

VI.5 Computation of transport coefficients

In this section, we show how the Boltzmann equation allows the computation of transport coefficients in a system that is slightly out of equilibrium, working within the relaxation-time approximation introduced in § [VI.4.3](#)

^(ci)P. L. BHATNAGAR, 1912–1976 ^(ej)E. P. GROSS, 1926–1991 ^(ck)M. KROOK, 1913–1985

VI.5.1 Electrical conductivity

As first example, consider a “gas” of mobile charged particles of mass m , in the presence of a constant and uniform electric field $\vec{\mathcal{E}}$. These charge carriers diffuse among a system of (oppositely charged) particles of a different species, which we shall not consider explicitly. As a result of the various possible types of (elastic) two-to-two collisions between the different particle species, the single-particle distribution $\bar{f}(t, \vec{r}, \vec{p})$ of the mobile charge carriers obeys the Boltzmann equation (VI.15), with the external force $\vec{F} = q\vec{\mathcal{E}}$ in the drift term, where q is the electric charge of the carriers.

We shall assume that the system is in a regime where the Boltzmann equation can be approximated by Eq. (VI.49) while the single-particle distribution can be written in the form (VI.50). For reasons that will be made clearer below, we search for a stationary particle distribution. Given the uniformity and stationarity of the electric field, it is consistent to consider a local equilibrium distribution $\bar{f}^{(0)}$ involving time- and position-independent local quantities n , T , \vec{v} , so that $\bar{f}^{(0)}$ only depends on momentum:

$$\bar{f}^{(0)}(\vec{p}) = n \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} e^{-(\vec{p}-m\vec{v})^2/2mk_B T}.$$

Assuming that the average velocity \vec{v} of the moving charges vanishes—which is only a matter of choosing the proper reference frame, since it is uniform across the system—, this local equilibrium distribution becomes

$$\bar{f}^{(0)}(\vec{p}) = n \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} e^{-\vec{p}^2/2mk_B T} \quad (\text{VI.51})$$

i.e. actually the Maxwell–Boltzmann distribution (VI.35). Given the homogeneity of the system, the relaxation time τ_r can be taken to be independent of position.

Inserting $\bar{f}(\vec{r}, \vec{p}) = \bar{f}^{(0)}(\vec{p}) + \bar{f}^{(1)}(\vec{r}, \vec{p})$ in Eq. (VI.49), the leading remaining term on the left-hand side is that involving $\vec{\nabla}_{\vec{p}} \bar{f}^{(0)}(\vec{p})$: there is no term involving either the time or space derivative of $\bar{f}^{(0)}$ —since $\bar{f}^{(0)}$ does not depend on either—, and the terms involving gradients of $\bar{f}^{(1)}$ are of subleading order—physically, the corresponding time scales [cf. Eq. (V.16)] are much larger than $\tau_r(\vec{p})$, since many more collisions are needed for smoothing out large-scale inhomogeneities than small-scale ones. All in all, Eqs. (VI.49) and (VI.50) thus give to leading order

$$q\vec{\mathcal{E}} \cdot \vec{\nabla}_{\vec{p}} \bar{f}^{(0)}(\vec{p}) = -\frac{\bar{f}^{(1)}(\vec{r}, \vec{p})}{\tau_r(\vec{p})}.$$

from where one reads off $\bar{f}^{(1)}$ at once:

$$\bar{f}^{(1)}(\vec{p}) = \frac{q}{mk_B T} \tau_r(\vec{p}) \bar{f}^{(0)}(\vec{p}) \vec{p} \cdot \vec{\mathcal{E}} \quad (\text{VI.52})$$

In particular, $\bar{f}^{(1)}$ is independent of \vec{r} .

Now, the electric current (density) is the sum over all carriers of their electric charge multiplied by their velocity

$$\vec{J}_{\text{el}}(t, \vec{r}) = \int_{\vec{p}} q\vec{v} \bar{f}(t, \vec{r}, \vec{p}) = \frac{q}{m} \int_{\vec{p}} \vec{p} \bar{f}(t, \vec{r}, \vec{p}).$$

Here the current is stationary and uniform, and one can replace \bar{f} by $\bar{f}^{(0)} + \bar{f}^{(1)}$, with Eqs. (VI.51) and (VI.52). The integral of the term involving the local equilibrium distribution $\bar{f}^{(0)}$ vanishes by symmetry.⁽⁹⁴⁾ There thus only remains the contribution of $\bar{f}^{(1)}$, which gives for the i -th component of \vec{J}_{el} .

$$J_{\text{el}}^i = \frac{q}{m} \int_{\vec{p}} p^i \bar{f}^{(1)}(\vec{p}) = \sum_{j=1}^3 \frac{q^2}{m^2 k_B T} \int_{\vec{p}} \bar{f}^{(0)}(\vec{p}) \tau_r(\vec{p}) p^i p^j \mathcal{E}^j.$$

⁽⁹⁴⁾Had we allowed for a non-vanishing average velocity \vec{v} , the $\bar{f}^{(0)}$ -term would have given a contribution $nq\vec{v}$ to \vec{J}_{el} .

