Chapter VI

Boltzmann equation

In the previous chapter, it has been shown that the Liouville equation describing the evolution in Γ-space of the probability density for a collection of many classical particles can be equivalently recast as a system of coupled evolution equations, the BBGKY hierarchy, for the successive reduced phase-space densities f_k. To become tractable, the hierarchy has to be truncated, by closing the system of equations on the basis of some physical ansatz.

A non-trivial example of such a prescription is the so-called assumption of *molecular chaos*, introduced by L. Boltzmann. This hypothesis provides a satisfactory recipe for systems of *weakly interacting* particles, the paradigmatic example thereof being a dilute gas. In such systems, the time scales characterizing the typical duration of a collision or the interval between two successive scatterings of a given particle are well separated. Accordingly, one can introduce a coarse-grained description of space and time, such that collisions become instantaneous (and localized) processes, as well as a corresponding coarse-grained single-particle phase-space density (Sec. VI.1). Together with an analysis at the microscopic level of the collision processes that induce changes in this single-particle distribution, Boltzmann's ansatz yields a generic kinetic equation for its evolution (Sec. VI.2).

Irrespective of the precise form of the interaction responsible for the scattering processes—at least as long as the latter remain elastic and are invariant under time and space parity—, the kinetic Boltzmann equation leads to balance relations for various macroscopic quantities, which are first introduced in Sec. VI.3. In addition, we shall see that the Boltzmann equation describes a macroscopic time evolution which is not invariant under time reversal, even though the underlying microscopic interactions are.

Once an equation has been obtained, comes the natural question of its solutions (Sec. VI.4). One easily shows that the Boltzmann equation admits of a stationary solution, which describes thermodynamic equilibrium at the microscopic level. It can even be shown that this solution often constitutes the long-time behavior of an evolution. Apart from that one, extremely few other analytical solutions are known, and one uses various methods to find distributions that approximate true solutions for out-of-equilibrium situations.

The latter distributions are especially interesting, inasmuch as they allow the computation within the framework of the Boltzmann equation of macroscopic quantities, for instance of transport coefficients (Sec. VI.5) and of the dissipative fluxes in a fluid (Sec. VI.6), thereby also yielding the form of the equations of motion for the fluid.

Throughout this chapter, $\vec{p}$ denotes the *linear* momentum, not the canonical one, so that the various equations hold irrespective of the presence of a external vector potential.

VI.1 Description of the system

The kinetic Boltzmann equation is to some extent a simplification of the BBGKY hierarchy (V.14), or equivalently of the N-particle Liouville equation (II.10b), which implies the introduction of assumptions. In this first section, we introduce the generic hypotheses underlying *weakly interacting*

systems of classical particles, starting with a discussion of the various length and time scales in the system. In a second step, we discuss the interactions in the system, adopting for the remainder of the chapter the most simple, non-trivial choice—which is that originally made by Boltzmann.

VI.1.1 Length and time scales

Throughout this chapter, we shall consider systems of classical particles, i.e. we assume that we may meaningfully use the notion of phase space and of distributions over it. As is known from equilibrium statistical mechanics, this holds at thermodynamic equilibrium provided the mean inter-particle distance $d \sim n^{-1/3}$, with n the particle number density in position space, is large compared to the thermal de Broglie[(ca)] wavelength $\lambda_{\text{th}} = 2\pi\hbar/\sqrt{2\pi m k_B T}$. In a non-equilibrium case, as we are interested in here, d should be much larger than the de Broglie wavelength $2\pi\hbar/\langle|\vec{p}|\rangle$, with $\langle|\vec{p}|\rangle$ the typical momentum of particles.

Since we want to allow for scatterings between particles, this condition is not always fulfilled. Colliding partners might come close enough to each other that their wave functions start overlapping significantly. In that regime, classical notions like the particle trajectories or the impact parameter of a scattering process become meaningless, as they have no (exact) equivalent in quantum mechanics.

