

CHAPTER IV

Boltzmann equation

IV.1 Description of the system

The kinetic Boltzmann equation is a simplification of the BBGKY hierarchy (III.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interactions in the system, adopting for the remainder of the chapter the most simple, non-trivial choice—which is that originally made by Boltzmann.

IV.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^(aj) wavelength $\lambda_{\text{th}} = 2\pi\hbar/\sqrt{2\pi mk_B T}$. 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 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 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. IV.4.

^(aj)L. DE BROGLIE, 1892–1987

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 $n r_0^3$ 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 travelled 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 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 [30], by restricting the temporal resolution of the description to some scale larger than the collision duration τ_0 , defined as the typical time which 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 dt —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 $n r_0^3 \ll 1$ 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 § III.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) $\bar{f}(t, \vec{r}, \vec{p})$, such that⁽³²⁾

$$\bar{f}(t, \vec{r}, \vec{p}) \frac{d^3 \vec{r} d^3 \vec{p}}{(2\pi\hbar)^3} \quad (\text{IV.1})$$

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

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

$$n(t, \vec{r}) = \int \bar{f}(t, \vec{r}, \vec{p}) \frac{d^3 \vec{p}}{(2\pi\hbar)^3} \quad (\text{IV.2})$$

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

⁽³²⁾In Sec. IV.2.1–IV.2.3 we shall also use the notation $\bar{f}_1$, emphasizing the “single-particle” aspect, instead of $\bar{f}$.

The notation $\bar{f}$ is naturally suggestive of an average, so one may wonder whether f_1 can be meaningfully decomposed as $f_1 = \bar{f} + \delta f$, with δf 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” $\bar{f}$ —which satisfies the assumptions leading to the Boltzmann equation, in particular the position-space locality and the Stöckzahlansatz (IV.14)—and a “non-kinetic part” δf , 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 Sec. IV.3.3, we shall define local equilibrium distributions, which depend on various local fields. The latter should be slowly varying functions of t and $\vec{r}$, which implicitly sets upper bounds on the size of local cells. Thus the typical time between two collisions of a particle should be much larger than the time 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.

IV.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.

Formulating 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⁽³³⁾, 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 linear momenta before

⁽³³⁾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.

and after the collision—i.e., to be precise, far from the collision zone—, the scattering process will be symbolically written $\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4$, and the conservation laws trivially read

$$\frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} = \frac{\vec{p}_3^2}{2m_3} + \frac{\vec{p}_4^2}{2m_4}, \quad \vec{p}_1 + \vec{p}_2 = \vec{p}_3 + \vec{p}_4, \quad (\text{IV.3})$$

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 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

$$\begin{aligned} \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) &\equiv \\ w(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \frac{2\pi}{\hbar} \delta\left(\frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} - \frac{\vec{p}_3^2}{2m_3} - \frac{\vec{p}_4^2}{2m_4}\right) (2\pi\hbar)^3 \delta^{(3)}(\vec{p}_1 + \vec{p}_2 - \vec{p}_3 - \vec{p}_4) \end{aligned} \quad (\text{IV.4a})$$

such that

$$\tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \frac{d^3\vec{p}_3}{(2\pi\hbar)^3} \frac{d^3\vec{p}_4}{(2\pi\hbar)^3} \quad (\text{IV.4b})$$

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 $d^3\vec{p}_3 d^3\vec{p}_4$.

Remarks:

* The various factors of 2π and $\hbar$ in relation (IV.4a) are there to ensure that $\tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)$ has a simple physical meaning, while $w(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)$ is a quantity which naturally emerges from a quantum mechanical calculation. As a matter of fact, $w(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)$ 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 (IV.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 $\tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)$ 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 $t \rightarrow -t$.

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

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

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

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

where we took into account both the transformations of the individual momenta and of the time direction of the scattering.

