## Boltzmann Equation


#### Abstract

Summary. We review some of the general properties of the semiclassical Boltzmann equation - not necessarily restricting ourselves to the dilute electron gas - paying special attention to its irreversible properties.


### 1.1 Heuristic Derivation of the Semiclassical Boltzmann Equation

The kinetic theory of Boltzmann which connects the regime of dynamics with that of thermodynamics has been a milestone in the development of theoretical physics. In order to describe the kinetics of, e.g., an atomic gas, Boltzmann [51] introduced, with great intuition, more than half a century before the rise of quantum mechanics, a probabilistic description for the evolution of a single-particle distribution which anticipated atomistic scattering concepts. Boltzmann introduced a single-particle probability distribution in the phase space of the canonical variables $\boldsymbol{r}$ and $\boldsymbol{p}$. This Boltzmann distribution function is usually denoted as $f(\boldsymbol{r}, \boldsymbol{p}, t)$. Obviously, this object is classical, because in quantum mechanics $\boldsymbol{r}$ and $\boldsymbol{p}$ are noncommuting operators so that they cannot be simultaneously measured with arbitrary precision. We will analyze in the following chapter how this conceptual difficulty affects the limits of validity of the Boltzmann equation. Here we will first present a heuristic derivation of the semiclassical Boltzmann equation. Later in this book we will pay special attention to the more detailed quantum mechanical justifications of the Boltzmann kinetics, present discussions of the limits of this semiclassical theory, and, most importantly, derive and study the quantum kinetics which has to be used instead of the Boltzmann kinetics on small length and/or short timescales. In the framework of the classical Hamilton theory the total change in time of this distribution function is

$$
\begin{align*}
\frac{\mathrm{d} f(\boldsymbol{r}, \boldsymbol{p}, t)}{\mathrm{d} t} & =\frac{\partial f}{\partial t}+\frac{\mathrm{d} \boldsymbol{r}}{\mathrm{~d} t} \cdot \nabla_{r} f+\frac{\mathrm{d} \boldsymbol{p}}{\mathrm{~d} t} \cdot \nabla_{p} f \\
& =\frac{\partial f}{\partial t}+\frac{\boldsymbol{p}}{m} \cdot \nabla_{r} f-\left[\nabla_{r} V(\boldsymbol{r})\right] \cdot \nabla_{p} f=\left.\frac{\partial f}{\partial t}\right|_{\text {coll }} \tag{1.1}
\end{align*}
$$

where $V(\boldsymbol{r})$ is a single-particle potential. The left-hand side of (1.1) describes the dynamics of a single particle. The influence of the other particles will give rise to a further change of the distribution function $\partial f /\left.\partial t\right|_{\text {coll }}$ which describes the effect of the collisions in the gas. We will not proceed historically, but include directly the proper quantum statistics for quantum gases, so that we are not limited to nondegenerate gases. This extension is necessary for the application of the Boltzmann kinetics to electron gases in semiconductors which are often degenerate, whether they are produced by doping, injection, or optical excitation. Fermi's golden rule gives us the transition probability per unit time and thus the wanted change of $f$ due to collisions. For an interacting Fermi gas we calculate this change by considering approximately free-particle collisions in which the particle is scattered from a momentum state $\boldsymbol{p}$ to a momentum state $\boldsymbol{p}^{\prime}$ and simultaneously another particle is scattered from state $\boldsymbol{p}_{1}$ to $\boldsymbol{p}_{1}^{\prime}$, as well as the inverse process

$$
\begin{align*}
\left.\frac{\partial f(\boldsymbol{p})}{\partial t}\right|_{\text {coll }}= & -\sum_{\boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}, \boldsymbol{p}_{1}^{\prime}} w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right)\left\{f(\boldsymbol{p}) f\left(\boldsymbol{p}_{1}\right)\left[1-f\left(\boldsymbol{p}^{\prime}\right)\right]\left[1-f\left(\boldsymbol{p}_{1}^{\prime}\right)\right]\right. \\
& \left.-[1-f(\boldsymbol{p})]\left[1-f\left(\boldsymbol{p}_{1}\right)\right] f\left(\boldsymbol{p}^{\prime}\right) f\left(\boldsymbol{p}_{1}^{\prime}\right)\right\} \tag{1.2}
\end{align*}
$$

