Lecture Note for the Boltzmann transport theory

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[2]This note is mainly got from Dr. Weiwei Chen

What is the core of statistical mechanics? What is the goal of statistical mechanics?

In my own understanding, statistical mechanics is to understand the macroscopic phenomenon in thermodynamics, from an angle of microscopic view based on the kinetic theory and probability assumption. According to the different kinetic theories, we have classical statistical mechanics and quantum statistical mechanics. The so-called classical statistical mechanics is based on the Newton's law, while the quantum statistical mechanics is based on the quantum mechanical law (please think about the examples we shown in previous chapters).

In a another way, statistical mechanics can be mainly divided into equilibrium statistics and non-equilibrium physics. The equilibrium part is widely accepted by the community, and the related theories are almost well done. Most of this lecture note focus on this part. In contrast, the non-equilibrium statistical mechanics is more challenging, where many topics are still under debate so far, such as transport processes, the process toward equilibrium. In this chapter, we will try to introduce some topic related to non-equilibrium physics, following the Boltzmann.

Think about the density inhomogeneous fluid, the density inhomogeneity leads to the diffusion of particles which drives the system towards homogeneity. The second-law in thermodynamics states that this diffusion process is irreversible, i.e. there is no way to reverse this diffusion process in real life. The similar example is the heat transport when the temperature is non-unifrom. Please note that, irreversibility in thermodynamic processes is at odd with the basic kinetic laws in statistical mechanics, because in kinetic theories the arrow of time is reversible. (If you check it in detail, you will find the second-law in thermodynamics has been questioned and attacked by many people.) How to understand this fundamental discrepancy? Is this a challenge to the statistical mechanics?

The first mechanical argument of the Kinetic theory of gases that molecular collisions entail an equalization of temperatures and hence a tendency towards equilibrium was due to James Clerk Maxwell in 1860; Ludwig Boltzmann with his H-theorem of 1872 also argued that due to collisions gases should over time tend toward the MaxwellBoltzmann distribution. Boltzmann believed that statistical mechanics gives an explanation for the second law by postulating that a material is composed of atoms and molecules which are in constant motion. Due to this, Boltzmann was attacked by the world since then. He spent all his life to fight with the other people on the so-called H-theorem. Finally, he ended his life by suicide in 1906. It is sad that such great people left the world, but his scientific ideas are still with us: Boltzmann distribution, Boltzmann machine, Boltzmann equation, Boltzmann constant.

Although the debate on the H-theorem remains, it has been accepted by most of the people. In this chapter, we will see how the H-theorem works. H-theorem provides a way to understand the irreversibility in the second-law of thermodynamics, which bridges the kinetic theory and thermodynamics.

PRELIMINARY

Liouville's Theorem

Consider a Hamiltonian dynamical system with canonical coordinates q_i and conjugate momenta p_i, where $i = 1, \ldots, n$ and n is the degrees of freedom of the system. Then the phase space distribution $\rho(q_1, \cdots, q_n, p_1, \cdots, p_n, t)$ determines the probability $\rho(q_1, \cdots, q_n, p_1, \cdots, p_n, t)dq_1 \cdots dq_n dp_1 \cdots dp_n$ that the system will be found in the infinitesimal phase space volume $d\Omega = dq_1 \cdots dq_n dp_1 \cdots dp_n$. The Liouville equation governs the evolution of $\rho(q_1, \cdots, q_n, p_1, \cdots, p_n)$ in time t:

$$\frac{d\rho(q_1, \cdots, q_n, p_1, \cdots, p_n, t)}{dt} = \frac{\partial \rho}{\partial t} + \boldsymbol{v} \cdot \nabla \rho = 0 \tag{.1}$$

where $\boldsymbol{v} = (\dot{q}_1, \cdots, \dot{q}_n, \dot{p}_1, \cdots, \dot{p}_n)$ and $\nabla = (\partial_{q_1}, \cdots, \partial_{q_n}, \partial_{p_1}, \cdots, \partial_{p_n})$ are the velocity and gradient operators of a state point in phase space. If one regard the motion of the ensemble in the phase space as a "fluid", then Liouville's theorem indicates that this "fluid" is incompressible. The condition for Liouville's theorem to hold is that Hamiltonian is not explicitly time-dependent (steady or stationary state).

Proof: From the continuity equation of state density, one can get

$$0 = \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = \frac{\partial \rho}{\partial t} + \boldsymbol{v} \cdot \nabla \rho + \rho(\nabla \cdot \boldsymbol{v}) = \frac{d\rho}{dt} + \rho(\nabla \cdot \boldsymbol{v}) \tag{.2}$$

For the conservative Hamiltonian system (not explicitly time-dependent), the state density flow in phase space is incompressible

$$\nabla \cdot \boldsymbol{v} = \sum_i \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \sum_i \frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial q_i \partial p_i} = 0 \tag{.3}$$

due to the canonical relations

$$\begin{aligned} \dot{q}_i &= \frac{1}{i\hbar}[q_i, H] = \frac{1}{i\hbar}(i\hbar)\frac{\partial H}{\partial p_i} = \frac{\partial H}{\partial p_i} && (.4) \\ \dot{p}_i &= \frac{1}{i\hbar}[p_i, H] = \frac{1}{i\hbar}(-i\hbar)\frac{\partial H}{\partial q_i} = -\frac{\partial H}{\partial q_i} && (.5) \end{aligned}$$

Under the canonical relations, one can rewrite the Liouville equation in another form

$$\frac{\partial \rho}{\partial t} + \sum_i \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} = \frac{\partial \rho}{\partial t} + iL^N \rho = 0 \qquad (.6)$$

where $L^N = -i\sum_{i=1}^{N} \frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i}$

Liouville's theorem applies only to Hamiltonian systems. The Hamiltonian is allowed to vary with time, and there are no restrictions regarding how strongly the degrees of freedom are coupled. Liouville's theorem is true even if the Hamiltonian is time dependent.

BBGKY Hierarchy

The observables we deal with in physics are general one- and two-body operators, and to find their expectation values we only need reduced one- and two-body probability densities and not the full N-body probability density. As mentioned above, the probability density satisfies Liouville equation:

$$\frac{\partial \rho(\boldsymbol{r}_1, \boldsymbol{k}_1, \cdot, \boldsymbol{r}_N, \boldsymbol{k}_N, t)}{\partial t} + \boldsymbol{v}_{1,\cdots,N} \cdot \nabla_{1,\cdots,N}\rho(\boldsymbol{r}_1, \boldsymbol{k}_1, \cdot, \boldsymbol{r}_N, \boldsymbol{k}_N, t) = 0 \qquad (.7)$$

where $\boldsymbol{v}_{1,\cdots,N} = (\dot{\boldsymbol{r}}_1, \cdots, \dot{\boldsymbol{r}}_N, \dot{\boldsymbol{k}}_1, \cdots, \dot{\boldsymbol{k}}_N)$ and $\nabla_{1,\cdots,N} = (\nabla_{\boldsymbol{r}_1}, \cdots, \nabla_{\boldsymbol{r}_N}, \nabla_{\boldsymbol{k}_1}, \cdots, \nabla_{\boldsymbol{k}_N})$. A reduced probability density, $f_s(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_s, \boldsymbol{k}_1, \cdots, \boldsymbol{k}_s, t)$, is defined as

$$f_s(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_s, \boldsymbol{k}_1, \cdots, \boldsymbol{k}_s, t) = \frac{N!}{(N-s)!}\int \cdots \int d\boldsymbol{r}_{s+1} d\boldsymbol{k}_{s+1} \cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \rho(\boldsymbol{r}_1, \boldsymbol{k}_1, \cdot, \boldsymbol{r}_N, \boldsymbol{k}_N, t) \qquad (.8)$$

Integrating the Eq. (.7) over $d\boldsymbol{r}_{s+1} d\boldsymbol{k}_{s+1} \cdots d\boldsymbol{r}_N d\boldsymbol{k}_N$, one get

$$\begin{aligned} 0 =& \frac{\partial f_s}{\partial t} + \frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1} d\boldsymbol{k}_{s+1} \cdots d\boldsymbol{r}_N d\boldsymbol{k}_N (\boldsymbol{v}_{1,\cdots,s} \cdot \nabla_{1,\cdots,s} + \boldsymbol{v}_{s+1,\cdots,N} \cdot \nabla_{s+1,\cdots,N})\rho \\ =& \frac{\partial f_s}{\partial t} + \frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1} d\boldsymbol{k}_{s+1} \cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \boldsymbol{v}_{1,\cdots,s} \cdot \nabla_{1,\cdots,s}\rho + \nabla_{s+1,\cdots,N} \cdot (\boldsymbol{v}_{s+1,\cdots,N}\rho) \\ & - \rho(\nabla_{s+1,\cdots,N} \cdot \boldsymbol{v}_{s+1,\cdots,N}) \\ =& \frac{\partial f_s}{\partial t} + \frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1} d\boldsymbol{k}_{s+1} \cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \boldsymbol{v}_{1,\cdots,s} \cdot \nabla_{1,\cdots,s}\rho \end{aligned} \qquad (.9)$$

where $\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \nabla_{s+1,\cdots,N}\cdot(\boldsymbol{v}_{s+1,\cdots,N}\rho)=0$ since the probability density vanishes at the boundary of the domain of definition and $\nabla_{s+1,\cdots,N}\cdot\boldsymbol{v}_{s+1,\cdots,N}=0$ due to the incompressibility.

Then one introduce the conserved Hamiltonian as

$$H = T + V^{(1)} + V^{(2)} + \cdots \tag{.10}$$

where $T=\sum_i T(\boldsymbol{k}_i)=\sum_i T_i$ denotes the kinetic energy. $V^{(1)}$ and $V^{(2)}$ represent single- and two-body potentials in the form of

$$V^{(1)}=\sum_{i=1}^{N} U(\boldsymbol{r}_i)=\sum_i U_i; \quad \text{and} \quad V^{(2)}=\sum_{i=1}^{N}\sum_{j\neq i}^{N} V(|\boldsymbol{r}_i-\boldsymbol{r}_j|)=\sum_{i=1}^{N}\sum_{j\neq i}^{N} V_{ij} \tag{.11}$$

We ignore ther interactions involving more than two particles.

Single-body potential If there only exists single-particle potential $V^{(1)}$, the $\boldsymbol{v}_{1,\cdots,s}$ will be independent with $(\boldsymbol{r}_{s+1},\cdots,\boldsymbol{r}_N,\boldsymbol{k}_{s+1},\cdots,\boldsymbol{k}_N)$, so that

$$\begin{aligned}
0 =& \frac{\partial f_s}{\partial t} + \frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \boldsymbol{v}_{1,\cdots,s}\cdot\nabla_{1,\cdots,s}\rho \\
=& \frac{\partial f_s}{\partial t} + (\boldsymbol{v}_{1,\cdots,s}\cdot\nabla_{1,\cdots,s})\frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\cdots d\boldsymbol{r}_N d\boldsymbol{k}_N\rho \\
=& \frac{\partial f_s}{\partial t} + \boldsymbol{v}_{1,\cdots,s}\cdot\nabla_{1,\cdots,s} f_s
\end{aligned} \tag{.12}$$

Thus, the equation of motion of the reduced probability density, which is also called **kinetic equation**, is obtained as

$$\frac{\partial f_1(\boldsymbol{r},\boldsymbol{k},t)}{\partial t} + \dot{\boldsymbol{r}}\cdot\nabla_{\boldsymbol{r}} f_1(\boldsymbol{r},\boldsymbol{k},t) + \dot{\boldsymbol{k}}\cdot\nabla_{\boldsymbol{k}} f_1(\boldsymbol{r},\boldsymbol{k},t) = 0 \tag{.13}$$

Two-body potential In the following, we take the two-body potential $V^{(2)}$ into account.

$$
\begin{aligned}
0 =& \frac{\partial f_s}{\partial t} + \frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \boldsymbol{v}_{1,\cdots,s}\cdot\nabla_{1,\cdots,s}\rho \\
=& \frac{\partial f_s}{\partial t} + \frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \sum_{i=1}^{s}\frac{\partial H}{\partial \boldsymbol{k}_i}\cdot\frac{\partial \rho}{\partial \boldsymbol{r}_i} - \frac{\partial H}{\partial \boldsymbol{r}_i}\cdot\frac{\partial \rho}{\partial \boldsymbol{k}_i} \\
=& \frac{\partial f_s}{\partial t} + \frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \times \\
& \left[\sum_{i=1}^{s}\frac{\partial T_i}{\partial \boldsymbol{k}_i}\cdot\frac{\partial \rho}{\partial \boldsymbol{r}_i} - \sum_{i=1}^{s}\sum_{j\neq i}^{s}\frac{\partial V_{ij}}{\partial \boldsymbol{r}_i}\cdot\frac{\partial \rho}{\partial \boldsymbol{k}_i} - \sum_{i=1}^{s}\sum_{j=s+1}^{N}\frac{\partial V_{ij}}{\partial \boldsymbol{r}_i}\cdot\frac{\partial \rho}{\partial \boldsymbol{k}_i}\right] \qquad (.14) \\
=& \frac{\partial f_s}{\partial t} + \boldsymbol{v}_{1,\cdots,s}\cdot\nabla_{1,\cdots,s}f_s - \frac{N!}{(N-s)!}\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \sum_{i=1}^{s}\sum_{j=s+1}^{N}\frac{\partial V_{ij}}{\partial \boldsymbol{r}_i}\cdot\frac{\partial \rho}{\partial \boldsymbol{k}_i} \\
=& \frac{\partial f_s}{\partial t} + \boldsymbol{v}_{1,\cdots,s}\cdot\nabla_{1,\cdots,s}f_s - \frac{N!(N-s)}{(N-s)!}\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\cdots d\boldsymbol{r}_N d\boldsymbol{k}_N \sum_{i=1}^{s}\frac{\partial V_{i,s+1}}{\partial \boldsymbol{r}_i}\cdot\frac{\partial \rho}{\partial \boldsymbol{k}_i} \\
=& \frac{\partial f_s}{\partial t} + \boldsymbol{v}_{1,\cdots,s}\cdot\nabla_{1,\cdots,s}f_s - \sum_{i=1}^{s}\int d\boldsymbol{r}_{s+1}d\boldsymbol{k}_{s+1}\frac{\partial V_{i,s+1}}{\partial \boldsymbol{r}_i}\cdot\frac{\partial f_{s+1}}{\partial \boldsymbol{k}_i}
\end{aligned}
$$

Thus, the equation of motion of the reduced probability density, which is also called **kinetic equation**, is obtained as

$$
\frac{\partial f_1(\boldsymbol{r},\boldsymbol{k},t)}{\partial t} + \dot{\boldsymbol{r}}\cdot\nabla_{\boldsymbol{r}}f_1(\boldsymbol{r},\boldsymbol{k},t) + \dot{\boldsymbol{k}}\cdot\nabla_{\boldsymbol{k}}f_1(\boldsymbol{r},\boldsymbol{k},t) = \int d\boldsymbol{r}'d\boldsymbol{k}'\frac{\partial V(|\boldsymbol{r}-\boldsymbol{r}'|)}{\partial \boldsymbol{r}'}\cdot\frac{\partial}{\partial \boldsymbol{k}'}f_2(\boldsymbol{r},\boldsymbol{k},\boldsymbol{r}',\boldsymbol{k}',t) \qquad (.15)
$$

Noticed that, for the many-body potential, the equations of motion for the reduced probability densities form a hierarchy of equations called the **BBGKY hierarchy** (after Born, Bogoliubov, Green, Kirkwood, Yvon, who discovered it). To deal with this kinetic equation, the hierarchy should be truncated approximately.