Combining both invariances together, one finds the identity

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

which relates scattering processes which are both space- and time-reversed with respect to each other. The process on the right-hand side of Eq. (IV.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 $\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4$. The description of the process is simpler in the center-of-momentum frame⁽³⁴⁾ of the colliding particles, where the linear momenta become $\vec{p}'_1 = -\vec{p}'_2$ and $\vec{p}'_3 = -\vec{p}'_4$. In that frame—in which kinematic quantities will be denoted with a prime—one defines the *differential scattering cross section* $d^2\sigma/d^2\Omega'$, which characterizes the number of particles from an incident flux density which are deflected per unit time into a solid angle element $d^2\Omega'$ around some direction with respect to the initial density. More precisely, the differential cross section is defined as

$$\frac{d^2\sigma}{d^2\Omega'}(\theta', \varphi') = \frac{|\vec{j}'_{\text{out}}(\theta', \varphi')|}{|\vec{j}'_{\text{in}}|} r^2, \quad (\text{IV.6})$$

where $\vec{j}'_{\text{in}}$ is the flux density falling on a single scattering center while $\vec{j}'_{\text{out}}(\theta, \varphi)$ is the outgoing flux density in the direction (θ', φ') , so that out of the $|\vec{j}'_{\text{in}}|$ particles crossing a unit area pro unit time, a number $|\vec{j}'_{\text{out}}(\theta, \varphi)| d^2S$ leave the collision zone through a surface element d^2S in the direction (θ', φ') situated at a distance r from the scattering center (see Fig. IV.1).

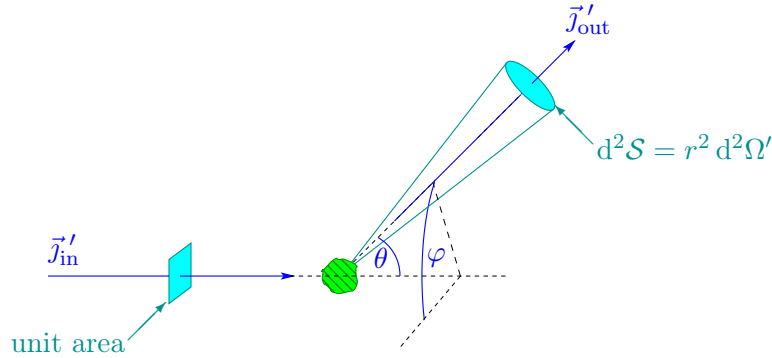


Figure IV.1 – Representation of the quantities entering the definition (IV.6) of the differential cross section.

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 $\vec{v}_4 - \vec{v}_3$.⁽³⁵⁾ The solid-angle element $d^2\Omega'$ is then equivalent to a volume element $d^3\vec{p}_3 d^3\vec{p}_4$ 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, $\tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) d^3\vec{p}_3 d^3\vec{p}_4$, is related to the differential cross section by the identity (in the sense of distributions)

$$\tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \frac{d^3\vec{p}_3}{(2\pi\hbar)^3} \frac{d^3\vec{p}_4}{(2\pi\hbar)^3} = |\vec{v}_2 - \vec{v}_1| \frac{d^2\sigma}{d^2\Omega'}(\theta', \varphi') d^2\Omega', \quad (\text{IV.7})$$

which may be seen as a definition for $w(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)$ 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, $\sigma_{\text{tot}} \sim r_0^2$. In turn, the total cross section allows to estimate the mean free path ℓ_{mfp} as $\ell_{\text{mfp}} \sim 1/n\sigma_{\text{tot}}$, with n the particle number density. The assumption

⁽³⁴⁾Remember that the “center of mass” has momentum $\vec{p}_1 + \vec{p}_2 = \vec{p}_3 + \vec{p}_4$ and mass $m_1 + m_2 = m_3 + m_4$.

⁽³⁵⁾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.

$n^{-1/3} \gg r_0$ is then equivalent to $\ell_{\text{mfp}} \gg n^{-1/3}$, i.e. the mean free path is much larger than the typical inter-particle distance.⁽³⁶⁾ Accordingly, the diluteness of the system is sometimes measured with the dimensionless parameter $n\ell_{\text{mfp}}^3$, instead of $nr_0^3 \sim n\sigma_{\text{tot}}^{3/2}$.

IV.2 Boltzmann equation

We now derive the equation governing the dynamics of the single-particle density $\bar{f}(t, \vec{r}, \vec{p})$ —denoted by $\bar{f}_1$ in Sec. IV.2.1–IV.2.3—for the system with the properties presented in the previous section, where we only consider elastic two-to-two scattering processes.

