuration in which $H = H_0$. During this evolution, H has increased, in contradiction with the H theorem.

This paradox relies on a wrong interpretation of the Stosszahlansatz: as time is reversed, the micro-reversibility implies that particles display *pre-collisional* correlations, but *post-collisional* chaos. Deriving Boltzmann equation with this modified hypothesis inverses the sign of the collision term: the entropy decreases (or the quantity H increases) during the evolution of the system. Qualitatively, the reverse evolution starts with correlated particles and every collision brings the system closer to the initial distribution, where all particles were uncorrelated; the decrease of entropy translates this loss of information. A further objection can then be formulated:

> The situation presented above shows that Boltzmann equation is not relevant to describe some systems, such as distributions with initial correlations.

The assessment is true, but does not constitute a paradox of any kind, as illustrated by spin echo experiments. However, these systems with strong initial correlations require a very delicate construction and a typical configuration, drawn at random in phase-space, is very unlikely to display such features. The story says that, as Boltzmann was confronted to Loschmidt's reversibility paradox, he answered: "Go ahead then, reverse them !".

- Poicaré-Zermelo's recurrent paradox [Zermelo 1896]

Poicaré demonstrated in 1889 the recurrence theorem [Poincaré 1890]:

> Let us consider a system which dynamics conserves the phase volume of any finite element and which evolution remains contained in a finite phase space volume. Then, after sufficiently long time (the so-called *Poincaré recurrence time*), the system will return to a state arbitrarily close to its initial state.

Owing to Liouville theorem and energy conservation, the two premesis are verified for most closed physical systems. Few years after the publication of Poincaré memoir, Zermelo formulated a paradox relying on his theorem:

> How can a system returns to its initial configuration, with the initial quantity H_0, if H can only increase during its evolution ?

Mathematically, the paradox comes from the applicability of the Poincaré theorem, which concerns finite systems of N particles. Boltzmann equation supposes an infinite number of degrees of freedom and is therefore not subject to the theorem.

Physically however, systems do contain a finite number of particles. Nevertheless, the recurrence time scales exponentially with N and for macroscopic samples, the corresponding periods are much longer than the age of the universe. What's more, Boltzmann equation remains valid only as long as the Stosszahlansatz is relevant. Long before the recurrence time is reached, the pre-collisional correlations might not be negligible and the system will exit the validity range of the H theorem.