A simple way is, by assumption, $f_2(\boldsymbol{r},\boldsymbol{k},\boldsymbol{r}',\boldsymbol{k}',t)$ can be expressed in terms of $f_1(\boldsymbol{r},\boldsymbol{k},t)$:

$$
\rho_2(r_1,v_1;r_2,v_2;t) = \rho_1(r_1,v_1,t)\rho_1(r_2,v_2,t) \qquad (.16)
$$

which means two particles are independent, i.e. molecule chaos assumption (usually it holds for dilute gas).

Master Equation

A fundamental study of the time evolution of probability distributions is the Markov approximation.

$P_1(y_1, t_1)$ is the **probability density** that the stochastic variable Y has value y_1 at time t_1; $P_{1|1}(y_1, t_1|y_2, t_2)$ is the **conditional probability density** for the stochastic variable Y to have value y_2 at time t_2 given that it has value y_1 at time t_1; $P_n(y_1, t_1; y_2, t_2; \cdots ; y_n, t_n)$ is the **joint probability density** that the stochastic variable Y have value y_1 at time t_1, y_2 at time t_2, ..., y_n at time t_n; $P_{k|l}(y_1, t_1; \cdots ; y_k, t_k|y_{k+1}, t_{k+1}; \cdots ; y_{k+l}, t_{k+l})$ is the **joint conditional probability density** that the stochastic variable Y has values $(y_{k+1}, t_{k+1}; \cdots ; y_{k+l}, t_{k+l})$ given that $(y_1, t_1; \cdots ; y_k, t_k)$ are fixed.

If the stochastic variable has memory only of its immediate past, which is called the **Markov process**, the joint conditional probability density must have the form

$$P_{n-1|1}(y_1, t_1; \cdots ; y_{n-1}, t_{n-1}|y_n, t_n) = P_{1|1}(y_{n-1}, t_{n-1}|y_n, t_n) \tag{.17}$$

where $t_1 < t_2 < \cdots < t_n$. The conditional probability density $P_{1|1}(y_{n-1}, t_{n-1}|y_n, t_n)$ in this identity is called the **transition probability**. The Markov character is exhibited by the fact that the probability of the two successive steps is the product of the probability of the individual steps. The successive steps are statistically independent. Two quantities $P(y_1, t_1)$ and $P_{1|1}(y_1, t_1|y_2, t_2)$ completely determine the evolution of a Markov chain. The time evolution of such processes is governed by the **master equation**

$$\frac{\partial P_1(n, t)}{\partial t} = \sum_m [P_1(m, t)W_{m,n} - P_1(n, t)W_{n,m}] \tag{.18}$$

which gives the rate of change of the probability $P_1(n, t)$ due to transitions into the state n from all others states (first term on the right) and due to transitions out of state n into all others states (second term on the right). Here, one assume that stochastic variable Y has discrete realizations $\{y(n)\}$ and the transition matrix $W_{m,n}$ is independent of time.

BOLTZMANN EQUATION

The aim of kinetic theory is to find the distribution function $f(\boldsymbol{r},\boldsymbol{k},t)$ for a given system with interactions. We would expect the form of $f(\boldsymbol{r},\boldsymbol{k},t)$ contains all the equilibrium properties of the system. One such kind of kinetic theory is the Boltzman equation. The Boltzmann equation can be derived from the BBGKY hierarchy, as shown above. That is, we truncate the BBGKY hierarchy up to two-body interaction and neglect higher body interactions, and we assume the two body-interaction induce a collision term in the equation. In short, the function to be determined by employing Boltzmann equation is a quantity: the one-particle reduced density, or one-particle non-equilibrium distribution function, $f(\boldsymbol{r},\boldsymbol{p},t)$. Given the phase-space volume $d\boldsymbol{r}d\boldsymbol{p}$, the quantity $f(\boldsymbol{r},\boldsymbol{p},t)d\boldsymbol{r}d\boldsymbol{p}$ means average number of particles that at time t is found in a phase-space volume $d\boldsymbol{r}d\boldsymbol{p}$, around the phase-space point $\boldsymbol{r},\boldsymbol{p}$. The total number of particles N is therefore

$$N=\int f(\boldsymbol{r},\boldsymbol{k},t)d\boldsymbol{r}d\boldsymbol{p}, \tag{.19}$$

where the integral is over all allowed space and momenta. Notable that the distribution function is not normalized. This is different from the probability density $\rho_s=\rho(\{q_i\},\{q_i\},t)$, which is normalized $\sum_s\rho_s=1$. In the framework of the classical Hamilton theory, the Boltzmann equation can be given by

$$\frac{df(\boldsymbol{r},\boldsymbol{p},t)}{dt}=\frac{\partial f}{\partial t}+\frac{d\boldsymbol{r}}{dt}\cdot\nabla_{\boldsymbol{r}}f+\frac{d\boldsymbol{p}}{dt}\cdot\nabla_{\boldsymbol{p}}f=\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} \tag{.20}$$

or

$$\frac{\partial f}{\partial t}+\boldsymbol{v}\cdot\nabla_{\boldsymbol{r}}f+\boldsymbol{F}\cdot\nabla_{\boldsymbol{p}}f=\frac{\partial f}{\partial t}+(\nabla_{\boldsymbol{p}}H)\cdot\nabla_{\boldsymbol{r}}f+(-\nabla_{\boldsymbol{r}}H)\cdot\nabla_{\boldsymbol{p}}f=\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} \tag{.21}$$

where we have used the canonical relations $\dot{q}_i=\frac{\partial H}{\partial p_i}$ and $\dot{p}_i=-\frac{\partial H}{\partial q_i}$.

The Boltzmann equation implies the change of distribution function through various mechanisms: intrinsic $\frac{\partial f}{\partial t}$, diffusion $\frac{\partial f}{\partial t}\big|_{\text{diff}}=\boldsymbol{v}\cdot\nabla_{\boldsymbol{r}}f$, external fields $\frac{\partial f}{\partial t}\big|_{\text{field}}=\boldsymbol{F}\cdot\nabla_{\boldsymbol{p}}f$, and collisions $\frac{\partial f}{\partial t}\big|_{\text{coll}}$. While the former three mechanisms describe the dynamics of a single particle, the last one denotes the influence of the other particles. The diffusion term means, if f varies from point to point, there will be a tendency for it to change with time due to its spatial velocity. The combination of the intrinsic and diffusion terms, $(\frac{\partial}{\partial t}+\boldsymbol{v}\cdot\nabla_{\boldsymbol{r}})f$, is analogous to the material derivation or substantial derivation of Eulerian method in fluid mechanics (hydrodynamics).

The single-particle scattering term is

$$\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} = \int [f_{\boldsymbol{k}'}(1-f_{\boldsymbol{k}}) - f_{\boldsymbol{k}}(1-f_{\boldsymbol{k}'})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' = \int (f_{\boldsymbol{k}'} - f_{\boldsymbol{k}})W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' \qquad (.22)$$

and the two-body scattering term is

$$\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} = \begin{cases} \int [f_{\boldsymbol{k}_2}f_{\boldsymbol{k}_3}(1-f_{\boldsymbol{k}})(1-f_{\boldsymbol{k}_1}) - f_{\boldsymbol{k}}f_{\boldsymbol{k}_1}(1-f_{\boldsymbol{k}_2})(1-f_{\boldsymbol{k}_3})]W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3; & \text{Fermion} \\ \int [f_{\boldsymbol{k}_2}f_{\boldsymbol{k}_3}(1+f_{\boldsymbol{k}})(1+f_{\boldsymbol{k}_1}) - f_{\boldsymbol{k}}f_{\boldsymbol{k}_1}(1+f_{\boldsymbol{k}_2})(1+f_{\boldsymbol{k}_3})]W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3; & \text{Boson} \\ \int (f_{\boldsymbol{k}_2}f_{\boldsymbol{k}_3} - f_{\boldsymbol{k}}f_{\boldsymbol{k}_1})W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3; & \text{Classical} \end{cases} \qquad (.23)$$

where $W(\boldsymbol{k},\boldsymbol{k}') = W(\boldsymbol{k}',\boldsymbol{k})$ is the elastic scattering probability between state $\boldsymbol{k}$ to state $\boldsymbol{k}'$. The former term in square bracket represents the probability of the number of particles entering the volume $d\boldsymbol{k}$ within the time interval dt, while the latter represents the probability of leaving. (The form of collision term is meaningful. It equals to the difference between the particle gain and the particle loss due to collision (interaction).) Naively, here we assume, the phase space dk is small enough, so the collision leads to particle in or out of the phase space dk. For two-body interaction, $W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3) = W(\boldsymbol{k}_2,\boldsymbol{k}_3;\boldsymbol{k},\boldsymbol{k}_1)$. One should consider the Pauli exclusion principle when writing the collision term of fermions.

The single-body scattering is easy to understand. The two-body scattering can be understood as follows. The number of transitions $\mathbf{k}+\mathbf{k}_1 \to \mathbf{k}_2+\mathbf{k}_3$ in a volume element d^3r, owing to the collisions during the time interval δt is

$$dN_{k,k_1} W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)\delta t \qquad (.24)$$

where N_{k,k_1} is the initial number of colliding pairs $(\mathbf{k},\mathbf{k}_1)$. The number can be obtained by

$$dN_{k,k_1} = f_2(r,k,k_1,t)d^3r d^3k d^3k_1 \qquad (.25)$$

The particle number leaving the phase element after the collision will be

$$R_{leaving}\delta t d^3r d^3k = \delta t d^3r d^3k \int d^3k_1 \int d^3k_2 \int d^3k_3 W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3) f_2(r,k,k_1,t) \qquad (.26)$$

Similarly, the particle number entering the phase element is

$$R_{entering}\delta t d^3r d^3k = \delta t d^3r d^3k \int d^3k_1 \int d^3k_2 \int d^3k_3 W(\boldsymbol{k}_2,\boldsymbol{k}_3;\boldsymbol{k},\boldsymbol{k}_1) f_2(r,k_2,k_3,t) \qquad (.27)$$

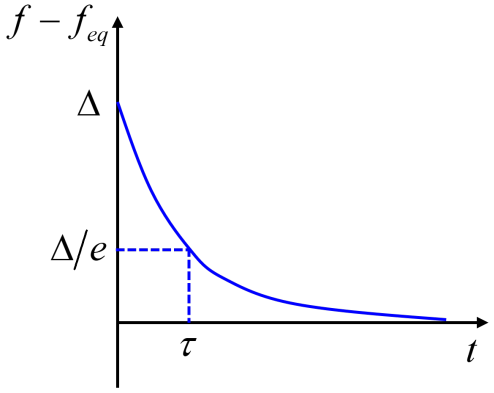

FIG. .1:

By applying molecule chaos assumption, we set $f_2(r, k_2, k_3, t) = f_1(r, k_2, t) f_1(r, k_3, t)$. So we have

$$\frac{\partial f}{\partial t}\bigg|_{\text{coll}} \sim (R_{entering} - R_{leaving}) \sim \int (f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3} - f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \qquad (.28)$$

Relaxation Time Approximation

The **relaxation time approximation** assume that the nonequilibrium state caused by the external action will return to the original equilibrium state due to the collisions of the internal particles after the external action is removed.

$$\frac{d}{dt}[f(t) - f_{eq}] = -\frac{f(t) - f_{eq}}{\tau} \quad \Longrightarrow \quad f(t) - f_{eq} = [f(0) - f_{eq}] e^{-t/\tau} \qquad (.29)$$

where the relaxation time τ characterizes the resilience of the system. (Equivalently, relaxation is introduced here. Or, statistical property enters here due to collision term.) In this condition, there are no diffusion and field terms in the Boltzmann equation, only the collision term. Based on this assumption, a simple to deal with the collision term is the relaxation time approximation

$$\frac{\partial f}{\partial t}\Big|_{\text{coll}} \approx -\frac{f_{\boldsymbol{k}} - f_{eq}}{\tau} \qquad (.30)$$

If we suppose that there is a uniform temperature gradient ∇T in the system, the diffusion term in the Boltzmann equation will become

$$\frac{\partial f}{\partial t}\Big|_{\text{diff}} = \boldsymbol{v} \cdot \nabla_{\boldsymbol{r}} f = \boldsymbol{v} \cdot \frac{\partial f}{\partial T} \nabla T \approx \boldsymbol{v} \cdot \frac{\partial f_{eq}}{\partial T} \nabla T \qquad (.31)$$

The effect of electric field can be considered through two ways. One can express it in the diffusion term bu using electric potential gradient $\nabla\phi$

$$\frac{\partial f}{\partial t}\Big|_{\text{diff}} = \boldsymbol{v}\cdot\nabla_{\boldsymbol{r}} f = \boldsymbol{v}\cdot\frac{\partial f}{\partial \phi}\nabla\phi \tag{.32}$$

One can also express it the field term

$$\frac{\partial f}{\partial t}\Big|_{\text{field}} = e\boldsymbol{E}\cdot\nabla_{\boldsymbol{p}} f = e\boldsymbol{E}\cdot\frac{\partial f}{\partial \varepsilon_{\boldsymbol{p}}}\nabla_{\boldsymbol{p}}\varepsilon_{\boldsymbol{p}} \approx e\boldsymbol{E}\cdot\boldsymbol{v}_{\boldsymbol{p}}\frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{p}}} \tag{.33}$$

The latter is somewhat simplified.