IV.2.1 General formulation

Since $\bar{f}_1(t, \vec{r}, \vec{p})$ is an instance of single-particle density—admittedly, on a coarse-grained version of space-time, yet this makes no difference here—, its evolution equation could be derived in the same manner as in the previous chapter III. Accordingly, in the absence of collisions $\bar{f}_1$ obeys the single-particle Liouville equation [cf. (III.15)]

$$\frac{\partial \bar{f}_1(t, \vec{r}, \vec{p})}{\partial t} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} \bar{f}_1(t, \vec{r}, \vec{p}) + \vec{F} \cdot \vec{\nabla}_{\vec{p}} \bar{f}_1(t, \vec{r}, \vec{p}) = 0.$$

This result can also be derived by counting particles within a volume $d^3\vec{r} d^3\vec{p}$ around point $(\vec{r}, \vec{p})$ at time t , then by investigating where these particles are at a later time $t + dt$, invoking Liouville's theorem (II.15) to equate the new volume they occupy to the old one.⁽³⁷⁾

Traditionally, the influence of collisions on the evolution is expressed by introducing a symbolic *collision term* $(\partial \bar{f}_1 / \partial t)_{\text{coll}}$ in the right member

$$\frac{\partial \bar{f}_1}{\partial t} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} \bar{f}_1 + \vec{F} \cdot \vec{\nabla}_{\vec{p}} \bar{f}_1 = \left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{coll}}. \quad (\text{IV.8})$$

The role of the collision term is to describe the change induced by scatterings in the number of particles $\bar{f}_1(t, \vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p}$ inside an infinitesimal volume element around point $(\vec{r}, \vec{p})$.

The purpose of next subsection will be to give substance to this as yet empty notation. In particular, we shall split the collision term into a “gain term”—describing the particles that enter the volume $d^3\vec{r} d^3\vec{p}$ after a collision—and a “loss term”—corresponding to the particles which are scattered away from $d^3\vec{r} d^3\vec{p}$:

$$\left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{coll}} \equiv \left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{gain}} - \left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{loss}}. \quad (\text{IV.9})$$

Remark: In the same spirit as the right-hand side of Eq. (IV.8), one can designate the second and third terms of the left member as the rates of change of $\bar{f}_1$ respectively caused by the motion of the particles and by the external force:

$$\frac{\partial \bar{f}_1}{\partial t} = - \left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{motion}} - \left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{force}} + \left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{coll}}. \quad (\text{IV.10})$$

IV.2.2 Computation of the collision term

We now derive the form of the two contributions to the collision term (IV.9), starting with the loss term.

⁽³⁶⁾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.

⁽³⁷⁾This proof can for instance be found in Huang [29, Chap. 3.1] or Reif [31, Chap. 13.2].

IV.2.2a Loss term

Consider a volume element $d^3\vec{r} d^3\vec{p}_1$ around a point $(\vec{r}, \vec{p}_1)$ at time t . A particle inside this range can scatter on a partner also situated at $\vec{r}$ —collisions are local—having a momentum $\vec{p}_2$ up to $d^3\vec{p}_2$. After the collision, the outgoing particles have momenta $\vec{p}_3, \vec{p}_4$, with a probability related to the transition rate $\tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)$. Integrating over all possible final momenta yields the total scattering probability for initial particles with momenta $\vec{p}_1, \vec{p}_2$. Since $d^3\vec{p}_1$ is infinitesimally small, any scattering process will give both colliding particles a different final momentum, so that any collision automatically leads to a decrease of the number of particles inside $d^3\vec{p}_1$.

To obtain the number of particles which are scattered away from $d^3\vec{p}_1$, one has to multiply the transition rate per unit volume for the collision of one pair of particles with momenta $\vec{p}_1, \vec{p}_2$ by the total number of particles 1 and 2 per unit volume in the respective momentum ranges at time t . Very generally, this number is given by⁽³⁸⁾

$$\bar{f}_2(t, \vec{r}, \vec{p}_1, \vec{r}, \vec{p}_2) d^3\vec{r} \frac{d^3\vec{p}_1}{(2\pi\hbar)^3} \frac{d^3\vec{p}_2}{(2\pi\hbar)^3},$$

with $\bar{f}_2$ the (coarse-grained) joint two-particle density. Eventually, one integrates over all possible momenta $\vec{p}_2$ of the partner, which yields, after dividing by $d^3\vec{r} d^3\vec{p}_1 / (2\pi\hbar)^3$

$$\left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{loss}}(t, \vec{r}, \vec{p}_1) = \int \bar{f}_2(t, \vec{r}, \vec{p}_1, \vec{r}, \vec{p}_2) \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \frac{d^3\vec{p}_2}{(2\pi\hbar)^3} \frac{d^3\vec{p}_3}{(2\pi\hbar)^3} \frac{d^3\vec{p}_4}{(2\pi\hbar)^3}. \quad (\text{IV.11a})$$