As we discuss shortly, the kinetic equations we shall consider hereafter hold for dilute systems, in which the successive collisions of a given particle are independent—in the sense of separated—of each other. Accordingly, one only need to consider the ingoing and outgoing states of a scattering event, as well as the probability rate to transition from the former to the latter, irrespective of the detailed description of the process. In particular, even though the scattering rate may (and indeed should!) be computed quantum mechanically, the evolution of a particle between successive collisions remains classical.

> As we shall see in Chap. ??, it is possible to formulate fully quantum-mechanical kinetic equations, from which the classical Boltzmann equation can be recovered in a specific limit. In that respect, the assumption of classical particles is only a simplification, not a necessity.

A more crucial assumption underlying kinetic approaches is that of the "diluteness" of the system under consideration. More precisely, the typical distance $n^{-1/3}$ between two neighboring particles is assumed to be much larger than the characteristic range r_0 of the force between them. Again, this obviously cannot hold when the particles collide. Yet the requirement $r_0 \ll n^{-1/3}$ ensures that scatterings remain rare events, i.e. that most of the time any given particle is moving freely. Accordingly, the potential energy associated with the interactions between particles is much smaller than their kinetic energy: this condition defines a *weakly interacting* system. The paradigm for such a system is a dilute gas, yet we shall see further examples in Sec. VI.5.

> The reader should be aware of the difference between "weakly interacting"—which is a statement on the diluteness of the system, as measured by a dimensionless number (*diluteness parameter*) like nr_0^3 or $n\sigma_{\text{tot}}^{3/2}$ which should be much smaller than unity, where σ_{tot} denotes the total cross section—and "weakly coupled", which relates to the characteristic strength of the coupling of the interactions at play.

Thanks to the assumption of diluteness, the typical distance traveled by a particle between two successive collisions, the mean free path ℓ_{mfp}, must be much larger than the interaction range r_0. In consequence, any scattering event will happen long after the previous collisions (with different partners) of each of the two participating particles; that is, the successive scatterings of any particle are independent processes, they are said to be *incoherent*.

Since we do not wish to describe the details of collisions, which involve length scales of the order of r_0 and smaller, we may simply consider a *coarse-grained* version of position space, in which

[(ca)] L. de Broglie, 1892–1987

points separated by a distance of the order of r_0 or smaller are taken as one and the same. In the coarse-grained position space, scatterings thus only take place when two particles are at the same point, i.e. they are *local* processes.

In parallel, we introduce a coarse-grained version of the time axis [55], by restricting the temporal resolution of the description to some scale larger than the collision duration τ_0, defined as the typical time that a particle needs to travel a distance r_0. As scatterings actually take place on a time scale of the order of τ_0, they are instantaneous in the coarse-grained time. Conversely, all the time intervals δt we shall consider—even infinitesimal ones, which will as usual be denoted as $\mathrm{d}t$—will implicitly fulfill the condition $\delta t \gg \tau_0$.

Remark: If the particles interact through long-range interactions, as e.g. the Coulomb force, the diluteness condition $nr_0^3 \ll 1$ is clearly violated. For such systems, the proper approach is to leave out such interactions from the term in the evolution equation that describes collision processes, and to reintroduce them "on the left-hand side of the equation" in the form of a mean field in which the particles are moving, as was done in § V.2.3 b when writing down the Vlasov equation.

Let $\vec{p}$ denote the linear momentum of a particle. We introduce the dimensionless single-particle distribution (or density) $\bar{\mathsf{f}}(t,\vec{r},\vec{p})$, such that[(78)]

$$\bar{\mathsf{f}}(t,\vec{r},\vec{p})\,\frac{\mathrm{d}^3\vec{r}\;\mathrm{d}^3\vec{p}}{(2\pi\hbar)^3} \tag{VI.1}$$

is the average number of particles which are at time t in the infinitesimal (coarse-grained) volume element $\mathrm{d}^3\vec{r}$ around position $\vec{r}$ and possess a momentum equal to $\vec{p}$ up to $\mathrm{d}^3\vec{p}$. The kinetic equation we shall derive and study hereafter will be the equation that governs the dynamics of $\bar{\mathsf{f}}(t,\vec{r},\vec{p})$.