Then, the typical Boltzmann equation is written as

$$v_{\boldsymbol{k}}\cdot\frac{\partial f_{eq}}{\partial T}\nabla T + e\boldsymbol{E}\cdot\boldsymbol{v}_{\boldsymbol{k}}\frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} = \int [f_{\boldsymbol{k}'} - f_{\boldsymbol{k}}]Q_{\boldsymbol{k}}^{\boldsymbol{k}'}d\boldsymbol{k}' \approx -\frac{f_{\boldsymbol{k}} - f_{eq}}{\tau} \tag{.34}$$

Transport coefficient: Electric Conductivity, Thermal Conductivity, Viscosity

Example 1: Conductivity We calculate the conductivity of 2DEG in the presence of the electric field $\boldsymbol{E} = E\hat{e}_x$. Boltzmann equation will reduce to

$$\frac{\partial f}{\partial t} + \mathbf{v}\cdot\nabla_{\mathbf{r}} f + \mathbf{F}\cdot\nabla_{\mathbf{k}} f = -\frac{f - f_{eq}}{\tau} \to -e\mathbf{E}\cdot\nabla_{\mathbf{k}} f = -\frac{f - f_{eq}}{\tau}. \tag{.35}$$

We assume the derivation from the equilibrium is small $f^{(1)} \ll f_{eq}$, so (neglecting $\nabla_{\mathbf{k}} f^{(1)}$)

$$-e\mathbf{E}\cdot\nabla_{\mathbf{k}} f_{eq} = -\frac{f^{(1)}}{\tau} \tag{.36}$$

which gives the nonequilibrium distribution based on relaxation time approximation as

$$f_{\boldsymbol{k}} \approx f_{eq} + f^{(1)} = f_{eq} + \tau e\boldsymbol{E}\cdot\boldsymbol{v}_{\boldsymbol{k}}\frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} \tag{.37}$$

where $f_{eq} = \frac{1}{e^{\alpha+\beta\varepsilon_{\boldsymbol{k}}}+1} = \frac{1}{e^{\beta(\varepsilon_{\boldsymbol{k}}-\mu)}+1}$. The electric current induced by electric field can be obtained by

$$\begin{aligned} J_x =&(-e)\int\frac{d^2\boldsymbol{k}}{(2\pi)^2}v_{\boldsymbol{k},x}f_{\boldsymbol{k}} = -e^2\tau E\int\frac{d^2\boldsymbol{k}}{(2\pi)^2}v_x^2\frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} = Ee^2\tau\int\frac{d^2\boldsymbol{k}}{(2\pi)^2}v_x^2[-\frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}}] \\ =&E\frac{ne^2\tau}{m} \end{aligned} \tag{.38}$$

where $v_x^2 = v^2/3 = 2\varepsilon/3m, -\frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} \overset{T=0}{=} \delta(\varepsilon - \mu)$. The longitudinal conductivity is defined by $\boldsymbol{J} = \sigma\boldsymbol{E}$, so that

$$\sigma = \frac{ne^2\tau}{m} \tag{.39}$$

Example 2: Thermal Conductivity We consider 2DEG with a uniform temperature gradient $\frac{dT}{dx}$. The nonequilibrium distribution based on relaxation time approximation is

$$f_{\boldsymbol{k}} \approx f_{eq} - \tau v_{\boldsymbol{k},x} \frac{\partial f_{eq}}{\partial T} \frac{dT}{dx} = f_{eq} + \tau v_{\boldsymbol{k},x} \frac{\varepsilon_{\boldsymbol{k}} - \mu}{T} \frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} \frac{dT}{dx} \tag{.40}$$

where $f_{eq} = \frac{1}{e^{\alpha+\beta\varepsilon_{\boldsymbol{k}}}+1} = \frac{1}{e^{\beta(\varepsilon_{\boldsymbol{k}}-\mu)}+1}$ and $\boldsymbol{v}_{\boldsymbol{k}} = \hbar\boldsymbol{k}/m$. The heat current induced by the temperature gradient $\frac{dT}{dx}$ is evaluated by

$$\begin{aligned} J_{q,x} =& \int \frac{d^2\boldsymbol{k}}{(2\pi)^2}(\varepsilon_{\boldsymbol{k}} - \mu) v_{\boldsymbol{k},x} f_{\boldsymbol{k}} = \int \frac{d^2\boldsymbol{k}}{(2\pi)^2}(\varepsilon_{\boldsymbol{k}} - \mu) v_{\boldsymbol{k},x} \tau v_{\boldsymbol{k},x} \frac{\varepsilon_{\boldsymbol{k}} - \mu}{T} \frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} \frac{dT}{dx} \\ =& \frac{dT}{dx} \frac{\tau}{\hbar^2 T} \int \frac{d\varepsilon_{\boldsymbol{k}}}{2\pi} (\varepsilon_{\boldsymbol{k}} - \mu)^2 \varepsilon_{\boldsymbol{k}} \frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} = -\frac{dT}{dx} \frac{\tau}{\hbar^2 T} \int \frac{d\varepsilon_{\boldsymbol{k}}}{2\pi} (3\varepsilon_{\boldsymbol{k}}^2 - 4\varepsilon_{\boldsymbol{k}}\mu + \mu^2) f_{eq} \\ =& -\frac{dT}{dx} \frac{\tau}{\hbar^2 T} \frac{\pi\mu}{6} (k_B T)^2 = -\frac{dT}{dx} \frac{\pi^2 n \tau k_B}{3m} (k_B T) \end{aligned} \tag{.41}$$

where we have used the expression of particle number concentration

$$n = \int \frac{d^2\boldsymbol{k}}{(2\pi)^2} f_{eq} = \int \frac{d^2\boldsymbol{k}}{(2\pi)^2} \frac{1}{e^{\beta(\varepsilon_{\boldsymbol{k}}-\mu)}+1} = \frac{m}{\hbar^2} \int \frac{d\varepsilon_{\boldsymbol{k}}}{2\pi} f_{eq} = \frac{m}{\hbar^2} \frac{\mu}{2\pi} = \frac{m\mu}{2\pi\hbar^2}, \tag{.42}$$

and Sommerfeld Expansion generating functions

$$\int \frac{d\varepsilon}{2\pi} f_{eq} = \frac{\mu}{2\pi} \tag{.43}$$

$$\int \frac{d\varepsilon}{2\pi} \frac{\varepsilon}{2\pi} f_{eq} = \frac{1}{2!} \left(\frac{\mu}{2\pi}\right)^2 + \frac{(k_B T)^2}{4!} \tag{.44}$$

$$\int \frac{d\varepsilon}{2\pi} \frac{1}{2!} \left(\frac{\varepsilon}{2\pi}\right)^2 f_{eq} = \frac{1}{3!} \left(\frac{\mu}{2\pi}\right)^3 + \left(\frac{\mu}{2\pi}\right) \frac{(k_B T)^2}{4!} \tag{.45}$$

The thermal conductivity is defined by $\boldsymbol{J}_q = -\kappa \nabla T$, so that

$$\kappa = \frac{\pi^2 n \tau k_B}{3m} (k_B T) = \frac{\pi^2 k_B^2}{3e^2} \sigma T \tag{.46}$$

from which one can get Wiedemann-Franz law

$$\frac{\kappa}{\sigma T} = L_0 = \frac{\pi^2 k_B^2}{3e^2} \tag{.47}$$

where the righthand side is purely physical constant.

If we apply the classical equipartition of energy theorem $\frac{1}{2} m v_i^2 = \frac{1}{2} k_B T$, we can get other expression of thermal conductivity

$$\kappa = \frac{\pi^2 n \tau k_B}{3m} \frac{1}{2} m \bar{v}^2 = \frac{\pi^2 k_B}{6} n \bar{v}^2 \tau = \frac{\pi^2 k_B}{6} n \bar{v} l \tag{.48}$$

where $l = \bar{v}\tau$ is mean free path.

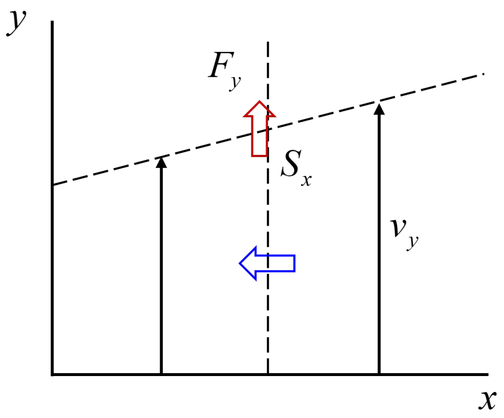

FIG. .2: Sketch of viscous flow. Red arrow denotes the direction of force. Blue arrow denotes the particle moving.

Example 3: Shear Viscosity We assume a 2DEG with the group velocity $\boldsymbol{u} = u_y(x)\hat{e}_y$. The Boltzmann equation is

$$\boldsymbol{v} \cdot \nabla_{\boldsymbol{r}} f = -\frac{f_{\boldsymbol{k}} - f_{eq}}{\tau} \tag{.49}$$

The nonequilibrium distribution based on relaxation time approximation is arrived at

$$\begin{aligned} f_{\boldsymbol{k}} \approx & f_{\boldsymbol{k}}^{(0)} - \tau v_{\boldsymbol{k},x} \frac{\partial f_{\boldsymbol{k}}^{(0)}}{\partial x} = f_{\boldsymbol{k}}^{(0)} - \tau v_{\boldsymbol{k},x} \frac{-e^{\alpha+\beta(\varepsilon_{\boldsymbol{k}} - \hbar k_y u_y)}}{[e^{\alpha+\beta(\varepsilon_{\boldsymbol{k}} - \hbar k_y u_y)} + 1]^2} (-\beta\hbar k_y) \frac{\partial u_y}{\partial x} \\ = & f_{\boldsymbol{k}}^{(0)} + \tau m v_{\boldsymbol{k},x} v_{\boldsymbol{k},y} \frac{-\beta e^{\alpha+\beta(\varepsilon_{\boldsymbol{k}} - \hbar k_y u_y)}}{[e^{\alpha+\beta(\varepsilon_{\boldsymbol{k}} - \hbar k_y u_y)} + 1]^2} \frac{\partial u_y}{\partial x} \\ \approx & f_{eq} + \tau m v_{\boldsymbol{k},x} v_{\boldsymbol{k},y} \frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} \frac{\partial u_y}{\partial x} \end{aligned} \tag{.50}$$

where $\alpha = -\beta\mu$, $\boldsymbol{v}_{\boldsymbol{k}} = \hbar\boldsymbol{k}/m$ is the velocity of state $\boldsymbol{k}$, $f_{eq} = \frac{1}{e^{\alpha+\beta\varepsilon_{\boldsymbol{k}}}+1}$ is the equilibrium distribution function with $\boldsymbol{u} = 0$ and $f_{\boldsymbol{k}}^{(0)} = \frac{1}{e^{\alpha+\beta[\varepsilon_{\boldsymbol{k}} - \hbar k_y u_y(x)]}+1}$ (derived in Section below). The shear stress in a viscous flow (shown in Fig. .2) is defined by

$$T_{xy} = \frac{F_y}{S_x} = \frac{1}{S_x}\frac{\Delta p_y}{\Delta t} = \frac{1}{S_x}\frac{-m v_y \Delta N}{\Delta t} = \int f_{\boldsymbol{k}} d\boldsymbol{k} \frac{1}{S_x} \frac{-m v_y (S_x v_x dt)}{dt} = -\int m v_x v_y f_{\boldsymbol{k}} d\boldsymbol{k} \tag{.51}$$

Here, the minus sign of $T_{xy} = -\int \frac{d^2\boldsymbol{k}}{(2\pi)^2} m v_{\boldsymbol{k},x} v_{\boldsymbol{k},y} f_{\boldsymbol{k}}$ indicates that the particles are moving in the opposite direction to the momentum gradient. The liquid with higher velocity experiences a frictional force by virtue of the fact that it suffers a net loss of “y component of momentum” to the gas with slower velocity. This is the origin of friction.

Thus, the shear stress induced by strain rate $\frac{\partial u_y}{\partial x}$ can be obtained as

$$\begin{aligned} T_{xy} =& -\int \frac{d^2\boldsymbol{k}}{(2\pi)^2} m v_{\boldsymbol{k},x} v_{\boldsymbol{k},y} f_{\boldsymbol{k}} = -\tau \frac{\partial u_y}{\partial x} \int \frac{d^2\boldsymbol{k}}{(2\pi)^2} (m v_{\boldsymbol{k},x} v_{\boldsymbol{k},y})^2 \frac{-\beta e^{\alpha+\beta\varepsilon_{\boldsymbol{k}}}}{(e^{\alpha+\beta\varepsilon_{\boldsymbol{k}}}+1)^2} = -\tau \frac{\partial u_y}{\partial x} \int \frac{kdk}{2\pi} \frac{1}{8} \frac{\hbar^4 k^4}{m^2} \frac{m}{\hbar^2 k} \\ =& -\tau \frac{\partial u_y}{\partial x} \int dk \frac{\hbar^2 k^4}{16\pi m} \frac{\partial f_{eq}}{\partial k} = \tau \frac{\partial u_y}{\partial x} \left[\frac{\hbar^2 k^4}{16\pi m} f_{eq} \Big|_0^\infty - \int dk \frac{\hbar^2 k^3}{4\pi m} f_{eq} \right] \\ =& \frac{m}{2} \tau \frac{\partial u_y}{\partial x} \int \frac{d^2\boldsymbol{k}}{(2\pi)^2} v_{\boldsymbol{k}}^2 f_{eq} = \frac{1}{2} n m \bar{v}^2 \tau \frac{\partial u_y}{\partial x} \end{aligned} \tag{.52}$$

where $\bar{v} = \sqrt{\langle v^2 \rangle}$. The shear viscosity is defined by $T_{xy} = \eta_s \frac{\partial u_y}{\partial x}$, so that

$$\eta_s = \frac{1}{2} n m \bar{v}^2 \tau = \frac{1}{2} n m \bar{v} l \tag{.53}$$

where $l = \bar{v}\tau$ is mean free path.

Single-Particle Relaxation Time and Transport Relaxation Time

In all above examples, the results are determined by relaxation time τ, which is important. If we ask quantitative behavior, we need the value of τ. How to estimate the relaxation time? Here, usually we have two ways to estimate relaxation time: 1. Single-particle relaxation time; 2. Transport relaxation time.

Single-particle relaxation time

$$\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} = -\frac{f_{\boldsymbol{k}} - f_{eq}}{\tau} = \int (f_{\boldsymbol{k}'} - f_{\boldsymbol{k}}) W_{\boldsymbol{k}}^{\boldsymbol{k}'} d\boldsymbol{k}' \approx -\int (f_{\boldsymbol{k}} - f_{eq}) W_{\boldsymbol{k}}^{\boldsymbol{k}'} d\boldsymbol{k}' = -(f_{\boldsymbol{k}} - f_{eq}) \int W_{\boldsymbol{k}}^{\boldsymbol{k}'} d\boldsymbol{k}' \tag{.54}$$

Thus,

$$\frac{1}{\tau} = \int d\boldsymbol{k}' W(\boldsymbol{k}, \boldsymbol{k}') \overset{\text{Fermi-Golden Rule}}{=} \int d\boldsymbol{k}' \frac{2\pi}{\hbar} |\langle \boldsymbol{k}|V|\boldsymbol{k}'\rangle|^2 \delta(\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}'}) \tag{.55}$$

From this derivation, it can be easily found that the relaxation time approximation is analogous to the first order expansion of the collision term in the Boltzmann equation.