In terms of the differential cross section, this loss term reads

$$\left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{loss}}(t, \vec{r}, \vec{p}_1) = \int \bar{f}^{(2)}(t, \vec{r}, \vec{p}_1, \vec{r}, \vec{p}_2) |\vec{v}_2 - \vec{v}_1| \frac{d^2\sigma}{d^2\Omega'}(\theta', \varphi') d^2\Omega' \frac{d^3\vec{p}_2}{(2\pi\hbar)^3}. \quad (\text{IV.11b})$$

Remark: The integrand of the latter expression (IV.11b) actually involves quantities measured in different rest frames: $\vec{p}_1, \vec{p}_2$ are with respect to the rest frame in which the system is studied, while primed quantities are in the respective centre-of-momentum frames of the binary collisions—which, for a fixed $\vec{p}_1$, depend on $\vec{p}_2$!

IV.2.2b Gain term

The gain term describes particles which at time t acquire the momentum $\vec{p}_1$ up to $d^3\vec{p}_1$ in the final state of a collision. We thus need to consider scattering processes $\vec{p}_3, \vec{p}_4 \rightarrow \vec{p}_1, \vec{p}_2$, where the values of the initial momenta and of $\vec{p}_2$ are irrelevant and thus will be integrated over.

For fixed $\vec{p}_3, \vec{p}_4$ and for a given $\vec{p}_2$ known up to $d^3\vec{p}_2$, the number of particles with final momenta in the proper range for a unit number density of incoming particles is given by [cf. Eq. (IV.4b)]

$$\tilde{w}(\vec{p}_3, \vec{p}_4 \rightarrow \vec{p}_1, \vec{p}_2) \frac{d^3\vec{p}_1}{(2\pi\hbar)^3} \frac{d^3\vec{p}_2}{(2\pi\hbar)^3}.$$

Multiplying by the two-particle distribution $\bar{f}_2(t, \vec{r}, \vec{p}_3, \vec{r}, \vec{p}_4)$, which gives the density of particles with the respective momenta in the initial state, and integrating over these momenta as well as over the momentum $\vec{p}_2$ of the partner particle, one finds the number of “gained” particles per unit volume

$$\left(\frac{\partial \bar{f}_1}{\partial t} \right)_{\text{gain}}(t, \vec{r}, \vec{p}_1) \frac{d^3\vec{p}_1}{(2\pi\hbar)^3} = \frac{d^3\vec{p}_1}{(2\pi\hbar)^3} \int \bar{f}_2(t, \vec{r}, \vec{p}_3, \vec{r}, \vec{p}_4) \tilde{w}(\vec{p}_3, \vec{p}_4 \rightarrow \vec{p}_1, \vec{p}_2) \frac{d^3\vec{p}_2}{(2\pi\hbar)^3} \frac{d^3\vec{p}_3}{(2\pi\hbar)^3} \frac{d^3\vec{p}_4}{(2\pi\hbar)^3}.$$

⁽³⁸⁾ The reader upset by the presence of the factor $d^3\vec{r}$ despite the fact that we are interested in the number of pairs per unit volume may want to consider the number of pairs with both particles in the volume element $d^3\vec{r}$, writing it first in the form

$$\bar{f}_2(t, \vec{r}, \vec{p}_1, \vec{r}_2, \vec{p}_2) d^3\vec{r} d^3\vec{r}_2 \frac{d^3\vec{p}_1}{(2\pi\hbar)^3} \frac{d^3\vec{p}_2}{(2\pi\hbar)^3}$$

and then letting $\vec{r}_2 = \vec{r}$ —and accordingly $d^3\vec{r}_2 = d^3\vec{r}$. The announced number of pairs per unit volume is then obtained by dividing by (a single factor of) $d^3\vec{r}$.