where the intrinsic transition probalility per unit time is given by

$$
\begin{align*}
w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right)= & \frac{1}{2}\left|W_{\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}}-W_{\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}_{1}^{\prime}, \boldsymbol{p}^{\prime}}\right|^{2} \\
& \times \delta_{\boldsymbol{p}+\boldsymbol{p}_{1}, \boldsymbol{p}^{\prime}+\boldsymbol{p}_{1}^{\prime}} \frac{2 \pi}{\hbar} \delta\left(\varepsilon_{p}+\varepsilon_{p_{1}}-\varepsilon_{p^{\prime}}-\varepsilon_{p_{1}^{\prime}}\right) . \tag{1.3}
\end{align*}
$$

Here

$$
\begin{equation*}
W_{\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}}=\left\langle\boldsymbol{p} \boldsymbol{p}_{1}\right| W\left|\boldsymbol{p}^{\prime} \boldsymbol{p}_{1}^{\prime}\right\rangle \tag{1.4}
\end{equation*}
$$

is the interaction matrix element and $\varepsilon_{p}$ is the energy of the particle. The second matrix element in (1.3) is the exchange term in which $\boldsymbol{p}_{1}^{\prime}$ and $\boldsymbol{p}^{\prime}$ are interchanged. This form of the intrinsic transition probability is called the first Born approximation. The population factors take care that the initial states in the scattering event are populated and that the final states are empty in accordance with the Pauli principle. The scattering $\boldsymbol{p}+\boldsymbol{p}_{1} \rightarrow \boldsymbol{p}^{\prime}+\boldsymbol{p}_{1}^{\prime}$ is a loss term which reduces $f(\boldsymbol{p})$, while the inverse process $\boldsymbol{p}^{\prime}+\boldsymbol{p}_{1}^{\prime} \rightarrow \boldsymbol{p}+\boldsymbol{p}_{1}$ increases the distribution function. For shortness of notation, the parametric dependencies on the spatial coordinate $\boldsymbol{r}$ and time $t$ are not shown in the collision integral. The form of the collision integral leads to five conservation laws for: (a) the
number of particles, (b) the vector of the total momentum, and (c) the total energy. In a dilute, nondegenerate gas the final state population can be neglected, so that (1.2) can be simplified by the approximation $1-f(\boldsymbol{p}) \simeq 1$.

A second important scattering rate for an electron gas in a perfect crystal is the scattering by emission or absorption of a phonon. Its form is

$$
\begin{align*}
\left.\frac{\partial f(\boldsymbol{p})}{\partial t}\right|_{\text {coll }}= & -\sum_{\boldsymbol{p}^{\prime}, \boldsymbol{q}} w\left(\boldsymbol{p}, \boldsymbol{p}^{\prime} ; \pm \boldsymbol{q}\right) \times\left\{f(\boldsymbol{p})\left[1-f\left(\boldsymbol{p}^{\prime}\right)\right]\left[\frac{1}{2}+n(\boldsymbol{q}) \pm \frac{1}{2}\right]\right. \\
& \left.-[1-f(\boldsymbol{p})] f\left(\boldsymbol{p}^{\prime}\right)\left[\frac{1}{2}+n(\boldsymbol{q}) \mp \frac{1}{2}\right]\right\} \tag{1.5}
\end{align*}
$$

where the intrinsic transition probabilty per unit time is given by

$$
\begin{equation*}
w\left(\boldsymbol{p}, \boldsymbol{p}^{\prime} ; \pm \boldsymbol{q}\right)=\left|M_{q}\right|^{2} \delta_{\boldsymbol{p}, \boldsymbol{p}^{\prime} \pm \boldsymbol{q}} \frac{2 \pi}{\hbar} \delta\left(\varepsilon_{p^{\prime}} \pm \hbar \omega_{q}-\varepsilon_{p}\right) \tag{1.6}
\end{equation*}
$$

