

Linear response in the Lorentz Gas

P Crowley

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Abstract

In this note we review the Lorentz gas model of electrons in a solid, its dynamical equation and equilibrium properties. We then use this to derive transport coefficients for the Lorentz Gas within the single scattering time approximation. We then calculate the transport coefficients in two examples: the current response to an electrochemical force, and to a temperature gradient.

1 Intro

The Lorentz Gas (aka the Drude-Lorentz gas) is a statistical model in which electrons are treated as classical particles with momenta and positions.

The precise predictions of the model turn out to have certain limitations due to the omission of Pauli exclusion. Nevertheless, when this effect is included, many of the techniques here generalise directly, and yield Boltzmann transport theory.

The Lorentz Gas model makes several assumptions which are summarised here:

- **Classical electrons:** Assume a system of electrons each characterised by their position and momentum (\mathbf{r}, \mathbf{p}) each with energy $\varepsilon = p^2/2m$.
- **Spatial uniformity:** In the absence of externally imposed forces or temperature gradients, neither the system's dynamical evolution or equilibrium properties depend on position.
- **Local charge neutrality:** the electron density is independent of position *even away from equilibrium*. *Note that this does not require the system's state is translationally invariant*
- **Dynamics:** the dynamics has two contributions:
 - **Electron free propagation:** electrons propagate as free classical particles between scattering events.
 - **Scattering:** Single electron-single ion scattering only. Each scattering event involves one electron, and causes that electron's momentum to change. Further assumptions regarding the collision term are discussed in Sec. 2.2.2
- **Maxwell-Boltzmann equilibrium:** the system relaxes to the Maxwell-Boltzmann equilibrium state.
- **Single scattering time approximation:** when computing the linear response transport coefficients, to obtain tractable calculations, we also make the single scattering time approximation, discussed in greater detail in Sec. 2.4

2 The distribution function

2.1 Definition

In class we consider the Lorentz Gas. In this model the electrons are treated as classical particles with momenta and positions $(\mathbf{r}_i, \mathbf{p}_i)$. The central object of the theory is the distribution function

$$f(\mathbf{r}, \mathbf{p}) := \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{p} - \mathbf{p}_i) \quad (1)$$

from which the properties of the gas may be calculated by integration. For example the total number of particles N , the total energy U and the total momentum \mathbf{P} are given by

$$\begin{aligned} N &= \int d^3\mathbf{r} d^3\mathbf{p} f(\mathbf{r}, \mathbf{p}) \\ U &= \int d^3\mathbf{r} d^3\mathbf{p} f(\mathbf{r}, \mathbf{p}) \varepsilon(\mathbf{p}) \\ \mathbf{P} &= \int d^3\mathbf{r} d^3\mathbf{p} f(\mathbf{r}, \mathbf{p}) \mathbf{p} \end{aligned} \quad (2)$$

A generic physical observable A is similarly given by

$$A = \int d^3\mathbf{r} d^3\mathbf{p} f(\mathbf{r}, \mathbf{p}) A_{\text{el.}}(\mathbf{r}, \mathbf{p}) \quad (3)$$

where A is the experimentally observed value, and $A_{\text{el.}}(\mathbf{r}, \mathbf{p})$ the contribution to A from a single electron with state (\mathbf{r}, \mathbf{p}) .

2.2 Dynamical equation

In this section we derive the dynamical equation

$$\boxed{\frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f + \dot{\mathbf{p}} \cdot \nabla_{\mathbf{p}} f = \int d^3\mathbf{q} \left(W_{\mathbf{q} \rightarrow \mathbf{p}} f(\mathbf{r}, \mathbf{q}) - W_{\mathbf{p} \rightarrow \mathbf{q}} f(\mathbf{r}, \mathbf{p}) \right)}. \quad (4)$$

this equation consists of two terms: the LHS which describes the dynamics of free electrons, and the RHS which describes the effect of collisions.