Transport relaxation time (vertex correction) We consider the Boltzmann equation of a system in the present of electric field

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \nabla_{\boldsymbol{r}} f + \boldsymbol{F} \cdot \nabla_{\boldsymbol{p}} f = q\boldsymbol{E} \cdot \nabla_{\boldsymbol{p}} \varepsilon_{\boldsymbol{k}} \frac{\partial f}{\partial \varepsilon_{\boldsymbol{k}}} \approx q\boldsymbol{E} \cdot \boldsymbol{v}_{\boldsymbol{k}} \frac{\partial f_{eq}}{\partial \varepsilon_{\boldsymbol{k}}} = \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} \tag{.56}$$

and use the relaxation time approximation in the collision term of Boltzmann equation as

$$\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} = -\frac{f_{\boldsymbol{k}} - f_{eq}}{\tau_{\boldsymbol{k}}^{\text{tr}}} \tag{.57}$$

Since the relaxation time introduced here is related to the momentum, it is also called the **transport relaxation time**. Combining the above two equation, one can get

$$f_{\boldsymbol{k}} = f_{eq} - \tau^{\text{tr}}_{\boldsymbol{k}} q\boldsymbol{E}\cdot\boldsymbol{v}_{\boldsymbol{k}}\frac{\partial f_{eq}}{\partial\varepsilon_{\boldsymbol{k}}} \tag{.58}$$

Then, we plug this expression of distribution function into the origin form of Boltzmann

$$q\boldsymbol{E}\cdot\boldsymbol{v}_{\boldsymbol{k}}\frac{\partial f_{eq}}{\partial\varepsilon_{\boldsymbol{k}}} = \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} = \int (f_{\boldsymbol{k}'} - f_{\boldsymbol{k}})W^{\boldsymbol{k}'}_{\boldsymbol{k}}d\boldsymbol{k}' = \int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}')q\boldsymbol{E}\cdot\left[\tau^{\text{tr}}_{\boldsymbol{k}}\boldsymbol{v}_{\boldsymbol{k}}\frac{\partial f_{eq}}{\partial\varepsilon_{\boldsymbol{k}}} - \tau^{\text{tr}}_{\boldsymbol{k}'}\boldsymbol{v}_{\boldsymbol{k}'}\frac{\partial f_{eq}}{\partial\varepsilon_{\boldsymbol{k}'}}\right] \tag{.59}$$

If $\frac{\partial f_{eq}}{\partial\varepsilon_{\boldsymbol{k}}} = \frac{\partial f_{eq}}{\partial\varepsilon_{\boldsymbol{k}'}}$, it can be further reduced to

$$\boldsymbol{v}_{\boldsymbol{k}} = \frac{\tau^{\text{tr}}_{\boldsymbol{k}}}{\tau}\boldsymbol{v}_{\boldsymbol{k}} - \int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}')\tau^{\text{tr}}_{\boldsymbol{k}'}\boldsymbol{v}_{\boldsymbol{k}'} \tag{.60}$$

It is remarkable that this self-consistent equation corresponds to the vertex correction in the Kubo formula.

For electron systems with a spherical or circled surface in $\boldsymbol{k}$-space, which means $\boldsymbol{v}_{\boldsymbol{k}}$ and $\boldsymbol{k}$ are both in the same direction, the above self-consistent equation Eq. .60 can be reduced to

$$\begin{aligned}\boldsymbol{v}_{\boldsymbol{k}} =& \tau^{\text{tr}}_{\boldsymbol{k}}\boldsymbol{v}_{\boldsymbol{k}}\int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}') - \int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}')\tau^{\text{tr}}_{\boldsymbol{k}'}\boldsymbol{v}_{\boldsymbol{k}'} = \tau^{\text{tr}}_{\boldsymbol{k}}\boldsymbol{v}_{\boldsymbol{k}}\int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}') - \boldsymbol{v}_{\boldsymbol{k}}\int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}')\cos\theta\tau^{\text{tr}}_{\boldsymbol{k}'}\\ =& \tau^{\text{tr}}_{\boldsymbol{k}}\boldsymbol{v}_{\boldsymbol{k}}\int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}') - \tau^{\text{tr}}_{\boldsymbol{k}}\boldsymbol{v}_{\boldsymbol{k}}\int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}')\cos\theta\end{aligned} \tag{.61}$$

where θ is the angle between $\boldsymbol{k}$ and $\boldsymbol{k}'$, $|\boldsymbol{k}| = |\boldsymbol{k}'|$ due to the elastic scattering, and $\tau^{\text{tr}}_{\boldsymbol{k}}(k) = \tau^{\text{tr}}_{\boldsymbol{k}'}(k')$. Thus, the relaxation time is obtained as

$$\frac{1}{\tau^{\text{tr}}} = \int d\boldsymbol{k}'W(\boldsymbol{k},\boldsymbol{k}')(1-\cos\theta) \tag{.62}$$

which is like a scheme that distinguishes the contributions of forward scattering and back scattering, so that this relaxation time is also called **transport relaxation time**.

EQUILIBRIUM STATE, ENTROPY BALANCE EQUATION AND H-THEOREM

Let us recall the second-law of thermodynamics: The entropy of an isolated system should be never reduced under the evolution. This law is quite meaningful, which implies the irreversibility of thermal processes. The most important contribution of Boltzmann is, he provides a microscopic way to prove the non-reduced entropy based on the Boltzmann equation. Although the original proof is based on the diluted gas system, people believe it true for many other cases.

Classical Particles: Single-Particle Scattering In 1872, Boltzmann proposed a H-function,

$$H=\int\int f(\boldsymbol{r},\boldsymbol{k},t)[\ln f(\boldsymbol{r},\boldsymbol{k},t)-1]d\boldsymbol{k}d\boldsymbol{r} \tag{.63}$$

where $f(\boldsymbol{r},\boldsymbol{k},t)$ is the distribution function obeying the Boltzmann equation:

$$\frac{\partial f}{\partial t}+\boldsymbol{v}_\Gamma\cdot\nabla_\Gamma f=-\frac{\partial f}{\partial t}\bigg|_{\text{coll}}=\int(f_{\boldsymbol{k}'}-f_{\boldsymbol{k}})W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' \tag{.64}$$

with the velocity $\boldsymbol{v}_\Gamma=(\frac{d\boldsymbol{r}}{dt},\frac{d\boldsymbol{k}}{dt})$ and gradient $\nabla_\Gamma=(\nabla_{\boldsymbol{r}},\nabla_{\boldsymbol{k}})$ in the phase space. Here we assume the external force is zero.

$$\begin{aligned}
\frac{dH}{dt}&=\int\int\frac{\partial f_{\boldsymbol{k}}}{\partial t}\ln f_{\boldsymbol{k}}d\boldsymbol{k}d\boldsymbol{r}\\
&\overset{Boltzmanneq.}{=}-\int\int(\boldsymbol{v}_\Gamma\cdot\nabla_\Gamma f)\ln f_{\boldsymbol{k}}d\boldsymbol{k}d\boldsymbol{r}-\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})W(\boldsymbol{k},\boldsymbol{k}')\ln f_{\boldsymbol{k}}d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}\\
&=-\int\int\nabla_\Gamma\cdot[\boldsymbol{v}_\Gamma(f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-f_{\boldsymbol{k}})]-(f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-f_{\boldsymbol{k}})(\nabla_\Gamma\cdot\boldsymbol{v}_\Gamma)d\boldsymbol{k}d\boldsymbol{r}-\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})W(\boldsymbol{k},\boldsymbol{k}')\ln f_{\boldsymbol{k}}d\boldsymbol{k}'\\
&=-\int\int\nabla_\Gamma\cdot[\boldsymbol{v}_\Gamma(f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-f_{\boldsymbol{k}})]d\boldsymbol{k}d\boldsymbol{r}-\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})W(\boldsymbol{k},\boldsymbol{k}')\ln f_{\boldsymbol{k}}d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}
\end{aligned} \tag{.65}$$

where we used the incompressible condition of phase space $\nabla_\Gamma\cdot\boldsymbol{v}_\Gamma=0$.

The first term

$$\frac{d_eH}{dt}=-\int\int\nabla_\Gamma\cdot[\boldsymbol{v}_\Gamma(f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-f_{\boldsymbol{k}})]d\boldsymbol{k}d\boldsymbol{r}=-\oint\boldsymbol{v}(f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-f_{\boldsymbol{k}})\cdot d\boldsymbol{\Sigma}\equiv-\frac{1}{k_B}\frac{d_eS}{dt} \tag{.66}$$

corresponds to the entropy increase due to flow of entropy current. The integral is along the surface of the system. For the simplicity, we assume there is no particle can go through the surface (i.e. it is an isolated system), so this integral should be vanishing.

The second term is

$$\begin{aligned}
\frac{d_iH}{dt}&=-\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})W(\boldsymbol{k},\boldsymbol{k}')\ln f_{\boldsymbol{k}}d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}=-\int\int\int(f_{\boldsymbol{k}'}-f_{\boldsymbol{k}})W(\boldsymbol{k},\boldsymbol{k}')\ln f_{\boldsymbol{k}'}d\boldsymbol{k}d\boldsymbol{k}'d\boldsymbol{r}\\
&=-\frac{1}{2}\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})(\ln f_{\boldsymbol{k}}-\ln f_{\boldsymbol{k}'})W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}\equiv-\frac{1}{k_B}\frac{d_iS}{dt}=-\frac{P}{k_B}
\end{aligned} \tag{.67}$$

where we have used the reversibility of scattering $W(\boldsymbol{k},\boldsymbol{k}')=W(\boldsymbol{k}',\boldsymbol{k})$.

Letting $x=\ln f_{\boldsymbol{k}}$ and $y=\ln f_{\boldsymbol{k}'}$, one can get

$$(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})(\ln f_{\boldsymbol{k}}-\ln f_{\boldsymbol{k}'})=(e^x-e^y)(x-y)\geq 0 \tag{.68}$$

thus,

$$\frac{d_i H}{dt} \le 0 \quad \Longrightarrow \quad P \ge 0 \tag{.69}$$

The equal symbol is reached when $f_{\boldsymbol{k}'} = f_{\boldsymbol{k}}$.

Note that the entropy can be expressed as

$$S = -k_B \sum_{\boldsymbol{k}} f_{\boldsymbol{k}} \ln f_{\boldsymbol{k}} - f_{\boldsymbol{k}} = -k_B H \tag{.70}$$

$$\Rightarrow \frac{dS}{dt} = -k_B \frac{dH}{dt} \ge 0 \tag{.71}$$

This is the so-called H-theorem, which proves the second law of thermodynamics from a microscopic perspective.

The entropy in the form of distribution function with Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics.

$$S = -k_B \sum_{\boldsymbol{k}} \begin{cases} f_{\boldsymbol{k}} \ln f_{\boldsymbol{k}} - f_{\boldsymbol{k}}; & \text{Classical} \\ f_{\boldsymbol{k}} \ln f_{\boldsymbol{k}} - (1+f_{\boldsymbol{k}}) \ln(1+f_{\boldsymbol{k}}); & \text{Bosons} \\ f_{\boldsymbol{k}} \ln f_{\boldsymbol{k}} + (1-f_{\boldsymbol{k}}) \ln(1-f_{\boldsymbol{k}}); & \text{Fermions} \end{cases} \tag{.72}$$

We can think about N classical particles grouped into several box:

$$N = \sum_m N_m \tag{.73}$$

The total possibilities are

$$\Omega = \frac{N!}{\prod_m N_m!} \tag{.74}$$

So, in the Stirling's approximation,

$$\ln \Omega \approx N \ln N - N - \sum_m N_m \ln N_m + \sum_m N_m = N \ln N - \sum_m N_m \ln N_m \tag{.75}$$

and thus the entropy is

$$S = k_B \ln \Omega = k_B N \ln N - k_B \sum_m N_m \ln N_m \tag{.76}$$

For momentum k, we have

$$S = k_B \ln \Omega \sim -k_B \sum_k f_k \ln f_k \sim -k_B \sum_k (f_k \ln f_k - f_k) = -k_B H \tag{.77}$$

Bosons: Single-Particle Scattering   For bosons, we need to write the form of H-function as

$$H=\int\int f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-(1+f_{\boldsymbol{k}})\ln(1+f_{\boldsymbol{k}})d\boldsymbol{k}d\boldsymbol{r} \tag{.78}$$

$$\begin{aligned}\frac{dH}{dt}&=\int\int\frac{\partial f_{\boldsymbol{k}}}{\partial t}[\ln f_{\boldsymbol{k}}-\ln(1+f_{\boldsymbol{k}})]d\boldsymbol{k}d\boldsymbol{r}\\ &=-\int\int(\boldsymbol{v}_\Gamma\cdot\nabla_\Gamma f)[\ln f_{\boldsymbol{k}}-\ln(1+f_{\boldsymbol{k}})]d\boldsymbol{k}d\boldsymbol{r}-\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}}-\ln(1+f_{\boldsymbol{k}})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}\\ &=-\int\int\nabla_\Gamma\cdot\{\boldsymbol{v}_\Gamma[f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-(1+f_{\boldsymbol{k}})\ln(1+f_{\boldsymbol{k}})]\}d\boldsymbol{k}d\boldsymbol{r}-\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}}-\ln(1+f_{\boldsymbol{k}})]W(\boldsymbol{k},\boldsymbol{k}'\end{aligned} \tag{.79}$$

$$\frac{d_eH}{dt}=-\int\int\nabla_\Gamma\cdot\{\boldsymbol{v}_\Gamma[f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-(1+f_{\boldsymbol{k}})\ln(1+f_{\boldsymbol{k}})]\}d\boldsymbol{k}d\boldsymbol{r} \tag{.80}$$

$$=-\oint\boldsymbol{v}[f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-(1+f_{\boldsymbol{k}})\ln(1+f_{\boldsymbol{k}})]\cdot d\boldsymbol{\Sigma}\equiv-\frac{1}{k_B}\frac{d_eS}{dt} \tag{.81}$$

$$\begin{aligned}\frac{d_iH}{dt}&=-\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}}-\ln(1+f_{\boldsymbol{k}})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}\\ &=-\int\int\int(f_{\boldsymbol{k}'}-f_{\boldsymbol{k}})[\ln f_{\boldsymbol{k}'}-\ln(1+f_{\boldsymbol{k}'})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}\\ &=-\frac{1}{2}\int\int\int(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}}-\ln(1+f_{\boldsymbol{k}})-\ln f_{\boldsymbol{k}'}+\ln(1+f_{\boldsymbol{k}'})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}\end{aligned} \tag{.82}$$