Here, $M_{q}$ is the electron-phonon interaction matrix element, and $n(\boldsymbol{q})$ and $\omega_{q}$ are the phonon distribution and frequency, respectively. Consider the upper sign first, then the first term in (1.5) describes a scattering of an electron from $\boldsymbol{p}$ into the state $\boldsymbol{p}^{\prime}$ accompanied with an emission of a phonon. The final state boson population factor $[1+n(\boldsymbol{q})]$ shows that the emission can be spontaneous or stimulated. The energy conservation also shows that the energy $\varepsilon_{p}$ of the initially populated state is shared between the particle in the final state and the phonon. The contribution of the lower sign in (1.5) describes a scattering from $\boldsymbol{p}$ to $\boldsymbol{p}^{\prime}$ via absorption of a phonon with an occupation factor $n(\boldsymbol{q})$. The form of (1.5) shows that for the electron-phonon scattering rate only the electron particle number is conserved, but no longer the total momentum and the total energy of the electron gas which both can be transferred to the phonon system. The phonon distribution in turn is also governed by a similar Boltzmann equation which we will not give explicitly here.

Obviously the semiclassical Boltzmann equation cannot be used on very short timescales because the assumption that the energy is conserved in an isolated collision (1.2), (1.5) breaks down. In a short time interval $\delta t$ the energy remains undetermined due to the uncertainty relation $\delta t \delta E \geq \hbar$. Therefore the strict energy conservation in an individual collision is not an inherent property of the quantum kinetic description.

The mathematical properties of the Boltzmann kinetics contained in (1.1), (1.2), and (1.5) have been thoroughly investigated. Its full theory is a wide subject in its own; we will discuss only a few properties here. For a much more complete treatment and for studies of its applications we have to refer to such excellent books as Ziman [380], Cercignani [76], and Smith and Jensen [327].

### 1.2 Approach to Equilibrium: H-Theorem

It is easy to convince oneself that the semiclassical Boltzmann equation (1.2) describes indeed an evolution toward the thermal equilibrium in the absence
of external fields. We introduce first an arbitrary function $F\left(\boldsymbol{p}, f_{\boldsymbol{p}}\right)$ which depends on the momentum and the distribution $f(\boldsymbol{r}, \boldsymbol{p}, t)$. Its local density is

$$
\begin{equation*}
\langle F(\boldsymbol{r}, t)\rangle=\sum_{\boldsymbol{p}} F\left(\boldsymbol{p}, f_{\boldsymbol{p}}\right) f_{\boldsymbol{p}} \tag{1.7}
\end{equation*}
$$

The change of this function due to the collisions is [here we consider explicitly the collision operator (1.2)]

$$
\begin{align*}
\left.\frac{\partial\langle F(\boldsymbol{r}, t)\rangle}{\partial t}\right|_{\text {coll }}= & \left.\sum_{\boldsymbol{p}}\left[\frac{\partial F(\boldsymbol{p})}{\partial f(\boldsymbol{p})}+F(\boldsymbol{p})\right] \frac{\partial f(\boldsymbol{p})}{\partial t}\right|_{\text {coll }} \\
= & -\sum_{\boldsymbol{p} \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}, \boldsymbol{p}_{1}^{\prime}} w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime} \boldsymbol{p}_{1}^{\prime}\right) \frac{\partial[F(\boldsymbol{p}) f(\boldsymbol{p})]}{\partial f(\boldsymbol{p})} \\
& \times\left\{f(\boldsymbol{p}) f\left(\boldsymbol{p}_{1}\right)\left[1-f\left(\boldsymbol{p}^{\prime}\right)\right]\left[1-f\left(\boldsymbol{p}_{1}^{\prime}\right)\right]\right. \\
& \left.-[1-f(\boldsymbol{p})]\left[1-f\left(\boldsymbol{p}^{\prime}\right)\right] f\left(\boldsymbol{p}_{1}\right) f\left(\boldsymbol{p}_{1}^{\prime}\right)\right\} \tag{1.8}
\end{align*}
$$