Here we use the usual notation in which the subscripts on $\nabla_{\mathbf{r}}$ and $\nabla_{\mathbf{p}}$ denote the variable we differentiate with respect to

$$\nabla_{\mathbf{r}} f = \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z} \right), \quad \nabla_{\mathbf{p}} f = \left(\frac{\partial f}{\partial p_x}, \frac{\partial f}{\partial p_y}, \frac{\partial f}{\partial p_z} \right). \quad (5)$$

The LHS in Eq. (4) is referred to as the *free evolution* term, while the RHS is the *collision integral*. In this language the above may be written as

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial t} \Big|_{\text{free}} + \frac{\partial f}{\partial t} \Big|_{\text{coll.}} \quad (6)$$

where

$$\frac{\partial f}{\partial t} \Big|_{\text{free}} = -\dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f - \dot{\mathbf{p}} \cdot \nabla_{\mathbf{p}} f, \quad \frac{\partial f}{\partial t} \Big|_{\text{coll.}} = \int d^3\mathbf{q} \left(W_{\mathbf{q} \rightarrow \mathbf{p}} f(\mathbf{r}, \mathbf{q}) - W_{\mathbf{p} \rightarrow \mathbf{q}} f(\mathbf{r}, \mathbf{p}) \right). \quad (7)$$

We derive each of these in turn.

2.2.1 Free evolution term

In this section we derive $\frac{\partial f}{\partial t} \Big|_{\text{free}}$, the LHS of (4). We assume that the electrons undergo a simple free evolution

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}(\mathbf{p}_i), \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}(\mathbf{r}_i) \quad (8)$$

where for classical electrons we will always use $\mathbf{v} = \mathbf{p}/m$.

We begin by differentiating the definition of f (see Eq. (1)) using the product rule

$$\begin{aligned} \frac{df}{dt} \Big|_{\text{free}} &= \frac{d}{dt} \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{p} - \mathbf{p}_i) \\ &= \sum_i \left[\delta(\mathbf{p} - \mathbf{p}_i) \frac{d}{dt} \delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i) \frac{d}{dt} \delta(\mathbf{p} - \mathbf{p}_i) \right] \end{aligned} \quad (9)$$

We start by considering the first term in the bracket and applying the chain rule

$$\begin{aligned}\delta(\mathbf{p} - \mathbf{p}_i) \frac{d}{dt} \delta(\mathbf{r} - \mathbf{r}_i) &= \delta(\mathbf{p} - \mathbf{p}_i) \frac{d\mathbf{r}_i}{dt} \cdot \nabla_{\mathbf{r}_i} \delta(\mathbf{r} - \mathbf{r}_i) \\ &= \delta(\mathbf{p} - \mathbf{p}_i) \mathbf{v}(\mathbf{p}) \cdot \nabla_{\mathbf{r}_i} \delta(\mathbf{r} - \mathbf{r}_i) \\ &= -\delta(\mathbf{p} - \mathbf{p}_i) \mathbf{v}(\mathbf{p}) \cdot \nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_i)\end{aligned}\tag{10}$$

in the penultimate line we have used that evaluating \mathbf{v} at \mathbf{p} and \mathbf{p}_i are equivalent (since they are forced to be the same momentum by the δ -function), in the last line we have used that

$$\nabla_{\mathbf{r}_i} \delta(\mathbf{r} - \mathbf{r}_i) = -\nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_i)\tag{11}$$

where the sign change is generated by applying the chain rule. Applying both of these results we find

$$\sum_i \delta(\mathbf{p} - \mathbf{p}_i) \frac{d}{dt} \delta(\mathbf{r} - \mathbf{r}_i) = -\mathbf{v}(\mathbf{p}) \cdot \sum_i \delta(\mathbf{p} - \mathbf{p}_i) \nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_i) = -\mathbf{v}(\mathbf{p}) \cdot \nabla_{\mathbf{r}} f(\mathbf{r}, \mathbf{p})\tag{12}$$

Repeating the same analysis for the second term in Eq. (9) (the momentum derivative) we obtain

$$\boxed{\left. \frac{df}{dt} \right|_{\text{free}} = -\mathbf{v} \cdot \nabla_{\mathbf{r}} f - \mathbf{F} \cdot \nabla_{\mathbf{p}} f.}\tag{13}$$

2.2.2 Collision term

In this section we derive $\left. \frac{\partial f}{\partial t} \right|_{\text{coll.}}$, corresponding to the RHS of Eq. (4).