Letting $x=\ln f_{\boldsymbol{k}}-\ln(1+f_{\boldsymbol{k}})$ and $y=\ln f_{\boldsymbol{k}'}-\ln(1+f_{\boldsymbol{k}'})$, one can get

$$(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}}-\ln(1+f_{\boldsymbol{k}})-\ln f_{\boldsymbol{k}'}+\ln(1+f_{\boldsymbol{k}'})]=(\frac{1}{e^{-x}-1}-\frac{1}{e^{-y}-1})(x-y)\geq 0 \tag{.83}$$

thus,

$$\frac{d_iH}{dt}\leq 0\quad\Longrightarrow\quad P\geq 0 \tag{.84}$$

Note that the entropy of boson can be expressed as

$$S=-k_B\sum_{\boldsymbol{k}}f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}-(1+f_{\boldsymbol{k}})\ln(1+f_{\boldsymbol{k}})=\frac{dH}{dt}=-k_BH \tag{.85}$$

Fermions: Single-Particle Scattering   For fermion, H-function is defined as

$$H=\int\int f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}}+(1-f_{\boldsymbol{k}})\ln(1-f_{\boldsymbol{k}})d\boldsymbol{k}d\boldsymbol{r} \tag{.86}$$

$$\begin{aligned}\frac{dH}{dt} &= \int\int \frac{\partial f_{\boldsymbol{k}}}{\partial t}[\ln f_{\boldsymbol{k}} - \ln(1-f_{\boldsymbol{k}})]d\boldsymbol{k}d\boldsymbol{r} \\ &= -\int\int(\boldsymbol{v}_\Gamma\cdot\nabla_\Gamma f)[\ln f_{\boldsymbol{k}} - \ln(1-f_{\boldsymbol{k}})]d\boldsymbol{k}d\boldsymbol{r} - \int\int\int(f_{\boldsymbol{k}} - f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}} - \ln(1-f_{\boldsymbol{k}})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r} \\ &= -\int\int\nabla_\Gamma\cdot\{\boldsymbol{v}_\Gamma[f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}} + (1-f_{\boldsymbol{k}})\ln(1-f_{\boldsymbol{k}})]\}d\boldsymbol{k}d\boldsymbol{r} - \int\int\int(f_{\boldsymbol{k}} - f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}} - \ln(1-f_{\boldsymbol{k}})]W(\boldsymbol{k},\boldsymbol{k}'\end{aligned} \tag{.87}$$

$$\frac{d_eH}{dt} = -\int\int\nabla_\Gamma\cdot\{\boldsymbol{v}_\Gamma[f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}} + (1-f_{\boldsymbol{k}})\ln(1-f_{\boldsymbol{k}})]\}d\boldsymbol{k}d\boldsymbol{r} \tag{.88}$$

$$= -\oint\boldsymbol{v}[f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}} + (1-f_{\boldsymbol{k}})\ln(1-f_{\boldsymbol{k}})]\cdot d\boldsymbol{\Sigma} = -\frac{1}{k_B}\frac{d_eS}{dt} \tag{.89}$$

$$\begin{aligned}\frac{d_iH}{dt} &= -\int\int\int(f_{\boldsymbol{k}} - f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}} - \ln(1-f_{\boldsymbol{k}})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r} \\ &= -\int\int\int(f_{\boldsymbol{k}'} - f_{\boldsymbol{k}})[\ln f_{\boldsymbol{k}'} - \ln(1-f_{\boldsymbol{k}'})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r} \\ &= -\frac{1}{2}\int\int\int(f_{\boldsymbol{k}} - f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}} - \ln(1-f_{\boldsymbol{k}}) - \ln f_{\boldsymbol{k}'} + \ln(1-f_{\boldsymbol{k}'})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}'d\boldsymbol{k}d\boldsymbol{r}\end{aligned} \tag{.90}$$

Letting $x = \ln f_{\boldsymbol{k}} - \ln(1-f_{\boldsymbol{k}})$ and $y = \ln f_{\boldsymbol{k}'} - \ln(1-f_{\boldsymbol{k}'})$, one can get

$$(f_{\boldsymbol{k}} - f_{\boldsymbol{k}'})[\ln f_{\boldsymbol{k}} - \ln(1-f_{\boldsymbol{k}}) - \ln f_{\boldsymbol{k}'} + \ln(1-f_{\boldsymbol{k}'})] = (\frac{1}{e^{-x}+1} - \frac{1}{e^{-y}+1})(x-y) \geq 0 \tag{.91}$$

thus,

$$\frac{d_iH}{dt} \leq 0 \quad\Longrightarrow\quad P \geq 0 \tag{.92}$$

Note that the entropy of fermion can be expressed as

$$S = -k_B\sum_{\boldsymbol{k}} f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}} - (1-f_{\boldsymbol{k}})\ln(1-f_{\boldsymbol{k}}) = \frac{dH}{dt} = -k_BH \tag{.93}$$

Classical Particles: Two-Body Scattering

$$H = \int\int f(\boldsymbol{r},\boldsymbol{k},t)[\ln f(\boldsymbol{r},\boldsymbol{k},t) - 1]d\boldsymbol{k}d\boldsymbol{r} \tag{.94}$$

$$\begin{aligned}\frac{dH}{dt} &= \int\int\frac{\partial f_{\boldsymbol{k}}}{\partial t}\ln f_{\boldsymbol{k}}d\boldsymbol{k}d\boldsymbol{r} \\ &= -\int\int(\boldsymbol{v}_\Gamma\cdot\nabla_\Gamma f)\ln f_{\boldsymbol{k}}d\boldsymbol{k}d\boldsymbol{r} - \int\ln f_{\boldsymbol{k}}[f_{\boldsymbol{k}}f_{\boldsymbol{k}_1} - f_{\boldsymbol{k}_2}f_{\boldsymbol{k}_3}]W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)d\boldsymbol{k}d\boldsymbol{k}_1d\boldsymbol{k}_2d\boldsymbol{k}_3d\boldsymbol{r} \\ &= -\int\int\nabla_\Gamma\cdot[\boldsymbol{v}_\Gamma(f_{\boldsymbol{k}}\ln f_{\boldsymbol{k}} - f_{\boldsymbol{k}})]d\boldsymbol{k}d\boldsymbol{r} - \int\ln f_{\boldsymbol{k}}[f_{\boldsymbol{k}}f_{\boldsymbol{k}_1} - f_{\boldsymbol{k}_2}f_{\boldsymbol{k}_3}]W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)d\boldsymbol{k}d\boldsymbol{k}_1d\boldsymbol{k}_2d\boldsymbol{k}_3d\boldsymbol{r}\end{aligned} \tag{.95}$$

$$\frac{d_eH}{dt} = -\int\int \nabla_\Gamma \cdot [\boldsymbol{v}_\Gamma(f_{\boldsymbol{k}} \ln f_{\boldsymbol{k}} - f_{\boldsymbol{k}})] d\boldsymbol{k} d\boldsymbol{r} = -\frac{1}{k_B}\frac{d_eS}{dt} \tag{.96}$$

$$\begin{aligned}
\frac{d_iH}{dt} =& -\int \ln f_{\boldsymbol{k}} (f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} - f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \\
=& -\int \ln f_{\boldsymbol{k}_1} (f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} - f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \\
=& -\frac{1}{2}\int \ln f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} (f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} - f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \\
=& -\frac{1}{2}\int \ln f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3} (f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3} - f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \\
=& -\frac{1}{4}\int (\ln f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} - \ln f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3})(f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} - f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r}
\end{aligned} \tag{.97}$$

Letting $x = \ln f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}$ and $y = \ln f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}$, one can get

$$(\ln f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} - \ln f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3})(f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} - f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}) = (e^x - e^y)(x - y) \geq 0 \tag{.98}$$

thus,

$$\frac{d_iH}{dt} \leq 0 \quad \Longrightarrow \quad P \geq 0 \tag{.99}$$

Fermions: Two-Body Scattering

$$\begin{aligned}
\frac{d_iH}{dt} =& -\int [\ln f_{\boldsymbol{k}} - \ln(1 - f_{\boldsymbol{k}})][f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}(1 - f_{\boldsymbol{k}_2})(1 - f_{\boldsymbol{k}_3}) - f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}(1 - f_{\boldsymbol{k}})(1 - f_{\boldsymbol{k}_1})] W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k} \\
=& -\int \ln \frac{f_{\boldsymbol{k}}}{1 - f_{\boldsymbol{k}}} \left(\frac{f_{\boldsymbol{k}}}{1 - f_{\boldsymbol{k}}}\frac{f_{\boldsymbol{k}_1}}{1 - f_{\boldsymbol{k}_1}} - \frac{f_{\boldsymbol{k}_2}}{1 - f_{\boldsymbol{k}_2}}\frac{f_{\boldsymbol{k}_3}}{1 - f_{\boldsymbol{k}_3}}\right) \tilde{W}(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \\
=& -\int \ln \frac{f_{\boldsymbol{k}_1}}{1 - f_{\boldsymbol{k}_1}} \left(\frac{f_{\boldsymbol{k}}}{1 - f_{\boldsymbol{k}}}\frac{f_{\boldsymbol{k}_1}}{1 - f_{\boldsymbol{k}_1}} - \frac{f_{\boldsymbol{k}_2}}{1 - f_{\boldsymbol{k}_2}}\frac{f_{\boldsymbol{k}_3}}{1 - f_{\boldsymbol{k}_3}}\right) \tilde{W}(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \\
=& -\frac{1}{2}\int \ln\left(\frac{f_{\boldsymbol{k}}}{1 - f_{\boldsymbol{k}}}\frac{f_{\boldsymbol{k}_1}}{1 - f_{\boldsymbol{k}_1}}\right)\left(\frac{f_{\boldsymbol{k}}}{1 - f_{\boldsymbol{k}}}\frac{f_{\boldsymbol{k}_1}}{1 - f_{\boldsymbol{k}_1}} - \frac{f_{\boldsymbol{k}_2}}{1 - f_{\boldsymbol{k}_2}}\frac{f_{\boldsymbol{k}_3}}{1 - f_{\boldsymbol{k}_3}}\right) \tilde{W}(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \\
=& -\frac{1}{2}\int \ln\left(\frac{f_{\boldsymbol{k}_2}}{1 - f_{\boldsymbol{k}_2}}\frac{f_{\boldsymbol{k}_3}}{1 - f_{\boldsymbol{k}_3}}\right)\left(\frac{f_{\boldsymbol{k}_2}}{1 - f_{\boldsymbol{k}_2}}\frac{f_{\boldsymbol{k}_3}}{1 - f_{\boldsymbol{k}_3}} - \frac{f_{\boldsymbol{k}}}{1 - f_{\boldsymbol{k}}}\frac{f_{\boldsymbol{k}_1}}{1 - f_{\boldsymbol{k}_1}}\right) \tilde{W}(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \\
=& -\frac{1}{4}\int d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 d\boldsymbol{r} \tilde{W}(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) \\
& \left[\ln\left(\frac{f_{\boldsymbol{k}}}{1 - f_{\boldsymbol{k}}}\frac{f_{\boldsymbol{k}_1}}{1 - f_{\boldsymbol{k}_1}}\right) - \ln\left(\frac{f_{\boldsymbol{k}_2}}{1 - f_{\boldsymbol{k}_2}}\frac{f_{\boldsymbol{k}_3}}{1 - f_{\boldsymbol{k}_3}}\right)\right]\left(\frac{f_{\boldsymbol{k}}}{1 - f_{\boldsymbol{k}}}\frac{f_{\boldsymbol{k}_1}}{1 - f_{\boldsymbol{k}_1}} - \frac{f_{\boldsymbol{k}_2}}{1 - f_{\boldsymbol{k}_2}}\frac{f_{\boldsymbol{k}_3}}{1 - f_{\boldsymbol{k}_3}}\right) \\
\leq& 0
\end{aligned} \tag{.100}$$

where $\tilde{W}(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) = \frac{W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3)}{(1 - f_{\boldsymbol{k}})(1 - f_{\boldsymbol{k}_1})(1 - f_{\boldsymbol{k}_2})(1 - f_{\boldsymbol{k}_3})}$.

In conclusion, we have proved the entropy balance equation using statistical mechanics,

$$\frac{dS}{dt} = -\int \nabla \cdot \boldsymbol{J}_s d\boldsymbol{r} + P \quad \text{or} \quad \frac{ds}{dt} = -\nabla \cdot \boldsymbol{J}_s + \Theta \tag{.101}$$

where $P, \Theta \leq 0$ and the equal sign applies to quasi-static processes. For equilibrium state, the $\frac{ds}{dt} = 0$ results from both $\nabla \cdot \boldsymbol{J}_s = 0$ and $\Theta = 0$.

Remarks on the H-theorem

H-theorem itself is meaningful on the statistical level, i.e. H-function is a functional of f which is a statistical averaged function. f describes the averaged distribution over the large size or scale. In the same way, the time evolution of H-function can be also viewed as meaningful on the statistical level. The results from H-theorem, for example, the detailed balance, are also on the statistical properties.

It is very intriguing to consider the reversibility of microscopic kinetic theory and irreversibility of theomaldynamics on the level of macroscopic systems. Kinetic theory always has reversibility (e.q. Newton's equation of motion, Schrodinger equation), if someone could reverse the time arrow, it looks like entropy should decrease, as it should return to the initial condition. This is called Loschmidt's paradox. To resolve this paradox, it is better to give a time scale for H-theorem.

On the reversibility, one would expect that the a system with finite number of particle will return to the initial condition in the phase space under time evolution, in the condition that the return time scale is quite quite long. For example, please check the Ehrenfest model as shown below, the return time is longer than the lifetime of universe.