Dividing both sides by $d^3\vec{p}_1/(2\pi\hbar)^3$ and invoking the microreversibility property (IV.5c), this may be recast as

$$\left(\frac{\partial \bar{f}_1}{\partial t}\right)_{\text{gain}}(t, \vec{r}, \vec{p}_1) = \int \bar{f}_2(t, \vec{r}, \vec{p}_3, \vec{r}, \vec{p}_4) \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \frac{d^3\vec{p}_2}{(2\pi\hbar)^3} \frac{d^3\vec{p}_3}{(2\pi\hbar)^3} \frac{d^3\vec{p}_4}{(2\pi\hbar)^3}. \quad (\text{IV.12a})$$

Equivalently, one may write

$$\left(\frac{\partial \bar{f}_1}{\partial t}\right)_{\text{gain}}(t, \vec{r}, \vec{p}_1) = \int \bar{f}_2(t, \vec{r}, \vec{p}_3, \vec{r}, \vec{p}_4) |\vec{v}_2 - \vec{v}_1| \frac{d^2\sigma}{d^2\Omega'}(\theta', \varphi') d^2\Omega' \frac{d^3\vec{p}_2}{(2\pi\hbar)^3}, \quad (\text{IV.12b})$$

where relation (IV.7) was used.

IV.2.3 Closure prescription: molecular chaos

Gathering the loss and gain terms (IV.11a) and (IV.12a) together, the collision term, or *collision integral*, in the right-hand side of the Boltzmann equation reads

$$\left(\frac{\partial \bar{f}_1}{\partial t}\right)_{\text{coll.}}(t, \vec{r}, \vec{p}_1) = \int [\bar{f}_2(t, \vec{r}, \vec{p}_3, \vec{r}, \vec{p}_4) - \bar{f}_2(t, \vec{r}, \vec{p}_1, \vec{r}, \vec{p}_2)] \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \frac{d^3\vec{p}_2}{(2\pi\hbar)^3} \frac{d^3\vec{p}_3}{(2\pi\hbar)^3} \frac{d^3\vec{p}_4}{(2\pi\hbar)^3}, \quad (\text{IV.13a})$$

or equivalently [cf. Eqs (IV.11b) and (IV.12b)]

$$\left(\frac{\partial \bar{f}_1}{\partial t}\right)_{\text{coll.}}(t, \vec{r}, \vec{p}_1) = \int [\bar{f}_2(t, \vec{r}, \vec{p}_3, \vec{r}, \vec{p}_4) - \bar{f}_2(t, \vec{r}, \vec{p}_1, \vec{r}, \vec{p}_2)] |\vec{v}_2 - \vec{v}_1| \frac{d^2\sigma}{d^2\Omega'}(\theta', \varphi') d^2\Omega' \frac{d^3\vec{p}_2}{(2\pi\hbar)^3}. \quad (\text{IV.13b})$$

As anticipated from the discussion of the BBGKY hierarchy in the previous chapter, the collision integral for the evolution of the single-particle density involves the two-particle density $\bar{f}_2$. In turn, one can derive the collision term for the dynamics of the latter, which depends on $\bar{f}_3$, and so forth.

Boltzmann's proposal was to transform the collision integral (IV.13a) into a term involving $\bar{f}_1$ only, by invoking the assumption of *molecular chaos*, or *Stoßzahlansatz*, according to which the velocities of the particles *before the collision* are uncorrelated

$$\bar{f}_2(t, \vec{r}, \vec{p}_1, \vec{r}, \vec{p}_2) = \bar{f}_1(t, \vec{r}, \vec{p}_1) \bar{f}_1(t, \vec{r}, \vec{p}_2) \quad \text{before a collision at instant } t. \quad (\text{IV.14})$$

Just after a collision, two particles which have scattered on each other are correlated—inverting their velocities, one makes them collide, which is a rare event. Yet before they meet and collide again, they will undergo many scatterings with other, random particles, which wash out any trace of this correlation, and justifies the above assumption.

Remark: Molecular chaos is thus a weaker assumption than the factorization (III.23) in the Vlasov equation, which holds at any instant and for all positions of the two particles.

Under this assumption and inserting the resulting collision integral in the right-hand side of Eq. (IV.8), one obtains the *Boltzmann kinetic equation*⁽³⁹⁾

$$\begin{aligned} \frac{\partial \bar{f}(t, \vec{r}, \vec{p}_1)}{\partial t} + \vec{v}_1 \cdot \vec{\nabla}_{\vec{r}} \bar{f}(t, \vec{r}, \vec{p}_1) + \vec{F} \cdot \vec{\nabla}_{\vec{p}_1} \bar{f}(t, \vec{r}, \vec{p}_1) = \\ \left(1 - \frac{\delta_{1,2}}{2}\right) \int [\bar{f}(t, \vec{r}, \vec{p}_3) \bar{f}(t, \vec{r}, \vec{p}_4) - \bar{f}(t, \vec{r}, \vec{p}_1) \bar{f}(t, \vec{r}, \vec{p}_2)] \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \frac{d^3\vec{p}_2}{(2\pi\hbar)^3} \frac{d^3\vec{p}_3}{(2\pi\hbar)^3} \frac{d^3\vec{p}_4}{(2\pi\hbar)^3}, \end{aligned} \quad (\text{IV.15a})$$