Integrating $\bar{\mathsf{f}}(t,\vec{r},\vec{p})$ over all possible momenta yields the local particle-number density on the coarse-grained position space at time t:

$$n(t,\vec{r}) = \int \bar{\mathsf{f}}(t,\vec{r},\vec{p})\,\frac{\mathrm{d}^3\vec{p}}{(2\pi\hbar)^3} \tag{VI.2}$$

[cf. Eq. (V.3b)]. In turn, the integral of $n(t,\vec{r})$ over position yields the total number N of particles in the system, which will be assumed to remain constant.

Remarks:

∗ The distribution $\bar{\mathsf{f}}(t,\vec{r},\vec{p})$ is obviously a coarse-grained version of the dimensionless single-particle density on μ-space $\mathsf{f}_1(t,\vec{r},\vec{p})$ introduced in the previous chapter[(79)]. One might already anticipate that f_1 provides a better description than $\bar{\mathsf{f}}$, since it corresponds to an increased resolution. The implicit loss of information when going from f_1 to $\bar{\mathsf{f}}$ should manifest itself when measuring the knowledge associated with each distribution for a given physical situation, i.e. when considering the corresponding statistical entropies.

> The notation $\bar{\mathsf{f}}$ is naturally suggestive of an average, so one may wonder whether f_1 can be meaningfully decomposed as $\mathsf{f}_1 = \bar{\mathsf{f}} + \delta\mathsf{f}$, with $\delta\mathsf{f}$ a "fluctuating part" whose coarse-grained value vanishes. That is, there might be a well-defined prescription for splitting f_1—which obeys the exact BBGKY hierarchy—into a "kinetic part" $\bar{\mathsf{f}}$—which satisfies the assumptions leading to the Boltzmann equation, in particular the position-space locality and the Stoßzahlansatz (VI.14)—and a "non-kinetic part" $\delta\mathsf{f}$, which should be irrelevant for weakly interacting systems. This decomposition can indeed be performed, with the help of projection operators (Chap. ??).

∗ Till now, no upper bounds were specified for the scales of the space-time cells which constitute the points $(t,\vec{r})$ in the coarse-grained description. In § VI.4.1, we shall define local equilibrium distributions, which depend on various local fields. The latter should be slowly varying functions

(78) In § VI.2.1–VI.2.3 we shall also use the notation $\bar{\mathsf{f}}_1$, instead of $\bar{\mathsf{f}}$, thus emphasizing the "single-particle" aspect of the distribution.

(79) See the second remark below Eq. (V.3a).

of t and $\vec{r}$, which implicitly sets upper bounds on the size of local cells. Thus, the typical duration between two collisions of a particle should be much larger than the temporal size of a local cell, while accordingly the mean free path ℓ_{mfp}—i.e. the characteristic length traveled by a particle between two collisions—should be much larger than the spatial size of a local cell.

VI.1.2 Collisions between particles

Let us now discuss the interactions between particles. As already stated above, in the coarse-grained description the collisions between particles are local and instantaneous, i.e. the participants have to be at the same space-time point $(t, \vec{r})$. If we allow the presence of an external potential—which for the sake of consistency has to vary slowly, so that the coarse-graining procedure makes sense—, then it is assumed to have no influence on the microscopic scattering processes.

Translating the assumption of a weakly interacting system at the particle-scattering level, it implies that the probability that two particles collide is already small, so that the probability for collisions between three or more particles becomes totally negligible. Accordingly, we shall from now on only consider *binary collisions* in the system.

For the sake of simplicity, we shall assume that the collisions are *elastic*. That is, we consider that the energy exchanged in a collision can neither excite internal degrees of freedom of the particles—which are thus considered structureless—, nor can it be transformed from kinetic into mass energy or vice-versa. As a consequence, the conservation of energy in a collision becomes the conservation of kinetic energy.