Detailed Balance of H-Theorem

Based on the scattering of two particles, one can obtain the condition that allows $\frac{dH}{dt} = 0$ of a closed system in Maxwell-Boltzmann statistics (classical particle, two-body scattering) is

$$\ln f_{\boldsymbol{k}_1} + \ln f_{\boldsymbol{k}_2} = \ln f'_{\boldsymbol{k}_1} + \ln f'_{\boldsymbol{k}_2} \tag{.102}$$

which manifests as a form of conservation law in the collisions process. Thus, it has specific solutions

$$\text{constant}; \quad \text{momentum}: \hbar\boldsymbol{k}; \quad \text{energy}: \varepsilon_{\boldsymbol{k}} \tag{.103}$$

Combining them linearly, we get the general solution

$$\ln f_{\boldsymbol{k}} = -\alpha - \beta\varepsilon_{\boldsymbol{k}} - \boldsymbol{\gamma}\cdot\hbar\boldsymbol{k} \quad \Longrightarrow \quad f_{\boldsymbol{k}} = e^{-\alpha-\beta\varepsilon_{\boldsymbol{k}}-\boldsymbol{\gamma}\cdot\hbar\boldsymbol{k}} \tag{.104}$$

Similarly, the general solution of equilibrium distribution function of Bosons and Fermions are obtained as

$$\begin{aligned} \textbf{Bosons:} \quad & \ln\frac{f_{\boldsymbol{k}}}{1+f_{\boldsymbol{k}}} = -\alpha - \beta\varepsilon_{\boldsymbol{k}} - \boldsymbol{\gamma}\cdot\hbar\boldsymbol{k} \quad \Longrightarrow \quad f_{\boldsymbol{k}} = \frac{1}{e^{\alpha+\beta\varepsilon_{\boldsymbol{k}}+\boldsymbol{\gamma}\cdot\hbar\boldsymbol{k}}-1} \\ \textbf{Fermions:} \quad & \ln\frac{f_{\boldsymbol{k}}}{1-f_{\boldsymbol{k}}} = -\alpha - \beta\varepsilon_{\boldsymbol{k}} - \boldsymbol{\gamma}\cdot\hbar\boldsymbol{k} \quad \Longrightarrow \quad f_{\boldsymbol{k}} = \frac{1}{e^{\alpha+\beta\varepsilon_{\boldsymbol{k}}+\boldsymbol{\gamma}\cdot\hbar\boldsymbol{k}}+1} \end{aligned} \tag{.105}$$

◇ How to determine the coefficients α, β, γ here?

Linearized Boltzmann equation

Instead of regarding the distribution function in each region of the gas as just the local-equilibrium function $f^0_{\boldsymbol{k}}$, we shall allow for a slight derivation of $f_{\boldsymbol{k}}$ from $f^0_{\boldsymbol{k}}$ by introducing a new function $\Phi_{\boldsymbol{k}}$ (Chapman-Enskog approach)

$$f_{\boldsymbol{k}} \equiv f^0_{\boldsymbol{k}} - \frac{\partial f^0_{\boldsymbol{k}}}{\partial\varepsilon_{\boldsymbol{k}}}\Phi_{\boldsymbol{k}} = \begin{cases} f^0_{\boldsymbol{k}} + \frac{f^0_{\boldsymbol{k}}}{k_BT}\Phi_{\boldsymbol{k}}; & \text{Boltzmann-Maxwell} \\ f^0_{\boldsymbol{k}} + \frac{f^0_{\boldsymbol{k}}(1+f^0_{\boldsymbol{k}})}{k_BT}\Phi_{\boldsymbol{k}}; & \text{Bose-Einstein} \\ f^0_{\boldsymbol{k}} + \frac{f^0_{\boldsymbol{k}}(1-f^0_{\boldsymbol{k}})}{k_BT}\Phi_{\boldsymbol{k}}; & \text{Fermi-Dirac} \end{cases} \tag{.106}$$

where we have used the identities for equilibrium classical particles, Bosons and Fermions

$$-\frac{\partial f^0_{\boldsymbol{k}}}{\partial\varepsilon_{\boldsymbol{k}}}\bigg|_{\text{classical}} = \frac{f^0_{\boldsymbol{k}}}{k_BT}; \quad -\frac{\partial f^0_{\boldsymbol{k}}}{\partial\varepsilon_{\boldsymbol{k}}}\bigg|_{\text{Boson}} = \frac{f^0_{\boldsymbol{k}}(1+f^0_{\boldsymbol{k}})}{k_BT}; \quad -\frac{\partial f^0_{\boldsymbol{k}}}{\partial\varepsilon_{\boldsymbol{k}}}\bigg|_{\text{Fermion}} = \frac{f^0_{\boldsymbol{k}}(1-f^0_{\boldsymbol{k}})}{k_BT} \tag{.107}$$

Collision Term

Single-particle scattering Taking the fermions as an example, the collision term in the Boltzmann equation Eq.(.22) is obtained as

$$\begin{aligned} \frac{\partial f}{\partial t}\bigg|_{\text{coll}} &= \int (f_{\boldsymbol{k}'} - f_{\boldsymbol{k}})W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' = -\frac{1}{k_BT}\int(\Phi_{\boldsymbol{k}} - \Phi_{\boldsymbol{k}'})f^0_{\boldsymbol{k}}(1-f^0_{\boldsymbol{k}})W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' \\ &= -\frac{1}{k_BT}\int P(\boldsymbol{k},\boldsymbol{k}')(\Phi_{\boldsymbol{k}} - \Phi_{\boldsymbol{k}'})d\boldsymbol{k}' \\ &= -P\Phi \end{aligned} \tag{.108}$$

where $P(\boldsymbol{k},\boldsymbol{k}') = f^0_{\boldsymbol{k}}(1-f^0_{\boldsymbol{k}})W(\boldsymbol{k},\boldsymbol{k}')$ is the scattering operator, which transforms the function Φ into another function of $\boldsymbol{k}$ by integration and $f^0_{\boldsymbol{k}} = f^0_{\boldsymbol{k}'}$ since $W(\boldsymbol{k},\boldsymbol{k}')$ stands for an elastic scattering which do not change the energy.

Two-body scattering Similarly, we take the fermions as an example and obtain the collision term in the Boltzmann equation Eq.(.23), which is maintained to the linear order of Φ, as

$$\begin{aligned}
\frac{\partial f}{\partial t}\bigg|_{\text{coll}} =& \int [f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}(1-f_{\boldsymbol{k}})(1-f_{\boldsymbol{k}_1}) - f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}(1-f_{\boldsymbol{k}_2})(1-f_{\boldsymbol{k}_3})] W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3) d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
\approx& \int d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3) \\
& \{[f^0_{\boldsymbol{k}_2} + \frac{f^0_{\boldsymbol{k}_2}(1-f^0_{\boldsymbol{k}_2})}{k_BT}\Phi_{\boldsymbol{k}_2}][f^0_{\boldsymbol{k}_3} + \frac{f^0_{\boldsymbol{k}_3}(1-f^0_{\boldsymbol{k}_3})}{k_BT}\Phi_{\boldsymbol{k}_3}][1 - f^0_{\boldsymbol{k}} - \frac{f^0_{\boldsymbol{k}}(1-f^0_{\boldsymbol{k}})}{k_BT}\Phi_{\boldsymbol{k}}][1 - f^0_{\boldsymbol{k}_1} - \frac{f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_1}}{k_BT} \\
& - [f^0_{\boldsymbol{k}} + \frac{f^0_{\boldsymbol{k}}(1-f^0_{\boldsymbol{k}})}{k_BT}\Phi_{\boldsymbol{k}}][f^0_{\boldsymbol{k}_1} + \frac{f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_1})}{k_BT}\Phi_{\boldsymbol{k}_1}][1 - f^0_{\boldsymbol{k}_2} - \frac{f^0_{\boldsymbol{k}_2}(1-f^0_{\boldsymbol{k}_2})}{k_BT}\Phi_{\boldsymbol{k}_2}][1 - f^0_{\boldsymbol{k}_3} - \frac{f^0_{\boldsymbol{k}_3}(1-f}{k_BT} \\
\approx& \int d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3) \\
& \{-\frac{f^0_{\boldsymbol{k}}(1-f^0_{\boldsymbol{k}})}{k_BT}\Phi_{\boldsymbol{k}}[f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_2})(1-f^0_{\boldsymbol{k}_3}) + f^0_{\boldsymbol{k}_2} f^0_{\boldsymbol{k}_3}(1-f^0_{\boldsymbol{k}_1})] \\
& - \frac{f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_1})}{k_BT}\Phi_{\boldsymbol{k}_1}[f^0_{\boldsymbol{k}}(1-f^0_{\boldsymbol{k}_2})(1-f^0_{\boldsymbol{k}_3}) + f^0_{\boldsymbol{k}_2} f^0_{\boldsymbol{k}_3}(1-f^0_{\boldsymbol{k}})] \\
& + \frac{f^0_{\boldsymbol{k}_2}(1-f^0_{\boldsymbol{k}_2})}{k_BT}\Phi_{\boldsymbol{k}_2}[f^0_{\boldsymbol{k}_3}(1-f^0_{\boldsymbol{k}})(1-f^0_{\boldsymbol{k}_1}) + f^0_{\boldsymbol{k}} f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_3})] \\
& + \frac{f^0_{\boldsymbol{k}_3}(1-f^0_{\boldsymbol{k}_3})}{k_BT}\Phi_{\boldsymbol{k}_3}[f^0_{\boldsymbol{k}_2}(1-f^0_{\boldsymbol{k}})(1-f^0_{\boldsymbol{k}_1}) + f^0_{\boldsymbol{k}} f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_2})]\} \\
=& \int d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3) \frac{f^0_{\boldsymbol{k}} f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_2})(1-f^0_{\boldsymbol{k}_3})}{k_BT}(\Phi_{\boldsymbol{k}_3} + \Phi_{\boldsymbol{k}_2} - \Phi_{\boldsymbol{k}} - \Phi_{\boldsymbol{k}_1}) \\
=& -\frac{1}{k_BT}\int P(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)(\Phi_{\boldsymbol{k}} + \Phi_{\boldsymbol{k}_1} - \Phi_{\boldsymbol{k}_2} - \Phi_{\boldsymbol{k}_3}) d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
=& -P\Phi
\end{aligned} \tag{.109}$$

where $f^0_{\boldsymbol{k}} f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_2})(1-f^0_{\boldsymbol{k}_3}) = f^0_{\boldsymbol{k}_2} f^0_{\boldsymbol{k}_3}(1-f^0_{\boldsymbol{k}})(1-f^0_{\boldsymbol{k}_1})$ implies the detailed balance of equilibrium system and $P(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3) = f^0_{\boldsymbol{k}} f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_2})(1-f^0_{\boldsymbol{k}_3}) W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)$.

Diffusion Term

$$\frac{\partial f}{\partial t}\Big|_{\text{diff}} = \boldsymbol{v}\cdot\nabla_{\boldsymbol{r}} f = (\nabla_{\boldsymbol{p}} H)\cdot\nabla_{\boldsymbol{r}} f \tag{.110}$$

where we have used the canonical relations $\dot{q}_i = \frac{\partial H}{\partial p_i}$ and $\dot{p}_i = -\frac{\partial H}{\partial q_i}$.

Example 1: Shear Viscosity As an example, we derive the shear viscosity of a fermion system with linear spectrum $H = \varepsilon(p) = vp$ and equilibrium distribution of

$f_{eq} = \frac{1}{e^{(\varepsilon-\mu-\boldsymbol{p}\cdot\boldsymbol{u})/k_BT}+1}$. In this case, the leading-order diffusion term in Boltzmann equation is

$$\begin{aligned}\frac{\partial f_{eq}}{\partial t}\Big|_{\text{diff}} =&\frac{\partial H}{\partial p_i}\frac{\partial f_{eq}}{\partial x_i} = \frac{\partial \varepsilon}{\partial p_i}\frac{-e^{(\varepsilon-\mu-\boldsymbol{p}\cdot\boldsymbol{u})/k_BT}}{[e^{(\varepsilon-\mu-\boldsymbol{p}\cdot\boldsymbol{u})/k_BT}+1]^2}\frac{-p_j}{k_BT}\frac{\partial u_j}{\partial x_i} = \frac{vp_i}{p}f_{eq}(1-f_{eq})\frac{p_j}{k_BT}\frac{\partial u_j}{\partial x_i}\\ =&\frac{f_{eq}(1-f_{eq})}{k_BT}v\frac{p_ip_j}{p}u_{ij}\end{aligned} \tag{.111}$$

where $u_{ij} = \frac{1}{2}(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j})$. In the absence of an external field, the Boltzmann equation is approximately simplified as

$$\frac{\partial f_{eq}}{\partial t}\Big|_{\text{diff}} = \frac{\partial f}{\partial t}\Big|_{\text{coll}} \tag{.112}$$

For single-particle scattering

$$v\frac{p_ip_j}{p}u_{ij} = \int(\Phi_{\boldsymbol{k}'} - \Phi_{\boldsymbol{k}})W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' = I(\Phi) \tag{.113}$$

For two-body scattering

$$v\frac{p_ip_j}{p}u_{ij}f^0_{\boldsymbol{k}} = \int f^0_{\boldsymbol{k}_2}f^0_{\boldsymbol{k}_3}(1-f^0_{\boldsymbol{k}_1})(\Phi_{\boldsymbol{k}_2} + \Phi_{\boldsymbol{k}_3} - \Phi_{\boldsymbol{k}} - \Phi_{\boldsymbol{k}_1})W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)d\boldsymbol{k}_1d\boldsymbol{k}_2d\boldsymbol{k}_3 = I(\Phi) \tag{.114}$$

where $f^0_{\boldsymbol{k}} = f_{eq}$.