This is the i -th component of the relation

$$\vec{J}_{\text{el.}} = \boldsymbol{\sigma}_{\text{el.}} \cdot \vec{\mathcal{E}}, \quad (\text{VI.53a})$$

where the electrical-conductivity tensor $\boldsymbol{\sigma}_{\text{el.}}$ has the components

$$\sigma_{\text{el.}}^{ij} \equiv \frac{q^2}{m^2 k_B T} \int_{\vec{p}} \bar{f}^{(0)}(\vec{p}) \tau_r(\vec{p}) p^i p^j. \quad (\text{VI.53b})$$

If the relaxation time $\tau_r(\vec{p})$ only depends on the modulus $|\vec{p}|$ of momentum, not on its orientation, then the product $\bar{f}^{(0)}(\vec{p}) \tau_r(\vec{p})$ is an even function of the (Cartesian) components p^i . The integrand in Eq. (VI.53b) is then odd in p^i (or p^j) when $i \neq j$, so that the non-diagonal elements of the tensor vanish. In turn, all three diagonal elements are equal, i.e. the tensor is proportional to the identity. Assuming that the relaxation time is independent of momentum (BGK approximation), one obtains

$$\sigma_{\text{el.}}^{ii} = \frac{q^2 \tau_r}{m^2 k_B T} \int_{\vec{p}} (p^i)^2 \bar{f}^{(0)}(\vec{p}) = \frac{q^2 \tau_r}{m^2 k_B T} n m k_B T = \frac{n q^2 \tau_r}{m}.$$

All in all, one thus finds Ohm's law [cf. Eq. (I.43b)]

$$\vec{J}_{\text{el.}} = \sigma_{\text{el.}} \vec{\mathcal{E}} \quad \text{with} \quad \sigma_{\text{el.}} = \frac{n q^2 \tau_r}{m}. \quad (\text{VI.54})$$

Taking into account the dependence of the relaxation time on momentum gives a similar expression, with a different—yet in principle computable—expression of the electrical conductivity $\sigma_{\text{el.}}$, or more generally of the electrical-conductivity tensor $\boldsymbol{\sigma}_{\text{el.}}$ if $\tau_r(\vec{p})$ depends on the direction of \vec{p} .

Remarks:

* Our interest in the electrical conductivity, which as recalled in the first remark on page 13 is defined in the stationary regime, justifies a posteriori the restriction to time-independent solutions.

* In writing down the local equilibrium distribution $\bar{f}^{(0)}$ as uniform, we ignored the electrostatic potential which gives rise to the electric field $\vec{\mathcal{E}}$. The reason is again our interest in the electrical conductivity $\sigma_{\text{el.}}$, which is defined as the coefficient between $\vec{\mathcal{E}}$ and the electric current $\vec{J}_{\text{el.}}$ in the absence of a gradient in the number of charge carriers, i.e. for a uniform particle number density—the reader should compare with § I.2.3 c.

* The electrical conductivity (VI.54) computed within the relaxation-time approximation is proportional to the relaxation time τ_r . Since the latter is supposedly governed by collisions, it should be roughly proportional to the mean-free time between two successive scatterings, or equivalently to the mean-free path ℓ_{mfp} . In this picture, a larger ℓ_{mfp} results in a more efficient transport of charge carriers, which is consistent with the larger path length traveled by the moving charge carriers in each step.

VI.5.2 Diffusion coefficient and heat conductivity

As second application of the ideas of § VI.4.3, consider a Lorentz gas—i.e. a gas of light particles colliding on much heavier ones—, submitted to time-independent gradients in temperature and in chemical potential (or density)—which are imposed through the heavy, motionless collision partners.