Exploiting the symmetry of the intrinsic transition probability $w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}_{1}^{\prime} \boldsymbol{p}^{\prime}\right)$ with respect to the exchange of particle coordinates

$$
\begin{align*}
w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right) & =w\left(\boldsymbol{p}_{1}, \boldsymbol{p} ; \boldsymbol{p}_{1}^{\prime}, \boldsymbol{p}^{\prime}\right) \\
& =w\left(\boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime} ; \boldsymbol{p}, \boldsymbol{p}_{1}\right)=w\left(\boldsymbol{p}_{1}^{\prime}, \boldsymbol{p}^{\prime} ; \boldsymbol{p}_{1}, \boldsymbol{p}\right) \tag{1.9}
\end{align*}
$$

one finds that

$$
\begin{align*}
\left.\frac{\partial\langle F(\boldsymbol{r}, t)\rangle}{\partial t}\right|_{\text {coll }}= & -\frac{1}{4} \sum_{\boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}, \boldsymbol{p}_{1}^{\prime}} w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right) \\
& \times\left[\frac{\partial(F f)}{\partial f}+\frac{\partial(F f)}{\partial f_{1}}-\frac{\partial(F f)}{\partial f^{\prime}}-\frac{\partial(F f)}{\partial f_{1}^{\prime}}\right] \\
& \times\left[f f_{1}\left(1-f^{\prime}\right)\left(1-f_{1}^{\prime}\right)-(1-f)\left(1-f_{1}\right) f^{\prime} f_{1}^{\prime}\right] \tag{1.10}
\end{align*}
$$

In (1.10) we have introduced a shorthand notation, for example in $\partial(F f) / \partial f$ all involved functions are evaluated at the argument $\boldsymbol{p}$. Now consider the following choice for $F$ :

$$
\begin{equation*}
f(\boldsymbol{p}) F\left(\boldsymbol{p}, f_{\boldsymbol{p}}\right)=f(\boldsymbol{p}) \ln f(\boldsymbol{p})+[1-f(\boldsymbol{p})] \ln [1-f(\boldsymbol{p})] \tag{1.11}
\end{equation*}
$$

The partial derivative with repect to $f$ yields

$$
\begin{equation*}
\frac{\partial(F f)}{\partial f(\boldsymbol{p})}=\ln \frac{f(\boldsymbol{p})}{1-f(\boldsymbol{p})} \tag{1.12}
\end{equation*}
$$

Equation (1.10) becomes

$$
\begin{align*}
\frac{\partial}{\partial t} & \left.\right|_{\text {coll }} \sum_{\boldsymbol{p}} f(\boldsymbol{p}) \ln f(\boldsymbol{p})+[1-f(\boldsymbol{p})] \ln [1-f(\boldsymbol{p})]=\left.\frac{\partial}{\partial t} H(\boldsymbol{r}, t)\right|_{\text {coll }} \\
= & -\frac{1}{4} \sum_{\boldsymbol{p} \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}, \boldsymbol{p}_{1}^{\prime}} w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right) \ln \left[\frac{f f_{1}\left(1-f^{\prime}\right)\left(1-f_{1}^{\prime}\right)}{(1-f)\left(1-f_{1}\right) f^{\prime} f_{1}^{\prime}}\right] \\
& \times\left[f f_{1}\left(1-f^{\prime}\right)\left(1-f_{1}^{\prime}\right)-(1-f)\left(1-f_{1}\right) f^{\prime} f_{1}^{\prime}\right] \tag{1.13}
\end{align*}
$$

The integrand is of the form $(x-y) \ln (x / y)$, and hence nonnegative, because $x-y$ and $\ln (x / y)$ have the same sign. Thus the $H$-function (called "eta"-function, the capital greek eta looks like a latin $H$ ) always decreases in the approach to equilibrium. This is the content of Boltzmann's famous eta-theorem, generalized to a Fermi gas.

The eta-theorem shows that the entropy density, which for a Fermi gas is given by [226]

$$
\begin{align*}
s(\boldsymbol{r}, t) & =-k_{\mathrm{B}} H(\boldsymbol{r}, t) \\
& =-k_{\mathrm{B}} \sum_{\boldsymbol{p}}\{f(\boldsymbol{p}) \ln f(\boldsymbol{p})+[1-f(\boldsymbol{p})] \ln [1-f(\boldsymbol{p})]\} \tag{1.14}
\end{align*}
$$

reaches a maximum in the equilibrium. Here, $k_{\mathrm{B}}$ is Boltzmann's constant.
Finally, we will show that the Boltzmann equation (1.2) describes indeed an approach to the well-known Fermi equilibrium function. For this purpose we formalize the already mentioned conservation laws. We define the functions $F_{i}(\boldsymbol{p})$ with $i=1, \ldots, 5$ as