In addition to the free dynamics there will be processes in which electrons scatter from one state to another. For the collision term in the Lorentz gas we make several assumptions:

- We assume the collision term is describing processes where a single electron scatters off of an ion, and ignore processes that involve multiple electrons. Then we expect a collision integral that is linear in f , and does not include any higher power of f .
- We expect that a scattering event changes the momentum of a single electron, but not its position. That is, we expect only processes of the form

$$(\mathbf{r}, \mathbf{p}) \longrightarrow (\mathbf{r}, \mathbf{q})\tag{14}$$

where \mathbf{r} is unchanged.

- We expect the scattering to be uniform in space, i.e. that scattering events are occurring at the same rate everywhere in the metal.
- The scattering process should satisfy detailed balance. Detailed balance is a condition from statistical mechanics, any process that satisfies detailed balance will necessarily converge to a Boltzmann distribution. The technical requirement made by detailed balance is that $W_{\mathbf{p} \rightarrow \mathbf{q}}$ satisfies

$$\frac{W_{\mathbf{p} \rightarrow \mathbf{q}}}{W_{\mathbf{q} \rightarrow \mathbf{p}}} = e^{-\beta(\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{q}))}, \quad \varepsilon(\mathbf{p}) = \frac{p^2}{2m}\tag{15}$$

We describe these processes with a kernel W . Specifically: the expected number of electrons that scatters from the state (\mathbf{r}, \mathbf{p}) to the state (\mathbf{r}, \mathbf{q}) in a time interval of length dt is

$$[\# \text{ electrons that scatter from } (\mathbf{r}, \mathbf{p}) \rightarrow (\mathbf{r}, \mathbf{q}) \text{ in interval } dt] = W_{\mathbf{p} \rightarrow \mathbf{q}} f(\mathbf{r}, \mathbf{p}) dt.\tag{16}$$

Incorporating this into the dynamics we obtain the desired result

$$\boxed{\left. \frac{df(\mathbf{r}, \mathbf{p})}{dt} \right|_{\text{coll.}} = \int d^3 \mathbf{q} \left(W_{\mathbf{q} \rightarrow \mathbf{p}} f(\mathbf{r}, \mathbf{q}) - W_{\mathbf{p} \rightarrow \mathbf{q}} f(\mathbf{r}, \mathbf{p}) \right).}\tag{17}$$

where the first term describes the increase in $f(\mathbf{r}, \mathbf{p})$ due to electrons scattered into the state (\mathbf{r}, \mathbf{p}) from all other states, and the second term describes the decrease in $f(\mathbf{r}, \mathbf{p})$ due to electrons scattered out of (\mathbf{r}, \mathbf{p}) into any other state.

2.3 Equilibrium

The Lorentz gas assumes a Maxwell-Boltzmann equilibrium in the absence of any external forces $\mathbf{F} = 0$. This corresponds to an equilibrium distribution

$$f_0(\mathbf{r}, \mathbf{p}) = \frac{\bar{n} e^{-\beta \varepsilon(\mathbf{p})}}{(2\pi m k_B T)^{3/2}} \quad (18)$$

where $\bar{n} = N/V$ is the electron density, and $\varepsilon(\mathbf{p}) = p^2/(2m)$ as before. Notably this solution is spatially independent $\nabla_{\mathbf{r}} f_0 = 0$.