The evolution equation of the single-particle distribution $\bar{f}(t, \vec{r}, \vec{p})$ is again approximated as Eq. (VI.49), here without external force. As local equilibrium distribution, we take

$$\bar{f}^{(0)}(\vec{r}, \vec{p}) = n(\vec{r}) \left(\frac{2\pi\hbar^2}{mk_B T(\vec{r})} \right)^{3/2} e^{-\vec{p}^2/2mk_B T(\vec{r})},$$

where the local density $n(\vec{r})$ and temperature $T(\vec{r})$ are those imposed by the heavy partners. Instead of this “canonical” form of the Maxwell–Boltzmann velocity distribution, it will be more convenient to replace it by the “grand-canonical” expression⁽⁹⁵⁾

$$\bar{f}^{(0)}(\vec{r}, \vec{p}) = \exp\left[-\frac{\vec{p}^2/2m - \mu(\vec{r})}{k_B T(\vec{r})}\right], \quad (\text{VI.55})$$

with the local chemical potential $\mu(\vec{r})$ instead of the number density. This will enable us to make more easily contact with the formalism of non-equilibrium thermodynamics in the entropy representation of Chapter [II](#).

Looking for stationary solutions $\bar{f}(\vec{r}, \vec{p}) = \bar{f}^{(0)}(\vec{r}, \vec{p}) + \bar{f}^{(1)}(\vec{r}, \vec{p})$ with $|\bar{f}^{(1)}| \ll \bar{f}^{(0)}$, Eq. [\(VI.49\)](#) reads to leading order

$$\frac{\partial \bar{f}^{(1)}(\vec{r}, \vec{p})}{\partial t} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} \bar{f}^{(0)}(\vec{r}, \vec{p}) = -\frac{\bar{f}^{(1)}(\vec{r}, \vec{p})}{\tau_r(\vec{r}, \vec{p})},$$

i.e.

$$\bar{f}^{(1)}(\vec{r}, \vec{p}) = -\frac{\tau_r(\vec{r}, \vec{p})}{m} \vec{p} \cdot \vec{\nabla}_{\vec{r}} \bar{f}^{(0)}(\vec{r}, \vec{p}). \quad (\text{VI.56})$$

VI.5.2a Fluxes

With the help of the leading and subleading contributions [\(VI.55\)](#), [\(VI.56\)](#) to the single-particle distribution, we can first easily compute the fluxes of particle number and energy.

$$\begin{aligned} \vec{J}_N(t, \vec{r}) &= \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \vec{v} = \frac{1}{m} \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \vec{p}, \\ \vec{J}_E(t, \vec{r}) &= \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \frac{\vec{p}^2}{2m} \vec{v} = \frac{1}{m} \int_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \frac{\vec{p}^2}{2m} \vec{p}. \end{aligned}$$

The local equilibrium distribution $\bar{f}^{(0)}$ does not contribute for parity reasons—the integrands are odd in \vec{p} and integrated over all momentum space.

To handle the contribution of $\bar{f}^{(1)}$, we first use the chain rule to rewrite the gradient of $\bar{f}^{(0)}$ with respect to position as

$$\vec{\nabla}_{\vec{r}} \bar{f}^{(0)}(\vec{r}, \vec{p}) = -\frac{1}{k_B} \bar{f}^{(0)}(\vec{r}, \vec{p}) \left\{ \frac{\vec{p}^2}{2m} \vec{\nabla}_{\vec{r}} \left[\frac{1}{T(\vec{r})} \right] + \vec{\nabla}_{\vec{r}} \left[-\frac{\mu(\vec{r})}{T(\vec{r})} \right] \right\}.$$

As in [§ VI.5.1](#), inserting $\bar{f}^{(1)}$, given by Eq. [\(VI.56\)](#) with this gradient, into the flux densities \vec{J}_N , \vec{J}_E leads to linear relations between the latter and the gradients $\vec{\nabla}_{\vec{r}}(1/T)$, $\vec{\nabla}_{\vec{r}}(-\mu/T)$, where the coefficients are in the general case tensors of rank 2. If the relaxation time τ_r does not depend on the orientation of \vec{p} , as we assume from now on, the tensors are diagonal and proportional to the unit tensor. The integrand of the diagonal coefficients of any of these tensors involves $(p^i)^2$, which has to be averaged—with a weight involving $\bar{f}^{(0)}$, τ_r and various powers of \vec{p}^2 —over all directions. Such an average is simply $\frac{1}{3}$ of the corresponding average of \vec{p}^2 , so that one eventually obtains

$$\vec{J}_N(\vec{r}) = \frac{1}{3m^2 k_B} \int_{\vec{p}} \tau_r(\vec{r}, \vec{p}) \vec{p}^2 \bar{f}^{(0)}(\vec{r}, \vec{p}) \left\{ \frac{\vec{p}^2}{2m} \vec{\nabla}_{\vec{r}} \left[\frac{1}{T(\vec{r})} \right] + \vec{\nabla}_{\vec{r}} \left[-\frac{\mu(\vec{r})}{T(\vec{r})} \right] \right\}, \quad (\text{VI.57a})$$