$$
\begin{equation*}
F_{1}=1, \quad F_{i}=p_{i}, \quad i=2,3,4, \quad F_{5}=\varepsilon_{p} \tag{1.15}
\end{equation*}
$$

we see immediately from (1.10) that the corresponding $\left\langle F_{i}\right\rangle$ are not changed by the collisions. In equilibrium the term in curly brackets in (1.2) has to vanish:

$$
\begin{equation*}
\left[f^{0} f_{1}^{0}\left(1-f^{0^{\prime}}\right)\left(1-f_{1}^{0^{\prime}}\right)-\left(1-f^{0}\right)\left(1-f_{1}^{0}\right) f^{0^{\prime}} f_{1}^{0^{\prime}}\right]=0 \tag{1.16}
\end{equation*}
$$

From this relation one sees that

$$
\begin{equation*}
\ln \frac{f^{0}}{\left(1-f^{0}\right)}+\ln \frac{f_{1}^{0}}{\left(1-f_{1}^{0}\right)}=\ln \frac{f^{0^{\prime}}}{\left(1-f^{0^{\prime}}\right)}+\ln \frac{f_{1}^{0^{\prime}}}{\left(1-f_{1}^{0^{\prime}}\right)} \tag{1.17}
\end{equation*}
$$

In other words, $\ln \left[f^{0} /\left(1-f^{0}\right)\right]$ is also a conserved quantity. Because we have only five basic conservation laws, this quantity can be expressed as a linear combination of $1, \boldsymbol{p}$, and $\varepsilon_{p}$ :

$$
\begin{equation*}
\ln \frac{f^{0}}{\left(1-f^{0}\right)}=A+\boldsymbol{B} \cdot \boldsymbol{p}+C \varepsilon_{p} \tag{1.18}
\end{equation*}
$$

with

$$
\begin{equation*}
A=\beta \mu, \quad \boldsymbol{B}=\beta \boldsymbol{u}, \quad C=-\beta, \tag{1.19}
\end{equation*}
$$

where $\beta=1 /\left(k_{\mathrm{B}} T\right), \mu$ is the chemical potential and $\boldsymbol{u}$ is the drift velocity. All the expressions in (1.19) can still be - slowly varying - functions of $\boldsymbol{r}$ and $t$. Such a situation is called a local equilibrium. Equation (1.18) has the solution

$$
\begin{equation*}
f^{0}(\boldsymbol{p})=\frac{1}{\mathrm{e}^{\beta\left(\varepsilon_{p}-\boldsymbol{p} \cdot \boldsymbol{u}-\mu\right)}+1} \tag{1.20}
\end{equation*}
$$

which is the Fermi distribution function. A similar derivation for the Boltzmann equation with electron-phonon scattering results in an equilibrium phonon distribution function of the form

$$
\begin{equation*}
n^{0}(\boldsymbol{p})=\frac{1}{\mathrm{e}^{\beta\left(\hbar \omega_{p}-\boldsymbol{p} \cdot \boldsymbol{u}\right)}-1} \tag{1.21}
\end{equation*}
$$

because the chemical potential of bosons, whose total number is not conserved, is identical to zero.

### 1.3 Linearization: Eigenfunction Expansion

Close to thermal equilibrium the nonlinear Boltzmann equation, e.g., (1.2), can be linearized with respect to the deviation $\delta f \equiv f-f^{0}$ from the thermal equilibrium solution (1.20). For simplicity we consider here a spatially homogeneous electron gas without drift. It turns out that it is advantageous to use a normalized deviation $\phi(\boldsymbol{p}, t)$ which is introduced by writing

$$
\begin{equation*}
f(\boldsymbol{p}, t)=\frac{1}{\mathrm{e}^{\beta\left(\varepsilon_{p}-\mu\right)-\phi(\boldsymbol{p}, t)}+1} \tag{1.22}
\end{equation*}
$$

Expanding this function with respect to $\phi(\boldsymbol{p}, t)$ yields

$$
\begin{equation*}
\delta f(\boldsymbol{p}, t)=f^{0}(\boldsymbol{p})\left[1-f^{0}(\boldsymbol{p})\right] \phi(\boldsymbol{p}, t) . \tag{1.23}
\end{equation*}
$$