In addition, linear momentum is also conserved in each scattering process[(80)], as is angular momentum. However, the latter does not contribute any additional constraint on the kinematics—and since the collisions are from the start assumed to be elastic, it does not provide selection rules for the possible final states of a process.

Remarks:

∗ The statement of the separate conservation of kinetic energy is less innocent than it seems and is closely related to the weakly-interacting assumption, according to which potential energy is negligible compared to the kinetic one.

∗ In the (Boltzmann–)Lorentz model—that is, a special case of the Boltzmann-gas model with two (or more) types of particles, among which one species is assumed to consist of infinitely massive particles—momentum conservation takes a particular twist, since the momentum of one participant in the collision is infinite… which has the effect of lifting the corresponding kinematic constraint.

In summary, we only consider so-called "two-to-two elastic processes", with two particles labeled 1 and 2 in the initial state and the same two particles, now labeled 3 and 4 for reasons that will be explained below, in the final state. Denoting by $\vec{p}_1$, $\vec{p}_2$, $\vec{p}_3$ and $\vec{p}_4$ the particle momenta before and after the collision—i.e., to be precise, far from the collision zone—, the scattering process will be symbolically written $\vec{p}_1, \vec{p}_2 \to \vec{p}_3, \vec{p}_4$, and the conservation laws trivially read

$$\frac{\vec{p}_1^{\,2}}{2m_1} + \frac{\vec{p}_2^{\,2}}{2m_2} = \frac{\vec{p}_3^{\,2}}{2m_3} + \frac{\vec{p}_4^{\,2}}{2m_4}, \qquad \vec{p}_1 + \vec{p}_2 = \vec{p}_3 + \vec{p}_4, \tag{VI.3}$$

where m_1, m_2, m_3 and m_4 are the respective masses of the particles.

Given a specific model for the microscopic interactions, one can compute the transition rate from the initial state with two particles with momenta $\vec{p}_1$, $\vec{p}_2$, to the final state in which the particles acquire the momenta $\vec{p}_3$ and $\vec{p}_4$. For scatterings, this rate is characterized by a differential cross

[(80)] This follows from the conservation of canonical momentum and the fact that collisions are local: if the particles are charged, the contributions from the vector potential to their canonical momenta are identical in the initial and final states.

section, as we recall at the end of the section. Yet to be more general and use notations which easily generalize to the case where particles may decay, we introduce a related quantity

$$\widetilde{w}(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)\equiv w(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)\,\frac{2\pi}{\hbar}\delta\!\left(\frac{\vec{p}_1^{\,2}}{2m_1}+\frac{\vec{p}_2^{\,2}}{2m_2}-\frac{\vec{p}_3^{\,2}}{2m_3}-\frac{\vec{p}_4^{\,2}}{2m_4}\right)(2\pi\hbar)^3\delta^{(3)}(\vec{p}_1+\vec{p}_2-\vec{p}_3-\vec{p}_4) \quad \text{(VI.4a)}$$

such that

$$\widetilde{w}(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)\,\frac{\mathrm{d}^3\vec{p}_3}{(2\pi\hbar)^3}\frac{\mathrm{d}^3\vec{p}_4}{(2\pi\hbar)^3} \quad \text{(VI.4b)}$$

is the number of collisions per unit time for a unit density (in position space) of colliding particle pairs, with final momenta in the range $\mathrm{d}^3\vec{p}_3\,\mathrm{d}^3\vec{p}_4$, while the two Dirac[cb] distributions encode the conditions (VI.3)

Remarks:

∗ The various factors of 2π and $\hbar$ in relation (VI.4a) are there to ensure that $\widetilde{w}(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)$ has a simple physical meaning, while $w(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)$ is a quantity which naturally emerges from a quantum mechanical calculation. As a matter of fact, $w(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)$ is then the squared modulus of the relevant element of the T-matrix (transition matrix), computed for initial single-particle states normalized to one particle per unit volume. Accordingly, the identities (VI.5) below are actually relations between T-matrix elements.

