

VI.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 § VI.2.1–VI.2.3—for the system with the properties presented in the previous section, where we only consider elastic two-to-two scattering processes.

The derivation presented in this section is of a rather heuristic spirit, emphasizing the physical meaning of the terms on the right hand side of the Boltzmann equation. An alternative derivation, starting from the BBGKY hierarchy, is given in the appendix (VI.A) to this Chapter.

VI.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 V. Accordingly, in the absence of collisions \bar{f}_1 obeys the single-particle Liouville equation [cf. (V.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 $d^3\vec{r} d^3\vec{p}$ about 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 (84)

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

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

The role of the collision term is to describe the change induced by scatterings in the number of particles $\bar{f}_1(t, \vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p} / (2\pi\hbar)^3$ inside an infinitesimal volume element about 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 $d^3\vec{r} d^3\vec{p}$:

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

Remark: In the same spirit as the right-hand side of Eq. (VI.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:

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

VI.2.2 Computation of the collision term

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

VI.2.2a Loss term

Consider a volume element $d^3\vec{r} d^3\vec{p}_1$ about the point (\vec{r}, \vec{p}_1) . A particle inside this range at time t 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

(84) This proof can for instance be found in the textbooks by Huang [54, Chap. 3.1] or Reif [45, Chap. 13.2].

to the transition rate $w(\vec{p}_1, \vec{p}_2 \rightarrow \vec{p}_3, \vec{p}_4)$. 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 $d^3\vec{p}_1$ (unless the particles exactly exchange their momenta).

To obtain the number of particles that 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 ⁽⁸⁵⁾

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

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 $d^3\vec{r} d^3\vec{p}_1 / (2\pi\hbar)^3$

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

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

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

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

VI.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. ^(VI.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

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

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

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

⁽⁸⁵⁾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) $d^3\vec{r}$.

Equivalently, one may write

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

where relation (VI.7) was used.

VI.2.3 Closure prescription: molecular chaos

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

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

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

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

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 (VI.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

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

Just after a collision, two particles that have scattered off each other are correlated—reversing 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 (V.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. (VI.8), one obtains the *Boltzmann kinetic equation* or *Boltzmann transport equation* ⁽⁸⁶⁾

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

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 $\delta_{1,2} = 0$).

Equivalently, the Boltzmann equation may recast as

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

⁽⁸⁶⁾From now on, we drop the notation \bar{f}_1 and only use \bar{f} .

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

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

To shorten expressions even 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

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

* 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.

VI.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^(cc) exclusion principle between particles with half-integer spins.⁽⁸⁷⁾ Considering the two-to-two collision $\vec{p}_i, \vec{p}_j \rightarrow \vec{p}_k, \vec{p}_l$, where all particles are fermions,^(cd) the “repulsive” behavior 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. (VI.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

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

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

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

We shall see below that these seemingly ad hoc generalizations (VI.16)–(VI.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.

⁽⁸⁷⁾This idea seems to date back to Landau, in his work on the theory of Fermi liquids [56].

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VI.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 § VI.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. (VI.15).

Thanks to the time locality of the Boltzmann equation, the evolution of \bar{f} is “Markovian” in the wide sense of § I.2.1 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 (VI.14) provides a closed equation for \bar{f} , yet at the cost of introducing nonlinearity, whereas the successive equations of the BBGKY hierarchy (V.14) are all linear.