where the prefactor $1 - \delta_{1,2}/2$ was introduced to ensure that the formula also holds without double counting when particles 1 and 2 are identical (in which case $\delta_{1,2} = 1$, otherwise is $\delta_{1,2} = 0$).

⁽³⁹⁾From now on, we drop the notation $\bar{f}_1$ and only use $\bar{f}$.

Equivalently, the Boltzmann equation may recast as

$$\begin{aligned} \frac{\partial \bar{f}(t, \vec{r}, \vec{p}_1)}{\partial t} + \vec{v}_1 \cdot \vec{\nabla}_{\vec{r}} \bar{f}(t, \vec{r}, \vec{p}_1) + \vec{F} \cdot \vec{\nabla}_{\vec{p}_1} \bar{f}(t, \vec{r}, \vec{p}_1) = \\ \left(1 - \frac{\delta_{1,2}}{2}\right) \int [\bar{f}(t, \vec{r}, \vec{p}_3) \bar{f}(t, \vec{r}, \vec{p}_4) - \bar{f}(t, \vec{r}, \vec{p}_1) \bar{f}(t, \vec{r}, \vec{p}_2)] |\vec{v}_2 - \vec{v}_1| \frac{d^2 \sigma}{d^2 \Omega'}(\theta', \varphi') d^2 \Omega' \frac{d^3 \vec{p}_2}{(2\pi\hbar)^3}. \end{aligned} \quad (\text{IV.15b})$$

Remarks:

* One often introduces the abbreviations $\bar{f}(1) \equiv \bar{f}(t, \vec{r}, \vec{p}_1)$, $\bar{f}(2) \equiv \bar{f}(t, \vec{r}, \vec{p}_2)$, and so on, so that the collision integral is shortly written as

$$\left(\frac{\partial \bar{f}_1}{\partial t}\right)_{\text{coll.}} = \int [\bar{f}(3) \bar{f}(4) - \bar{f}(1) \bar{f}(2)] \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4) \frac{d^3 \vec{p}_2}{(2\pi\hbar)^3} \frac{d^3 \vec{p}_3}{(2\pi\hbar)^3} \frac{d^3 \vec{p}_4}{(2\pi\hbar)^3}. \quad (\text{IV.15c})$$

To shorten expressions further, we shall also use $\int_{\vec{p}_i} \equiv \int \frac{d^3 \vec{p}_i}{(2\pi\hbar)^3}$, leading for instance to

$$\left(\frac{\partial \bar{f}_1}{\partial t}\right)_{\text{coll.}} = \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} [\bar{f}(3) \bar{f}(4) - \bar{f}(1) \bar{f}(2)] \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4). \quad (\text{IV.15d})$$

* The generalization of the Boltzmann equation to the case of a mixture of substances is straightforward: in the collision term for the evolution of the position-velocity-space density of a component, one has to sum the contribution from the (elastic two-to-two) scattering processes of the particles of that substance with each other—taking into account the $\frac{1}{2}$ factor to avoid double-counting—, and the contributions from collisions with particles of other components.

IV.2.4 Phenomenological generalization to fermions and bosons

The collision term of the Boltzmann equation can easily be modified so as to accommodate the Pauli exclusion principle between particles with half-integer spins.⁽⁴⁰⁾ Considering the two-to-two collision $\vec{p}_i, \vec{p}_j \rightarrow \vec{p}_k, \vec{p}_l$, where all particles are fermions, the “repulsive” behaviour of the latter can be phenomenologically accounted for by preventing the scattering process to happen when one of the final states $\vec{p}_k$ or $\vec{p}_l$ is already occupied. That is, one postulates that the rate for the process is not only proportional to the product $\bar{f}(i)\bar{f}(j)$ of the phase-space densities of the initial particles—where we use the same shorthand notation as in Eq. (IV.15c)—, but also to the product $[1 - \bar{f}(k)][1 - \bar{f}(l)]$ involving the densities of the final state particles. The collision integral of the Boltzmann equation thus reads

$$\left(\frac{\partial \bar{f}_1}{\partial t}\right)_{\text{coll.}} = \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} (\bar{f}(3) \bar{f}(4) [1 - \bar{f}(1)] [1 - \bar{f}(2)] - \bar{f}(1) \bar{f}(2) [1 - \bar{f}(3)] [1 - \bar{f}(4)]) \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4). \quad (\text{IV.16})$$