∗ When the colliding partners are identical, and thus—to respect the underlying quantum mechanical description—indistinguishable, then two final states that only differ through the exchange of the particle labels are actually a single state. To account for this, we shall later have to divide $\widetilde{w}(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)$ by 2 when we integrate over both $\vec{p}_3$ and $\vec{p}_4$, to avoid double counting.

As is customary, we make a further assumption on the interactions involved in the scatterings, namely that they are invariant under space parity and under time reversal. The transition rates for processes are thus unchanged when all position vectors $\vec{r}$ are replaced by $-\vec{r}$, as well as under the transformation $t\to -t$.

Therefore, we first have, thanks to the invariance under space parity

$$w(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)=w(-\vec{p}_1,-\vec{p}_2\to-\vec{p}_3,-\vec{p}_4), \quad \text{(VI.5a)}$$

where we used that $\vec{p}=m\,\mathrm{d}\vec{r}/\mathrm{d}t$ is transformed into $-\vec{p}$. In turn, the invariance of the transition rate under time reversal yields

$$w(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)=w(-\vec{p}_3,-\vec{p}_4\to-\vec{p}_1,-\vec{p}_2), \quad \text{(VI.5b)}$$

where we took into account both the transformations of the individual momenta and of the time direction of the scattering process. Combining both properties together, one finds the identity

$$w(\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4)=w(\vec{p}_3,\vec{p}_4\to\vec{p}_1,\vec{p}_2), \quad \text{(VI.5c)}$$

which relates scattering processes that are both space- and time-reversed with respect to each other. The process on the right-hand side of Eq. (VI.5c) is often called the *inverse collision* to that on the left-hand side. The identity of the transition rates for a process and the "inverse" one is referred to as *microscopic reversibility* or *microreversibility*.

Reminder: Classical scattering theory

Consider the scattering $\vec{p}_1,\vec{p}_2\to\vec{p}_3,\vec{p}_4$. The description of the process is simpler in the center-of-momentum frame[81] of the colliding particles, where the linear momenta become $\vec{p}_1'=-\vec{p}_2'$ and

[81] Remember that the "center of mass" has momentum $\vec{p}_1+\vec{p}_2=\vec{p}_3+\vec{p}_4$ and mass $m_1+m_2=m_3+m_4$.

[cb] P. A. M. Dirac, 1902–1984

$\vec{p}_3' = -\vec{p}_4'$. In that frame—in which kinematic quantities will be denoted with a prime—one defines the *differential scattering cross section* $\mathrm{d}^2\sigma/\mathrm{d}^2\Omega'$, which characterizes the number of particles from an incident flux density which are deflected per unit time into a solid angle element $\mathrm{d}^2\Omega'$ around some direction with respect to the initial density. More precisely, the differential cross section is defined as

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}^2\Omega'}(\theta',\varphi') = \frac{|\vec{\jmath}_{\mathrm{out}}'(\theta',\varphi')|}{|\vec{\jmath}_{\mathrm{in}}'|}\, r^2, \tag{VI.6}$$

where $\vec{\jmath}_{\mathrm{in}}'$ is the flux density falling on a single scattering center while $\vec{\jmath}_{\mathrm{out}}'(\theta,\varphi)$ is the outgoing flux density in the direction (θ',φ'), so that out of the $|\vec{\jmath}_{\mathrm{in}}'|$ particles crossing a unit area pro unit time, a number $|\vec{\jmath}_{\mathrm{out}}'(\theta,\varphi)|\,\mathrm{d}^2\mathcal{S}$ leave the collision zone through a surface element $\mathrm{d}^2\mathcal{S}$ in the direction (θ',φ') situated at a distance r from the scattering center (see Fig. VI.1.1).