The linearized Boltzmann equation yields the following net scattering rate for the state $\boldsymbol{p}$ :

$$
\begin{align*}
\frac{\partial \phi(\boldsymbol{p}, t)}{\partial t}= & -\frac{2}{f^{0}(\boldsymbol{p})\left[1-f^{0}(\boldsymbol{p})\right]} \sum_{\boldsymbol{p}_{1}, \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}} w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right) \\
& \times\left\{\phi ( \boldsymbol { p } , t ) \left[f^{0}\left(1-f^{0}\right) f_{1}^{0}\left(1-f^{0^{\prime}}\right)\left(1-f_{1}^{0^{\prime}}\right)\right.\right. \\
& \left.\left.+f^{0}\left(1-f^{0}\right)\left(1-f_{1}^{0}\right) f^{0^{\prime}} f_{1}^{0^{\prime}}\right]+\cdots\right\} . \tag{1.24}
\end{align*}
$$

The dots indicate terms of similar structure proportional to $\phi\left(\boldsymbol{p}_{1}, t\right), \phi\left(\boldsymbol{p}^{\prime}, t\right)$, and $\phi\left(\boldsymbol{p}_{1}^{\prime}, t\right)$. In equilibrium

$$
\begin{equation*}
f^{0} f_{1}^{0}\left(1-f^{0^{\prime}}\right)\left(1-f_{1}^{0^{\prime}}\right)=\left(1-f^{0}\right)\left(1-f_{1}^{0}\right) f^{0^{\prime}} f_{1}^{0^{\prime}} \tag{1.25}
\end{equation*}
$$

Using relation (1.25), the linearized Boltzmann equation (1.24) reduces to

$$
\begin{align*}
\frac{\partial \phi(\boldsymbol{p}, t)}{\partial t}= & -\frac{2}{f^{0}(\boldsymbol{p})\left[1-f^{0}(\boldsymbol{p})\right]} \sum_{\boldsymbol{p}_{1}, \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}} \mathcal{W}\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right)  \tag{1.26}\\
& \times\left[\phi(\boldsymbol{p}, t)+\phi\left(\boldsymbol{p}_{1}, t\right)-\phi\left(\boldsymbol{p}^{\prime}, t\right)-\phi\left(\boldsymbol{p}_{1}^{\prime}, t\right)\right]=-\mathcal{L} \phi(\boldsymbol{p}, t) \tag{1.27}
\end{align*}
$$

with

$$
\begin{equation*}
\mathcal{W}\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right)=w\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right) f^{0} f_{1}^{0}\left(1-f^{0^{\prime}}\right)\left(1-f_{1}^{0^{\prime}}\right) \tag{1.28}
\end{equation*}
$$

The transition matrix $\mathcal{W}$ of the linearized Boltzmann equation has the following symmetry properties:

$$
\begin{align*}
\mathcal{W}\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right) & =\mathcal{W}\left(\boldsymbol{p}_{1}, \boldsymbol{p} ; \boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime}\right) \\
& =\mathcal{W}\left(\boldsymbol{p}^{\prime}, \boldsymbol{p}_{1}^{\prime} ; \boldsymbol{p}, \boldsymbol{p}_{1}\right)=\mathcal{W}\left(\boldsymbol{p}, \boldsymbol{p}_{1} ; \boldsymbol{p}_{1}^{\prime}, \boldsymbol{p}^{\prime}\right) \tag{1.29}
\end{align*}
$$

The linearized Boltzmann equation also conserves the total particle number, the total momentum, and the total energy. If one chooses a $\phi(\boldsymbol{p}, t)$ which is proportional to either $1, \boldsymbol{p}$, or $\varepsilon_{p}$, the r.h.s of the Boltzmann equation (1.26) vanishes. Thus, these particular forms of $\phi(\boldsymbol{p})$ are eigenfunctions to the collision operator $\mathcal{L}$ with a vanishing eigenvalue. The collision operator is an integral operator

$$
\begin{equation*}
\mathcal{L} \phi(\boldsymbol{p})=\sum_{\boldsymbol{p}^{\prime}} \mathcal{L}\left(\boldsymbol{p}, \boldsymbol{p}^{\prime}\right) \phi\left(\boldsymbol{p}^{\prime}\right) \tag{1.30}
\end{equation*}
$$