To see this is a solution to the equation of motion, we can substitute (18), $\nabla_{\mathbf{r}} f_0 = 0$, and $\mathbf{F} = 0$ into (4), which yields

$$\frac{\partial f}{\partial t} = \frac{\bar{n}}{(2\pi m k_B T)^{3/2}} \int d^3 \mathbf{q} \left(W_{\mathbf{q} \rightarrow \mathbf{p}} e^{-\beta \varepsilon(\mathbf{q})} - W_{\mathbf{p} \rightarrow \mathbf{q}} e^{-\beta \varepsilon(\mathbf{p})} \right). \quad (19)$$

The two terms in the integrand are equal by detailed balance (see Eq. (15)), and hence $\frac{\partial f}{\partial t} = 0$ as required for an equilibrium state.

2.4 Single scattering time approximation

In this section we discuss the single scattering time approximation, a useful simplifying assumption. The single scattering time approximation assumes that relaxation towards equilibrium is characterised by a single timescale τ . Specifically it assumes a simple form for the scattering kernel $W_{\mathbf{p} \rightarrow \mathbf{q}}$ given by

$$W_{\mathbf{p} \rightarrow \mathbf{q}} = \frac{f_0(\mathbf{r}, \mathbf{q})}{\bar{n} \tau} \quad (20)$$

where, as before $\bar{n} = N/V$ is the mean electron density.

The single scattering time approximation causes the collision term to simplify dramatically

$$\left. \frac{df(\mathbf{r}, \mathbf{p})}{dt} \right|_{\text{coll.}} = \int d^3 \mathbf{q} \left(W_{\mathbf{q} \rightarrow \mathbf{p}} f(\mathbf{r}, \mathbf{q}) - W_{\mathbf{p} \rightarrow \mathbf{q}} f(\mathbf{r}, \mathbf{p}) \right) = \frac{f_0(\mathbf{r}, \mathbf{p}) - f(\mathbf{r}, \mathbf{p})}{\tau} \quad (21)$$

Here we have used that charge neutrality requires that the Lorentz gas is uniform

$$\int d^3 \mathbf{p} f(\mathbf{r}, \mathbf{p}) = \bar{n}. \quad (22)$$

2.5 Linear response transport coefficients

Linear response analysis gives a way to determine the values of observables \mathbf{A} when the system is perturbed away from equilibrium by some generalised force \mathbf{X} . A useful standard example to keep in mind is the case of studying the electric current \mathbf{j} in response to an electrochemical field \mathcal{E} , in this case

$$\mathbf{A}(\mathbf{r}, \mathbf{p}) = \mathbf{j}_{\text{el.}} = -\frac{e\mathbf{p}}{m}, \quad \mathbf{X} = \mathcal{E}. \quad (23)$$

The linear response coefficients are then defined by

$$L_{\alpha\beta} = \left. \frac{\partial A_{\alpha}}{\partial X_{\beta}} \right|_{\mathbf{X}=0} \quad (24)$$

where the subscripts α, β index the components of the vectors \mathbf{A} and \mathbf{X} .

$$\mathbf{A} = (A_x, A_y, A_z), \quad \mathbf{X} = (X_x, X_y, X_z) \quad (25)$$

The linear response coefficients determine the value of A for small values of X

$$\mathbf{A} = \mathbf{A}_0 + L\mathbf{X} + O(X^2) \quad (26)$$

where here $\mathbf{A}_0 = \mathbf{A}|_{\mathbf{X}=0}$ is the zero field value of A , and L is the matrix with elements $L_{\alpha\beta}$.

The goal of the linear response analysis is to give a framework for determining the value of the matrix L . We proceed as follows: first we substitute the definition of A_α

$$L_{\alpha\beta} = \left. \frac{\partial A_\alpha}{\partial X_\beta} \right|_{\mathbf{X}=0} = \int d^3\mathbf{r} d^3\mathbf{p} A_{\text{el.},\alpha}(\mathbf{r}, \mathbf{p}) \left. \frac{\partial f}{\partial X_\beta} \right|_{\mathbf{X}=0}. \quad (27)$$

Where in the second line we have used that the force \mathbf{X} only alters the distribution function f . In order to proceed we must calculate $\left. \frac{\partial f}{\partial X_\beta} \right|_{\mathbf{X}=0}$. We discuss two simple cases: (1) a uniform external field, and (2) a uniform temperature gradient.