$$\vec{J}_E(\vec{r}) = \frac{1}{6m^3 k_B} \int_{\vec{p}} \tau_r(\vec{r}, \vec{p}) \vec{p}^4 \bar{f}^{(0)}(\vec{r}, \vec{p}) \left\{ \frac{\vec{p}^2}{2m} \vec{\nabla}_{\vec{r}} \left[\frac{1}{T(\vec{r})} \right] + \vec{\nabla}_{\vec{r}} \left[-\frac{\mu(\vec{r})}{T(\vec{r})} \right] \right\}. \quad (\text{VI.57b})$$

Note that since T and μ only depend on position, not on momentum, we may drop the \vec{r} subscripts from the $\vec{\nabla}$ operators without ambiguity.

⁽⁹⁵⁾ A simple mnemonic is to remember that it corresponds to the phase-space occupancy, as given by the Boltzmann factor, for a macrostate at temperature T and chemical potential μ .

VI.5.2b Kinetic and transport coefficients

In the language of Chapter II, the relations (VI.57) express the fluxes \vec{J}_N , \vec{J}_E as functions of the affinities $\vec{\nabla}(1/T)$ and $\vec{\nabla}(-\mu/T)$. Using the notation of Eq. (I.31), we may write these relations in the form

$$\begin{aligned}\vec{J}_N &= L_{NN}\vec{\nabla}\left(-\frac{\mu}{T}\right) + L_{NE}\vec{\nabla}\left(\frac{1}{T}\right), \\ \vec{J}_E &= L_{EN}\vec{\nabla}\left(-\frac{\mu}{T}\right) + L_{EE}\vec{\nabla}\left(\frac{1}{T}\right),\end{aligned}$$

with position-dependent kinetic coefficients L_{NN} , L_{NE} , L_{EN} and L_{EE} that can be directly read off Eqs. (VI.57):

$$\begin{cases} L_{NN}(\vec{r}) = \frac{1}{3m^2k_B} \int_{\vec{p}} \tau_r(\vec{r}, \vec{p}) \vec{p}^2 \bar{f}^{(0)}(\vec{r}, \vec{p}), \\ L_{EN}(\vec{r}) = L_{NE}(\vec{r}) = \frac{1}{6m^3k_B} \int_{\vec{p}} \tau_r(\vec{r}, \vec{p}) \vec{p}^4 \bar{f}^{(0)}(\vec{r}, \vec{p}), \\ L_{EE}(\vec{r}) = \frac{1}{12m^4k_B} \int_{\vec{p}} \tau_r(\vec{r}, \vec{p}) \vec{p}^6 \bar{f}^{(0)}(\vec{r}, \vec{p}). \end{cases} \quad (\text{VI.58})$$

In particular, we see that the Onsager reciprocal relation $L_{EN} = L_{NE}$ is fulfilled.

If we assume that the relaxation time is independent of position and momentum, $\tau_r(\vec{r}, \vec{p}) = \tau_r$, the integrals can be performed with the help of formula (A.1c) with $a = 1/2mk_B T(\vec{r})$ and $2n = 4, 6$ and 8 , and lead to

$$\begin{cases} L_{NN}(\vec{r}) = \frac{n(\vec{r})\tau_r T(\vec{r})}{m}, \\ L_{EN}(\vec{r}) = L_{NE}(\vec{r}) = \frac{5}{2} \frac{n(\vec{r})\tau_r T(\vec{r})}{m} k_B T(\vec{r}), \\ L_{EE}(\vec{r}) = \frac{35}{4} \frac{n(\vec{r})\tau_r T(\vec{r})}{m} [k_B T(\vec{r})]^2. \end{cases}$$

From these kinetic coefficients, one deduces expressions for various transport coefficients using relations which were derived in § I.2.3.

Thus, the diffusion coefficient of the particles of the Lorentz gas is related through Eq. (I.39c) to the kinetic coefficient L_{NN}

$$D = \frac{1}{T} \left(\frac{\partial \mu}{\partial n} \right)_T L_{NN} = \frac{\tau_r k_B T}{m},$$

where the second identity holds when the relaxation time is independent of position and momentum. In turn, inserting the above expressions of the kinetic coefficients in the heat conductivity (I.57) yields

$$\kappa = \frac{L_{NN}L_{EE} - L_{NE}L_{EN}}{T^2 L_{NN}} = \frac{5}{2} \frac{n k_B \tau_r}{m} k_B T.$$

For both transport coefficients, we now have expressions in terms of microscopic quantities.