At first, we consider the single-particle scattering. The solution of Eq. (.113) is to be sought in the form

$$\Phi = g_{ij}u_{ij} \tag{.115}$$

where the tensor g_{ij} depends only on the $\boldsymbol{k}$, since a factor u_{ij} results on both sides of Eq. (.115) when this substitution is made. Since the equation must be valid for any tensor u_{ij}, the coefficients of this on the two sides must be equal, and also we obtain for g_{ij} the equation

$$v\frac{p_ip_j}{p} = \int[g_{ij}(\boldsymbol{k}') - g_{ij}(\boldsymbol{k})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' = I(g_{ij}) \tag{.116}$$

The collision term can approximately derived as

$$I(g_{ij}) = \int[g_{ij}(\boldsymbol{k}') - g_{ij}(\boldsymbol{k})]W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' \approx -g_{ij}(\boldsymbol{k})\int W(\boldsymbol{k},\boldsymbol{k}')d\boldsymbol{k}' \approx -g_{ij}(\boldsymbol{k})\frac{1}{\tau} \tag{.117}$$

from which we get the distribution function over the strain rate u_{ij}

$$f_{\boldsymbol{k}} = f_{eq} - \frac{\partial f_{eq}}{\partial \varepsilon}\Phi_{\boldsymbol{k}} \approx f_{eq} + \frac{\partial f_{eq}}{\partial \varepsilon}\frac{p_ip_j}{p}v\tau u_{ij} \tag{.118}$$

Then, the viscous stress tensor induced by u_{xy} can be evaluated as

$$T_{xy} = -\int \frac{1}{2}(p_x v_y + p_y v_x) f_{\boldsymbol{k}} d\boldsymbol{k} = -u_{xy} \int \left(v \frac{p_x p_y}{p} \right)^2 \tau d\boldsymbol{k} \tag{.119}$$

For zero temperature, the shear viscosity defined by $T_{xy} = \eta_s u_{xy}$ is obtained

$$\eta_s = \int \frac{d^2\boldsymbol{k}}{(2\pi)^2} \left(v \frac{p_x p_y}{p} \right)^2 \tau \left(-\frac{\partial f_{eq}}{\partial \varepsilon} \right) = \frac{1}{8} E^2 \rho \tau \tag{.120}$$

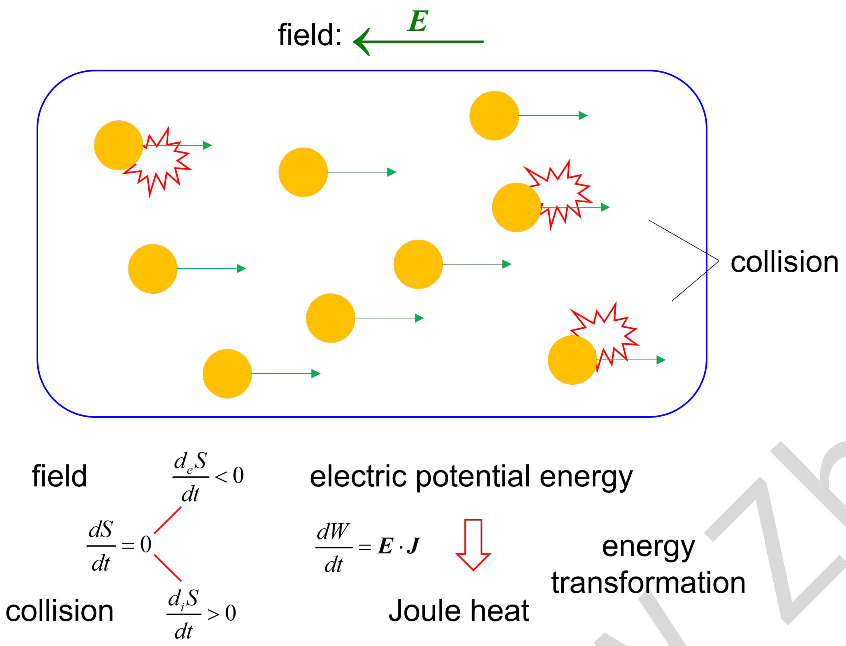

FIG. .3: Steady state of electrons in the presence of a electric field.

Steady State and Statistical Representation of Onsager Reciprocal Relations

The thermodynamic description of the steady state in linear nonequilibrium region are: (1) the rate of entropy production vanishes, i.e. $\frac{dP}{dt} = 0$ ($\frac{d\Theta}{dt} = 0$); (2) the $\frac{ds}{dt} = -\nabla \cdot \boldsymbol{J}_s + \Theta = 0$, which is different from $-\nabla \cdot \boldsymbol{J}_s = \Theta = 0$ for equilibrium state. This means that the balance of entropy of steady state is maintained between two equal and opposite trends. In the following, we will explore the properties of near-equilibrium steady state in statistical mechanics.

At first, for the steady state, the distribution function cannot explicitly contain time, i.e.

$$\frac{\partial f}{\partial t} = 0 \tag{.121}$$

so that the resulting Boltzmann equation is set down in the form of a balance between the sum of the diffusion and field terms and the collision term,

$$\left.\frac{\partial f}{\partial t}\right|_{\text{diff}} + \left.\frac{\partial f}{\partial t}\right|_{\text{field}} = \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} \tag{.122}$$

In this circumstance, the $\frac{ds}{dt} = 0$ is obviously satisfied for classical particles, Bosons, and Fermions, as shown in Eqs. (.65), (.79), and (.87).

In the previous section about the H-theorem, we have derived the expression of the rate of entropy according to the Boltzmann equation. Slightly different from the procedure of deriving the H-theorem, where the entropy production is expressed only by the collision term and the diffusion and field terms are partially offset by the canonical relation and partially classified as the entropy flow, we now also express the entropy production by the diffusion and field terms based on the new balanced Boltzmann equation Eq. (.122) and linear expansion of distribution function Eq. (.106).

Classical Particles For an assembly of classical particles, the entropy production density is derived as

$$\Theta = -k_B \int \left.\frac{\partial f}{\partial t}\right|_{\mathrm{coll}} \ln f_{\boldsymbol{k}} d\boldsymbol{k} \tag{.123}$$

and linearly expanded distribution function is

$$f_{\boldsymbol{k}} \approx f_{\boldsymbol{k}}^0 + \Phi_{\boldsymbol{k}} \frac{f_{\boldsymbol{k}}^0}{k_B T}, \quad \text{and} \quad f_{\boldsymbol{k}}^0 = e^{-(\varepsilon_{\boldsymbol{k}}-\mu)/k_B T} \tag{.124}$$

Thus,

$$\begin{aligned}\Theta \approx &- k_B \int \left.\frac{\partial f}{\partial t}\right|_{\mathrm{coll}} [\ln f_{\boldsymbol{k}}^0 + \ln(1+\frac{\Phi_{\boldsymbol{k}}}{k_B T})] d\boldsymbol{k} \approx -k_B \int \left.\frac{\partial f}{\partial t}\right|_{\mathrm{coll}} [-\frac{\varepsilon_{\boldsymbol{k}}-\mu}{k_B T} + \frac{\Phi_{\boldsymbol{k}}}{k_B T}] d\boldsymbol{k} \\ =& - \frac{1}{T} \int \left.\frac{\partial f}{\partial t}\right|_{\mathrm{coll}} \Phi_{\boldsymbol{k}} d\boldsymbol{k} + \frac{1}{T} \int \left.\frac{\partial f}{\partial t}\right|_{\mathrm{coll}} (\varepsilon_{\boldsymbol{k}}-\mu) d\boldsymbol{k}\end{aligned} \tag{.125}$$

The second term is vanishes for **elastic collisions** since collisions do not alter either the number of colliding particles or their total energy and momentum. It is also easy to prove it mathematically, for single scattering

$$\begin{aligned}\int \left.\frac{\partial f}{\partial t}\right|_{\mathrm{coll}} (\varepsilon_{\boldsymbol{k}}-\mu) d\boldsymbol{k} =& \int (\varepsilon_{\boldsymbol{k}}-\mu)(f_{\boldsymbol{k}'}-f_{\boldsymbol{k}}) W(\boldsymbol{k},\boldsymbol{k}') d\boldsymbol{k} d\boldsymbol{k'} = \int (\varepsilon_{\boldsymbol{k}'}-\mu)(f_{\boldsymbol{k}}-f_{\boldsymbol{k}'}) W(\boldsymbol{k},\boldsymbol{k}') d\boldsymbol{k} d\boldsymbol{k'} \\ =& \frac{1}{2} \int (\varepsilon_{\boldsymbol{k}}-\varepsilon_{\boldsymbol{k}'})(f_{\boldsymbol{k}'}-f_{\boldsymbol{k}}) W(\boldsymbol{k},\boldsymbol{k}') d\boldsymbol{k} d\boldsymbol{k'} \\ =& 0\end{aligned} \tag{.126}$$

and for two-body scattering

$$
\begin{aligned}
\int \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} (\varepsilon_{\boldsymbol{k}} - \mu) d\boldsymbol{k} =& \int (\varepsilon_{\boldsymbol{k}} - \mu)(f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3} - f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
=& \int (\varepsilon_{\boldsymbol{k}_1} - \mu)(f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3} - f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
=& \frac{1}{2} \int (\varepsilon_{\boldsymbol{k}} + \varepsilon_{\boldsymbol{k}_1} - 2\mu)(f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3} - f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
=& \frac{1}{2} \int (\varepsilon_{\boldsymbol{k}_2} + \varepsilon_{\boldsymbol{k}_3} - 2\mu)(f_{\boldsymbol{k}} f_{\boldsymbol{k}_1} - f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
=& \frac{1}{4} \int (\varepsilon_{\boldsymbol{k}} + \varepsilon_{\boldsymbol{k}_1} - \varepsilon_{\boldsymbol{k}_2} - \varepsilon_{\boldsymbol{k}_3})(f_{\boldsymbol{k}_2} f_{\boldsymbol{k}_3} - f_{\boldsymbol{k}} f_{\boldsymbol{k}_1}) W(\boldsymbol{k}, \boldsymbol{k}_1; \boldsymbol{k}_2, \boldsymbol{k}_3) d\boldsymbol{k} d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
=& 0
\end{aligned}
\tag{.127}
$$

At the microscopic level, **inelastic scattering** is the result of energy transfer, such as creation and annihilation of particle, the transitions between the translational mode (kinetic energy) and rotational and vibrational modes.

Bosons For an assembly of Bosons, the entropy production density is derived as

$$
\Theta = -k_B \int \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} [\ln f_{\boldsymbol{k}} - \ln(1 + f_{\boldsymbol{k}})] d\boldsymbol{k} \tag{.128}
$$

and linearly expanded distribution function is

$$
f_{\boldsymbol{k}} \approx f_{\boldsymbol{k}}^0 + \Phi_{\boldsymbol{k}} \frac{f_{\boldsymbol{k}}^0 (1 + f_{\boldsymbol{k}}^0)}{k_B T}, \quad \text{and} \quad f_{\boldsymbol{k}}^0 = \frac{1}{e^{(\varepsilon_{\boldsymbol{k}} - \mu)/k_B T} - 1} \tag{.129}
$$

Thus,

$$
\begin{aligned}
\Theta \approx & - k_B \int \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} \ln \frac{f_{\boldsymbol{k}}^0 + \frac{\Phi_{\boldsymbol{k}}}{k_B T} f_{\boldsymbol{k}}^0 (1 + f_{\boldsymbol{k}}^0)}{1 + f_{\boldsymbol{k}}^0 + \frac{\Phi_{\boldsymbol{k}}}{k_B T} f_{\boldsymbol{k}}^0 (1 + f_{\boldsymbol{k}}^0)} d\boldsymbol{k} = -k_B \int \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} \ln \frac{f_{\boldsymbol{k}}^0}{1 + f_{\boldsymbol{k}}^0} d\boldsymbol{k} - k_B \int \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} \ln \frac{1 + \frac{\Phi}{k_B}}{1 +} \\
\approx & - \frac{1}{T} \int \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} \Phi_{\boldsymbol{k}} d\boldsymbol{k} + \frac{1}{T} \int (\varepsilon_{\boldsymbol{k}} - \mu) \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} d\boldsymbol{k}
\end{aligned}
\tag{.130}
$$

where we have used relations

$$
\ln \frac{f_{\boldsymbol{k}}^0}{1 + f_{\boldsymbol{k}}^0} = \ln \frac{\frac{1}{e^{(\varepsilon_{\boldsymbol{k}} - \mu)/k_B T} - 1}}{1 + \frac{1}{e^{(\varepsilon_{\boldsymbol{k}} - \mu)/k_B T} - 1}} = -\frac{\varepsilon_{\boldsymbol{k}} - \mu}{k_B T} \tag{.131}
$$

$$
\ln \frac{1 + \frac{\Phi_{\boldsymbol{k}}}{k_B T}(1 + f_{\boldsymbol{k}}^0)}{1 + \frac{\Phi_{\boldsymbol{k}}}{k_B T} f_{\boldsymbol{k}}^0} \approx \frac{\Phi_{\boldsymbol{k}}}{k_B T}(1 + f_{\boldsymbol{k}}^0) - \frac{\Phi_{\boldsymbol{k}}}{k_B T} f_{\boldsymbol{k}}^0 = \frac{\Phi_{\boldsymbol{k}}}{k_B T} \tag{.132}
$$

Fermions For an assembly of Fermions, the entropy production density is derived as

$$\Theta = -k_B \int \frac{\partial f}{\partial t}\bigg|_{\text{coll}} [\ln f_{\boldsymbol{k}} + \ln(1 - f_{\boldsymbol{k}})] d\boldsymbol{k} \tag{.133}$$

and linearly expanded distribution function is

$$f_{\boldsymbol{k}} \approx f^0_{\boldsymbol{k}} + \Phi_{\boldsymbol{k}} \frac{f^0_{\boldsymbol{k}}(1 - f^0_{\boldsymbol{k}})}{k_B T}, \quad \text{and} \quad f^0_{\boldsymbol{k}} = \frac{1}{e^{(\varepsilon_{\boldsymbol{k}} - \mu)/k_B T} + 1} \tag{.134}$$

Thus,

$$\begin{aligned}\Theta \approx & - k_B \int \frac{\partial f}{\partial t}\bigg|_{\text{coll}} \ln \frac{f^0_{\boldsymbol{k}} + \frac{\Phi_{\boldsymbol{k}}}{k_B T} f^0_{\boldsymbol{k}}(1 - f^0_{\boldsymbol{k}})}{1 - f^0_{\boldsymbol{k}} - \frac{\Phi_{\boldsymbol{k}}}{k_B T} f^0_{\boldsymbol{k}}(1 - f^0_{\boldsymbol{k}})} d\boldsymbol{k} = -k_B \int \frac{\partial f}{\partial t}\bigg|_{\text{coll}} \ln \frac{f^0_{\boldsymbol{k}}}{1 - f^0_{\boldsymbol{k}}} d\boldsymbol{k} - k_B \int \frac{\partial f}{\partial t}\bigg|_{\text{coll}} \ln \frac{1 + \frac{\Phi}{k_B}}{1 -} \\ \approx & - \frac{1}{T} \int \frac{\partial f}{\partial t}\bigg|_{\text{coll}} \Phi_{\boldsymbol{k}} d\boldsymbol{k} + \frac{1}{T} \int (\varepsilon_{\boldsymbol{k}} - \mu) \frac{\partial f}{\partial t}\bigg|_{\text{coll}} d\boldsymbol{k}\end{aligned} \tag{.135}$$

where we have used relations

$$\ln \frac{f^0_{\boldsymbol{k}}}{1 - f^0_{\boldsymbol{k}}} = \ln \frac{\frac{1}{e^{(\varepsilon_{\boldsymbol{k}} - \mu)/k_B T} + 1}}{1 - \frac{1}{e^{(\varepsilon_{\boldsymbol{k}} - \mu)/k_B T} + 1}} = -\frac{\varepsilon_{\boldsymbol{k}} - \mu}{k_B T} \tag{.136}$$

$$\ln \frac{1 + \frac{\Phi_{\boldsymbol{k}}}{k_B T}(1 - f^0_{\boldsymbol{k}})}{1 - \frac{\Phi_{\boldsymbol{k}}}{k_B T} f^0_{\boldsymbol{k}}} \approx \frac{\Phi_{\boldsymbol{k}}}{k_B T}(1 - f^0_{\boldsymbol{k}}) + \frac{\Phi_{\boldsymbol{k}}}{k_B T} f^0_{\boldsymbol{k}} = \frac{\Phi_{\boldsymbol{k}}}{k_B T} \tag{.137}$$