A similar generalization, which simulates the “attractive” character of bosons, consists in enhancing the rate of the process $\vec{p}_i, \vec{p}_j \rightarrow \vec{p}_k, \vec{p}_l$, when there are already particles in the final state. This is done by multiplying the rate by the factor $[1 + \bar{f}(k)][1 + \bar{f}(l)]$, which yields

$$\left(\frac{\partial \bar{f}_1}{\partial t}\right)_{\text{coll.}} = \int_{\vec{p}_2} \int_{\vec{p}_3} \int_{\vec{p}_4} (\bar{f}(3) \bar{f}(4) [1 + \bar{f}(1)] [1 + \bar{f}(2)] - \bar{f}(1) \bar{f}(2) [1 + \bar{f}(3)] [1 + \bar{f}(4)]) \tilde{w}(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4). \quad (\text{IV.17})$$

We shall see below that these seemingly ad hoc generalizations (IV.16)–(IV.17) lead for instance to the proper equilibrium distributions.

An issue is naturally the actual meaning of $\bar{f}$ in the generalized kinetic equations obtained with the above collision terms, since phase space is usually not considered as an interesting concept in quantum mechanics, where the Heisenberg uncertainties prevent a particle from being localized at a well-defined point in μ -space.

⁽⁴⁰⁾ This idea seems to date back to Landau, in his work on the theory of Fermi liquids [32].

IV.2.5 Additional comments and discussions

Now that we have established the actual form of the Boltzmann equation, especially of its collision term, we wish to come back to the assumptions made in Sec. IV.1.1, to discuss their role in a new light.

An important point is the coarse graining of both time and position space. Thanks to it, the momenta of the colliding particles skip instantaneously from their initial values $\vec{p}_1, \vec{p}_2$ to the final ones, without going through intermediate values as would happen otherwise—except in the unrealistic case when the particles are modelled as hard spheres. If this transition were *not* instantaneous, particle 1—a similar reasoning holds for the other colliding particle (2), as well as for particles 3 and 4 in the gain term—would at the time t of the collision no longer have the momentum $\vec{p}_1$ it had “long” before the scattering. Accordingly, the distribution of particle 1 in the loss part of the collision integral should not be $\bar{f}(t, \vec{r}, \vec{p}_1)$, but rather one of the following possibilities:

- $\bar{f}$ evaluated at time t , yet for the position $\vec{r}'_1$ and momentum $\vec{p}'_1$ of particle 1 at that very instant: in a classical description of the scattering process, $\vec{r}'_1$ and $\vec{p}'_1$ depend for instance on the impact parameter of the collision; whereas they are not even well-defined in a quantum mechanical description.
- $\bar{f}$ evaluated at momentum $\vec{p}_1$, yet at a time $t - \tau$, before the collision, at which particle 1 still had this momentum, and accordingly at some position $\vec{r}_1 \neq \vec{r}$.

In the former case, one loses the locality in position space, while in the latter one has to abandon locality both in time and space. The advantage of adopting a coarse-grained description is thus to provide an evolution equation which is local both in t and $\vec{r}$, as is the case of Eq. (IV.15a).

Thanks to the time locality of the Boltzmann equation, the evolution of $\bar{f}$ is “Markovian” in the wide sense of Sec. ??, i.e. its rate of change is memoryless and only depends on $\bar{f}$ at the same instant.

Another assumption is that the time scale on which the coarse graining is performed is much smaller than the average duration between two successive collisions of a particle, and similarly that the spatial size of the coarse-grained cells is much smaller than the mean free path. This allows one to meaningfully treat $\bar{f}$ as a continuous—and even differentiable—function of t and $\vec{r}$, and thus amounts to assuming that the system properties do not change abruptly in time or spatially.

Eventually, one can note that the molecular chaos assumption (IV.14) provides a closed equation for $\bar{f}$, yet at the cost of introducing nonlinearity, whereas the successive equations of the BBGKY hierarchy (III.14) are all linear.