For the case of the electrical current response ($A_{\text{el.},\alpha}(\mathbf{r}, \mathbf{p}) = -e\mathbf{p}/m$), we find

$$\mathbf{j} = \sigma \left(\boldsymbol{\mathcal{E}} - \frac{k_B}{e} \nabla T \right), \quad \sigma = \frac{\bar{n}e^2\tau}{m} \quad (28)$$

2.5.1 Uniform electrochemical field $\mathbf{X} = \boldsymbol{\mathcal{E}}$

We start from Eq. (4), and use the condition for a stationary distribution ($\frac{\partial f}{\partial t} = 0$), and use the single scattering time approximation (21) to yield

$$\frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} f - e\boldsymbol{\mathcal{E}} \cdot \nabla_{\mathbf{p}} f = \frac{f_0 - f}{\tau}, \quad (29)$$

here we have used $\dot{\mathbf{r}} = \mathbf{p}/m$ and $\dot{\mathbf{p}} = -e\boldsymbol{\mathcal{E}}$. We then differentiate this with respect to \mathcal{E}_β to obtain

$$\frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} \frac{\partial f}{\partial \mathcal{E}_\beta} - e \frac{\partial f}{\partial p_\beta} - e\boldsymbol{\mathcal{E}} \cdot \nabla_{\mathbf{p}} \frac{\partial f}{\partial \mathcal{E}_\beta} = -\frac{1}{\tau} \frac{\partial f}{\partial \mathcal{E}_\beta} \quad (30)$$

Setting $\boldsymbol{\mathcal{E}} = 0$ simplifies things dramatically

$$-e \frac{\partial f_0}{\partial p_\beta} = -\frac{1}{\tau} \frac{\partial f}{\partial \mathcal{E}_\beta} \Big|_{\boldsymbol{\mathcal{E}}=0} \quad (31)$$

We note in particular that the $\nabla_{\mathbf{r}}$ term has gone, as, at equilibrium f is spatially uniform. Simplifying this relation further, using (18) we have

$$\left. \frac{\partial f}{\partial \mathcal{E}_\beta} \right|_{\boldsymbol{\mathcal{E}}=0} = e\tau \frac{\partial f_0}{\partial p_\beta} = -\frac{e\tau p_\beta}{mk_B T} f_0 \quad (32)$$

Using this result we obtain

$$L_{\alpha\beta} = -\frac{e\tau}{mk_B T} \int d^3\mathbf{r} d^3\mathbf{p} A_{\text{el.},\alpha}(\mathbf{r}, \mathbf{p}) p_\beta f_0 \quad (33)$$

For e.g. the case of electric current response $A_{\text{el.},\alpha}(\mathbf{r}, \mathbf{p}) = j_{\text{el.},\alpha}/V = -ep_\alpha/(mV)$, these integrals can be performed directly

$$\begin{aligned} L_{\alpha\beta} &= \frac{e^2\tau}{m^2 k_B T V} \int d^3\mathbf{r} d^3\mathbf{p} p_\alpha p_\beta f_0 \\ &= \frac{e^2\tau}{m^2 k_B T V} \frac{1}{3} \delta_{\alpha\beta} \int d^3\mathbf{r} d^3\mathbf{p} p^2 f_0 \\ &= \frac{e^2\tau}{m^2 k_B T V} \frac{1}{3} \delta_{\alpha\beta} 3\bar{n} m k_B T V \\ &= \frac{\bar{n}e^2\tau}{m} \delta_{\alpha\beta} \end{aligned} \quad (34)$$