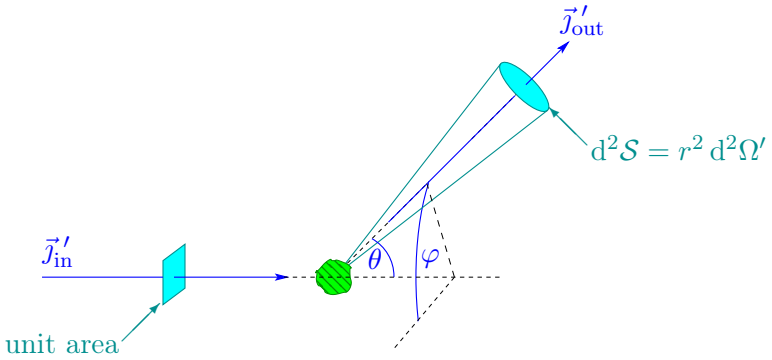

Figure VI.1.1 – Representation of the quantities entering the definition (VI.6) of the differential cross section.

If the colliding particles are non-identical, and thus distinguishable, say $m_3 = m_1 \neq m_2 = m_4$, then the scattering angle θ' is that between the (Galilei-invariant) incoming and outgoing relative velocities $\vec{v}_2 - \vec{v}_1$ and $\vec{v}_4 - \vec{v}_3$.[(82)] The solid-angle element $\mathrm{d}^2\Omega'$ is then equivalent to a volume element $\mathrm{d}^3\vec{p}_3\,\mathrm{d}^3\vec{p}_4$ in the joint momentum space of the two particles. More precisely, the number of collisions per unit time with final momenta in that range for a unit phase-space density of incoming particle pairs, $\widetilde{w}(\vec{p}_1,\vec{p}_2 \to \vec{p}_3,\vec{p}_4)\,\mathrm{d}^3\vec{p}_3\,\mathrm{d}^3\vec{p}_4$, is related to the differential cross section by the identity (in the sense of distributions)

$$\widetilde{w}(\vec{p}_1,\vec{p}_2 \to \vec{p}_3,\vec{p}_4)\,\frac{\mathrm{d}^3\vec{p}_3}{(2\pi\hbar)^3}\,\frac{\mathrm{d}^3\vec{p}_4}{(2\pi\hbar)^3} = |\vec{v}_2 - \vec{v}_1|\,\frac{\mathrm{d}^2\sigma}{\mathrm{d}^2\Omega'}(\theta',\varphi')\,\mathrm{d}^2\Omega', \tag{VI.7}$$

which may be viewed as a definition for $w(\vec{p}_1,\vec{p}_2 \to \vec{p}_3,\vec{p}_4)$ in the case of classical scattering.

Remark: Integrating the differential cross section over all possible directions of the scattered particle yields the total cross section σ_{tot}, which classically is the area of the effective... cross section of the target as seen by the projectile. For short-range interactions, this total cross section is of the order of the squared range of the interaction, $\sigma_{\mathrm{tot}} \sim r_0^2$. In turn, the total cross section allows to estimate the mean free path ℓ_{mfp} as $\ell_{\mathrm{mfp}} \sim 1/n\sigma_{\mathrm{tot}}$, with n the particle number density. The assumption $n^{-1/3} \gg r_0$ is then equivalent to $\ell_{\mathrm{mfp}} \gg n^{-1/3}$, i.e. the mean free path is much larger than the typical inter-particle distance.[(83)] Accordingly, the diluteness of the system is sometimes measured with the dimensionless parameter $n\ell_{\mathrm{mfp}}^3$, instead of $nr_0^3 \sim n\sigma_{\mathrm{tot}}^{3/2}$.

[(82)] For indistinguishable colliding particles, the final states with scattering angle θ' defined as above or with the supplementary angle $\pi - \theta'$, which is the angle between $\vec{v}_2 - \vec{v}_1$ and $\vec{v}_3 - \vec{v}_4$, are one and the same.

[(83)] In due fairness, the invoked relation between ℓ_{mfp} and σ_{tot} actually assumes that the system under study is dilute, so there is a kind of circular reasoning at play.