VI.6 From Boltzmann to hydrodynamics

In § VI.3.1, we have seen that if $\chi(t, \vec{r}, \vec{p})$ is an additive collisional invariant, then the integral over momentum space of its product with the collision term on the right-hand side of the Boltzmann equation is vanishing, Eq. (VI.19). This property can then be used to derive local conservation laws.

Here, we wish to exploit this idea again, rewriting the conservation laws in an alternative way (§ VI.6.1). We then apply the new forms of the balance equations to solutions $\bar{f}(t, \vec{r}, \vec{p})$ to the Boltzmann equation written as in Eq. (VI.50) as the sum of a local equilibrium distribution and

a (hopefully small) deviation. This leads to relations between the fields (number density, mean velocity, temperature) entering the expression of the local equilibrium solution, which are exactly the laws governing the (thermo)dynamics of a perfect (§ VI.6.2) or a Newtonian (§ VI.6.3) fluid. In the latter case, we can compute the various transport coefficients in terms of microscopic quantities.

VI.6.1 Conservation laws revisited

If $\chi(t, \vec{r}, \vec{p})$ denotes a quantity, carried by the colliding particles, which is locally conserved in elastic collisions, then

$$\int_{\vec{p}} \chi(t, \vec{r}, \vec{p}) \left(\frac{\partial \bar{f}}{\partial t} \right)_{\text{coll}}(t, \vec{r}, \vec{p}) = 0,$$

where $(\partial \bar{f} / \partial t)_{\text{coll}}$ denotes the collision integral of the Boltzmann equation, computed with *any* single-particle distribution $\bar{f}(t, \vec{r}, \vec{p})$ —that is, \bar{f} need not be a solution to the Boltzmann equation.

Now, if \bar{f} is a solution to the Boltzmann equation, then the collision term equals the left-hand side of Eq. (VI.8), resulting in the identity

$$\int_{\vec{p}} \chi(t, \vec{r}, \vec{p}) \left[\frac{\partial \bar{f}(t, \vec{r}, \vec{p})}{\partial t} + \vec{v} \cdot \vec{\nabla}_{\vec{r}} \bar{f}(t, \vec{r}, \vec{p}) + \vec{F} \cdot \vec{\nabla}_{\vec{p}} \bar{f}(t, \vec{r}, \vec{p}) \right] = 0,$$

Dropping the dependence of the functions on their variables and performing some straightforward algebra, this can be rewritten as

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

In the fourth term, the velocity is independent of the position, and can thus be taken out of the gradient, $\vec{\nabla}_{\vec{r}} \cdot (\chi \vec{v}) = \vec{v} \cdot \vec{\nabla}_{\vec{r}} \chi$. Similarly, if we from now on restrict ourselves to momentum-independent forces, then in the sixth term one may write $\vec{\nabla}_{\vec{p}} \cdot (\chi \vec{F}) = \vec{F} \cdot \vec{\nabla}_{\vec{p}} \chi$. Eventually, the fifth term, which is trivially integrated, is zero, since the single-particle density vanishes when $|\vec{p}| \rightarrow \infty$.

Exchanging the order of the integration over \vec{p} with the differentiation with respect to t or \vec{r} in the first and third terms, and introducing the notation

$$\langle \cdot \rangle_{\vec{p}} \equiv \frac{1}{n(t, \vec{r})} \int_{\vec{p}} (\cdot) \bar{f}(t, \vec{r}, \vec{p}),$$

which clearly represents an \bar{f} -weighted average over momenta, the above identity becomes

$$\frac{\partial(n \langle \chi \rangle_{\vec{p}})}{\partial t} - n \left\langle \frac{\partial \chi}{\partial t} \right\rangle_{\vec{p}} + \vec{\nabla}_{\vec{r}} \cdot \langle n \chi \vec{v} \rangle_{\vec{p}} - n \langle \vec{v} \cdot \vec{\nabla}_{\vec{r}} \chi \rangle_{\vec{p}} - n \vec{F} \cdot \langle \vec{\nabla}_{\vec{p}} \chi \rangle_{\vec{p}} = 0. \quad (\text{VI.59})$$

Note that since the particle-number density n is independent of velocity, it can be moved inside or outside of averages over \vec{p} at will.

We can now re-express the balance equations (VI.20)–(VI.22) in an equivalent, yet slightly different manner.