2.5.2 Uniform temperature gradient $\mathbf{X} = -\nabla T$

In the case of uniform temperature gradient we need to be careful: T has explicit position dependence it will get picked up by spatial derivatives $\nabla_{\mathbf{r}}$. We note that the temperature may be written as

$$T(\mathbf{r}) = T_0 + \mathbf{r} \cdot \nabla T = T_0 - \mathbf{r} \cdot \mathbf{X}. \quad (35)$$

We start from Eq. (4), and use the condition for a stationary distribution ($\frac{\partial f}{\partial t} = 0$), and use the single scattering time approximation (21) to yield

$$\frac{1}{m} \mathbf{p} \cdot \nabla_{\mathbf{r}} f = \frac{f_0 - f}{\tau}. \quad (36)$$

here we have used $\dot{\mathbf{r}} = \mathbf{p}/m$ and that a temperature gradient does not place external forces on the electrons during free evolution $\dot{\mathbf{p}} = \mathbf{0}$. We note the relation

$$\nabla_{\mathbf{r}} f = \nabla_{\mathbf{r}} T \frac{\partial f}{\partial T} = -\mathbf{X} \frac{\partial f}{\partial T} \quad (37)$$

We then use Eq. (37) and differentiate (36) with respect to $X_\beta = -\partial T / \partial r_\beta$ to obtain

$$-\frac{1}{m} p_\beta \frac{\partial f}{\partial T} + \frac{1}{m} \mathbf{p} \cdot \mathbf{X} X_\beta \frac{\partial^2 f}{\partial T^2} = -\frac{1}{\tau} \frac{\partial f}{\partial X_\beta}. \quad (38)$$

Then setting $\mathbf{X} = \mathbf{0}$ simplifies this to

$$-\frac{1}{m} p_\beta \frac{\partial f_0}{\partial T} = -\frac{1}{\tau} \frac{\partial f}{\partial X_\beta} \Big|_{\mathbf{X}=0}. \quad (39)$$

We rearrange and then use the definition of f_0 (Eq. (18))

$$\frac{\partial f}{\partial X_\beta} \Big|_{\mathbf{X}=0} = \frac{\tau}{m} p_\beta \frac{\partial f_0}{\partial T} = \frac{\tau}{m} p_\beta \frac{1}{k_B T^2} \left(\frac{p^2}{2m} - \frac{3}{2} k_B T \right) f_0 \quad (40)$$

which yields a linear response coefficient

$$L_{\alpha\beta} = \int d^3\mathbf{r} d^3\mathbf{p} A_{\text{el.},\alpha}(\mathbf{r}, \mathbf{p}) \frac{\partial f}{\partial X_\beta} \Big|_{\mathbf{X}=0} = \frac{\tau}{m k_B T^2} \int d^3\mathbf{r} d^3\mathbf{p} A_{\text{el.},\alpha}(\mathbf{r}, \mathbf{p}) p_\beta \left(\frac{p^2}{2m} - \frac{3}{2} k_B T \right) f_0 \quad (41)$$

For e.g. the case of electric current response $A_{\text{el.},\alpha}(\mathbf{r}, \mathbf{p}) = j_{\text{el.},\alpha}/V = -ep_\alpha/(mV)$, we may then calculate the linear response coefficient

$$\begin{aligned} L_{\alpha\beta} &= -\frac{e\tau}{m^2 k_B T^2 V} \int d^3\mathbf{r} d^3\mathbf{p} p_\alpha p_\beta \left(\frac{p^2}{2m} - \frac{3}{2} k_B T \right) f_0 \\ &= -\frac{e\tau}{m^2 k_B T^2 V} \frac{1}{3} \delta_{\alpha\beta} \int d^3\mathbf{r} d^3\mathbf{p} p^2 \left(\frac{p^2}{2m} - \frac{3}{2} k_B T \right) f_0 \\ &= -\frac{e\tau}{m^2 k_B T^2 V} \frac{1}{3} \delta_{\alpha\beta} 3\bar{n}m(k_B T)^2 V \\ &= -\frac{\bar{n}e^2\tau}{m} \frac{k_B}{e} \delta_{\alpha\beta} \end{aligned} \quad (42)$$