In general the eigenfunctions $\phi_{\lambda}(\boldsymbol{p})$ are solutions of the stationary equation

$$
\begin{equation*}
\mathcal{L} \phi_{\lambda}(\boldsymbol{p})=\lambda \phi_{\lambda}(\boldsymbol{p}) \tag{1.31}
\end{equation*}
$$

One can define a scalar product $\langle\sigma \mid \phi\rangle$ and a norm $|\phi|$ by

$$
\begin{equation*}
\langle\sigma \mid \phi\rangle=\sum_{\boldsymbol{p}} f^{0}(\boldsymbol{p})\left[1-f^{0}(\boldsymbol{p})\right] \sigma^{*}(\boldsymbol{p}) \phi(\boldsymbol{p}), \quad|\phi|^{2}=\langle\phi \mid \phi\rangle \tag{1.32}
\end{equation*}
$$

and span a Hilbert space by the eigenfunctions of $\mathcal{L}$. Using the symmetry relations of $\mathcal{W}$, one shows that $\mathcal{L}$ is a hermitian, real, and positive semidefinite operator in this Hilbert space, i.e.,

$$
\begin{equation*}
\langle\sigma \mid \mathcal{L} \phi\rangle=\langle\mathcal{L} \sigma \mid \phi\rangle ; \quad\langle\phi \mid \mathcal{L} \phi\rangle \geq 0 \tag{1.33}
\end{equation*}
$$

The equality sign holds, if $\phi$ is one of the five collision invariants. With these definitions the solution of the time-dependent linearized Boltzmann equation
with a given initial deviation $\phi(t=0)=\phi_{0}$ can be found by expanding $\phi_{0}$ in terms of the set of eigenfunctions $\phi_{\lambda}$ of $\mathcal{L}$. The solution is then of the form

$$
\begin{equation*}
\phi(\boldsymbol{p}, t)=\sum_{\lambda} A_{\lambda} \mathrm{e}^{-\lambda t} \phi_{\lambda}(\boldsymbol{p}) . \tag{1.34}
\end{equation*}
$$

The eigenvalues $\lambda$ are true relaxation frequencies for deviations $\phi_{\lambda}$. However, it is obvious from (1.34) that, in general, a description of the Boltzmann relaxation kinetics with only one relaxation time is not possible. Therefore the most frequently used linear approximation to the collision rate, the so-called relaxation-time approximation,

$$
\begin{equation*}
\left.\frac{\partial f(\boldsymbol{p})}{\partial t}\right|_{\mathrm{coll}} \simeq-\frac{\delta f(\boldsymbol{p})}{\tau} \tag{1.35}
\end{equation*}
$$

is only a very crude description of the relaxation kinetics toward equilibrium. The effective relaxation time $\tau$ in the resulting exponential decay of a deviation from the thermal equilibrium distribution has, in general, no well-defined meaning, and is known not to describe adequately the experimentally observed transport properties (e.g., viscosities and thermal conductivity of simple mono- and diatomic gases) [327]. Since the linearized collision operator commutes with the operator for the angular momentum in $\boldsymbol{p}$-space, the normalized deviation $\phi(\boldsymbol{p})$ can be factorized into a radial function and an angular part. Unfortunately, the eigenfunctions have to be evaluated numerically. Only for a nondegenerate system of Maxwell molecules with a repulsive interaction potential $\propto r^{-4}$ analytical eigenfunctions have been found. In the case of degenerate Fermi systems, where all momenta are confined to the neighborhood of $p_{\mathrm{F}}$, the eigenfunction expansions have provided rapidly converging series for various transport coefficients $[60,190]$.

We will illustrate in Chap. 2 the use of the eigenfunction expansion for the numerical evaluation of the relaxation kinetics due to Coulomb scattering in a quasi-two-dimensional (2D) electron gas. Such a 2D electron gas can be, for example, realized in a semiconductor quantum well structure. This example simultaneously addresses an important relaxation process of hot electrons in semiconductors, because in a dense electron gas in semiconductors the Coulomb scattering provides the fastest relaxation process.