In summary, Maxwell-Boltzmann statistic [Eq.(.125)], Bose-Einstein statistic [Eq. (.130)], and Fermi-Dirac statistic [Eq. (.135)] give the same result for the rate of change of entropy. The second term is vanishes for **elastic collisions** since collisions do not alter either the number of colliding particles or their total energy and momentum. Thus, combined with the new balanced Boltzmann equation Eq. (.122) for steady (stationary) state, one get

$$\Theta = -\frac{1}{T} \int \Phi_{\boldsymbol{k}} \frac{\partial f}{\partial t}\bigg|_{\text{coll}} d\boldsymbol{k} = -\frac{1}{T} \int \Phi_{\boldsymbol{k}} \left(\frac{\partial f}{\partial t}\bigg|_{\text{diff}} + \frac{\partial f}{\partial t}\bigg|_{\text{field}} \right) d\boldsymbol{k} \tag{.138}$$

In the previous section, we have derived a linear approximation of the collision term using fermions as example. Here, we write down the expressions for all three types statistics and two types of scattering, for single-particle scattering

$$\begin{aligned}\frac{\partial f}{\partial t}\bigg|_{\text{coll}} = & - \frac{1}{k_B T} \int P(\boldsymbol{k}, \boldsymbol{k}')(\Phi_{\boldsymbol{k}} - \Phi_{\boldsymbol{k}'}) d\boldsymbol{k}' \\ = & - \frac{1}{k_B T} P \Phi\end{aligned} \tag{.139}$$

with

$$P(\boldsymbol{k}, \boldsymbol{k}') = \begin{cases} f^0_{\boldsymbol{k}} W(\boldsymbol{k}, \boldsymbol{k}'); & \text{classical} \\ f^0_{\boldsymbol{k}}(1 - f^0_{\boldsymbol{k}}) W(\boldsymbol{k}, \boldsymbol{k}'); & \text{Boson} \\ f^0_{\boldsymbol{k}}(1 + f^0_{\boldsymbol{k}}) W(\boldsymbol{k}, \boldsymbol{k}'); & \text{Fermion} \end{cases} \tag{.140}$$

for two-body scattering

$$
\begin{aligned}
\left.\frac{\partial f}{\partial t}\right|_{\text{coll}} &= -\frac{1}{k_B T}\int P(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)(\Phi_{\boldsymbol{k}}+\Phi_{\boldsymbol{k}_1}-\Phi_{\boldsymbol{k}_2}-\Phi_{\boldsymbol{k}_3})d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
&= -\frac{1}{k_B T}P\Phi
\end{aligned}
\tag{.141}
$$

with

$$
P(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3) = \begin{cases} f^0_{\boldsymbol{k}} f^0_{\boldsymbol{k}_1} W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3); & \text{classical} \\ f^0_{\boldsymbol{k}} f^0_{\boldsymbol{k}_1}(1+f^0_{\boldsymbol{k}_2})(1+f^0_{\boldsymbol{k}_3}) W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3); & \text{Boson} \\ f^0_{\boldsymbol{k}} f^0_{\boldsymbol{k}_1}(1-f^0_{\boldsymbol{k}_2})(1-f^0_{\boldsymbol{k}_3}) W(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3); & \text{Fermion} \end{cases}
\tag{.142}
$$

where $P\Phi$ is abbreviation.

Plugging these expressions into Eq. .138, one can get the linearly approximated entropy production, for single-particle scattering

$$
\begin{aligned}
\Theta =& \frac{1}{k_B T^2}\int \Phi_{\boldsymbol{k}} P(\boldsymbol{k},\boldsymbol{k}')(\Phi_{\boldsymbol{k}}-\Phi_{\boldsymbol{k}'})d\boldsymbol{k}d\boldsymbol{k}' = \frac{1}{2k_B T^2}\int P(\boldsymbol{k},\boldsymbol{k}')(\Phi_{\boldsymbol{k}}-\Phi_{\boldsymbol{k}'})^2 d\boldsymbol{k}d\boldsymbol{k}' \\
=& \frac{1}{2k_B T^2}\langle \Phi, P\Phi\rangle
\end{aligned}
\tag{.143}
$$

and for two-body scattering

$$
\begin{aligned}
\Theta =& \frac{1}{k_B T^2}\int \Phi_{\boldsymbol{k}} P(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)(\Phi_{\boldsymbol{k}}+\Phi_{\boldsymbol{k}_1}-\Phi_{\boldsymbol{k}_2}-\Phi_{\boldsymbol{k}_3})d\boldsymbol{k}d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
=& \frac{1}{4k_B T^2}\int P(\boldsymbol{k},\boldsymbol{k}_1;\boldsymbol{k}_2,\boldsymbol{k}_3)(\Phi_{\boldsymbol{k}}+\Phi_{\boldsymbol{k}_1}-\Phi_{\boldsymbol{k}_2}-\Phi_{\boldsymbol{k}_3})^2 d\boldsymbol{k}d\boldsymbol{k}_1 d\boldsymbol{k}_2 d\boldsymbol{k}_3 \\
=& \frac{1}{2k_B T^2}\langle \Phi, P\Phi\rangle
\end{aligned}
\tag{.144}
$$

In effect, it is easy to see that we have also proved Boltzmann's H-theorem ($\Theta \geq 0$) with linear approximation.

If we introduce a inner product of two functions as

$$
\langle \Psi, P\Phi\rangle \equiv \int\int \Psi_{\boldsymbol{k}} P(\boldsymbol{k},\boldsymbol{k}')(\Phi_{\boldsymbol{k}}-\Phi_{\boldsymbol{k}'})d\boldsymbol{k}d\boldsymbol{k}'
\tag{.145}
$$

P is *symmetric* or *self-adjoint* for any two functions Φ and Ψ, $\langle \Psi, P\Phi\rangle = \langle \Phi, P\Psi\rangle$, since $P(\boldsymbol{k},\boldsymbol{k}') = P(\boldsymbol{k}',\boldsymbol{k})$ and

$$
\begin{aligned}
\langle \Psi, P\Phi\rangle \equiv& \int\int \Psi_{\boldsymbol{k}} P(\boldsymbol{k},\boldsymbol{k}')(\Phi_{\boldsymbol{k}}-\Phi_{\boldsymbol{k}'})d\boldsymbol{k}d\boldsymbol{k}' = \int\int \Psi_{\boldsymbol{k}'} P(\boldsymbol{k}',\boldsymbol{k})(\Phi_{\boldsymbol{k}'}-\Phi_{\boldsymbol{k}})d\boldsymbol{k}d\boldsymbol{k}' \\
=& \frac{1}{2}\int\int (\Psi_{\boldsymbol{k}}-\Psi_{\boldsymbol{k}'}) P(\boldsymbol{k},\boldsymbol{k}')(\Phi_{\boldsymbol{k}}-\Phi_{\boldsymbol{k}'})d\boldsymbol{k}d\boldsymbol{k}'
\end{aligned}
\tag{.146}
$$

Then, we label the terms in the Boltzmann equation contributed by mechanisms other than collisions as X,

$$X = \frac{\partial f}{\partial t}\bigg|_{\text{diff}} + \frac{\partial f}{\partial t}\bigg|_{\text{field}}, \tag{.147}$$

so that the Boltzmann equation is retained in

$$X = P\Phi \tag{.148}$$

Ehrenfest model

The Ehrenfest model was proposed by Tatiana and Paul Ehrenfest to explain the second law of thermodynamics. The model considers N particles in two containers. Particles independently change container at a rate. Suppose we have two boxes, labeled A and B, and a total of 2N distinguishable particles to distribute between the two boxes. At a given point in time, let n_0 particles in box A, and hence $2N - n_0$ particles in box B. Now, we repeatedly apply the following procedure (as one step):

1) Randomly choose one of the 2N particles (with equal probability);

2) Move the chosen particle from whichever box it happens to be into the other box.

The question is, what is the probability that there are n_0 particles in box A, after s steps?

After s steps, the probability of n particles in box A is $\langle n|P(s)|n_0\rangle$, so $\sum_n \langle n|P(s)|n_0\rangle = 1$. We deduce this process is like some "Markov process":

$$\langle n|P(s)|n_0\rangle = \langle n+1|P(s-1)|n_0\rangle \frac{n+1}{2N} + \langle n-1|P(s-1)|n_0\rangle (1 - \frac{n+1}{2N}) \tag{.149}$$

First, we can calculate the averaged particle number in box A:

$$\begin{aligned}
\langle n\rangle_s &= \sum_{n=0}^{2N} n\langle n|P(s)|n_0\rangle && (.150)\\
&= \sum_{n=0}^{2N} n \times \langle n+1|P(s-1)|n_0\rangle \frac{n+1}{2N} + n \times \langle n-1|P(s-1)|n_0\rangle (1 - \frac{n+1}{2N}) && (.151)\\
&= \frac{1}{2N}[\langle n^2\rangle_{s-1} - \langle n\rangle_{s-1}] + \langle n\rangle_{s-1} + 1 - \frac{1}{2N}[\langle n^2\rangle_{s-1} + \langle n\rangle_{s-1}] && (.152)\\
&= \langle n\rangle_{s-1}(1 - \frac{1}{N}) + 1 && (.153)
\end{aligned}$$

This is a iterative equation. One can check the form should be

$$\langle n\rangle_s = a + b(1 - \frac{1}{N})^s \tag{.154}$$

where $a = N, b = N - n_0$.

Thus in the infinite time, $s \to \infty$, $(1 - \frac{1}{N})^s \to 0$, so

$$\lim_{s\to\infty} \langle n\rangle_s \to N \tag{.155}$$

the averaged number of particle in each box is N, independent of n_0 (initial condition).

The next question is, how long should we observe n_0 particle in box A?

Again, we write the iterative relation as matrix form:

$$\langle n|P(s)|n_0\rangle = \sum_{n'=0}^{2N} M_{n,n'} \langle n'|P(s-1)|n_0\rangle \tag{.156}$$

$$= (A\Lambda A^{-1})...(A\Lambda A^{-1})\langle n_0|P(0)|n_0\rangle = A\Lambda^s A^{-1}\langle n_0|P(0)|n_0\rangle \tag{.157}$$

$$M = \begin{pmatrix} 0 & \frac{1}{2N} & 0 & ... & 0 & 0 \\ 1 & 0 & \frac{2}{2N} & 0 & ... & 0 \\ 0 & 1-\frac{1}{2N} & 0 & \frac{3}{2N} & ... & 0 \\ .... & & & & & \\ 0 & 0 & ...0 & 0 & 0 & 1 \\ 0 & 0 & ... & 0 & \frac{2}{2N} & 0 \end{pmatrix} \tag{.158}$$

where A contains the eigenvectors $\{\phi_{i=0,..,2N}(m)\}$ of M and $\Lambda = diag\lambda_1, \lambda_2, ...\lambda_m, ...$ are eigenvalues.

The iteration relation in the basis of eigenvector is:

$$(1 - \frac{n-1}{N})\phi_{n-1}(m) + \frac{n+1}{2N}\phi_{n+1}(m) = \lambda(m)\phi_n(m) \tag{.159}$$

To solve it, we can multiply both sizes by a factor z^n and sum over n:

$$zf_m(z) - \frac{1}{2N}z^2\frac{df_m(z)}{dz} + \frac{1}{2N}\frac{df_m(z)}{dz} = \lambda(m)f_m(z) \tag{.160}$$

$$f_m(z) \equiv \sum_{n=0}^{2N} \phi_n(m)z^n \tag{.161}$$

which leads to

$$\ln f_m = N[(1-\lambda)\ln(1-z) + (1+\lambda(m))\ln(1+z)] + const. \tag{.162}$$

$$\Rightarrow f_m(z) = const. \times (1-z)^{N(1-\lambda(m))}(1+z)^{N(1+\lambda(m))} = \sum_n \phi_n(m)z^n \tag{.163}$$

Note that the last equation requires $f_m(z)$ must be the z^{2N} polynomial, where the power index should be integer, so one get

$$\lambda(m) = -1 + \frac{m}{N}, m = 0, 1, ..., 2N \tag{.164}$$

Please note that $A_{nm} = \phi_n(m)$ is coefficient of z^n in function $f_m(z)$, i.e. coefficient of z^n in $(1-z)^{2N-m}(1+z)^m$.

Next we can prove that $A^{-1}_{ml} = \frac{(-)^{l+m}}{2^{2N}}\phi_m(l)$:

$$AA^{-1} = I \rightarrow \sum_m \phi_n(m)A^{-1}_{ml} = \delta_{nl} \tag{.165}$$

$$\xrightarrow{z^n} \sum_m f_m(z)A^{-1}_{ml} = z^l \tag{.166}$$

$$(1-z)^{2N}\sum_m(\frac{1+z}{1-z})^m A^{-1}_{ml} = z^l \tag{.167}$$

$$\xrightarrow{\zeta=-\frac{1+z}{1-z}} \sum_m(-1)^m A^{-1}_{ml} = \frac{(-1)^l}{2^{2N}}(1-\zeta)^{2N-l}(1+\zeta)^l \tag{.168}$$

Comparing the line with $f_m(z) = const. \times (1-z)^{N(1-\lambda(m))}(1+z)^{N(1+\lambda(m))}$, we get

$$A^{-1}_{ml} = \frac{(-)^{l+m}}{2^{2N}}\phi_m(l) \tag{.169}$$

Then we got

$$(M^s)_{nn_0} = \sum_m A_{nm}\lambda^s_m A^{-1}_{mn_0} \tag{.170}$$

$$= \sum_m \phi_n(m)\phi_m(n_0)\frac{(-)^{n_0+m}}{2^{2N}}\lambda^s(m) \tag{.171}$$

$$= \frac{(-1)^{n_0}}{2^{2N}}\sum_m \phi_n(m)\phi_m(n_0)(-1)^m(-1+\frac{m}{N})^s \tag{.172}$$

Next we consider a specific case, $n_0 = 2N$, where all particles are in box A at the initial time. We would like to ask the (average) time to return this state. For $n_0 = 2N$, $\phi_m(2N) = \frac{(2N)!}{m!(2N-m)!}$ is the coefficient of z^m in $(1+z)^{2N}$. And $\phi_{2N}(m) = (-1)^{2N-m}$ is the coefficient z^{2N} in $(1-z)^{2N-m}(1+z)^m$. So the probability is

$$P(s) = \langle 2N|P(s)|2N\rangle = \frac{1}{2^{2N}}\sum_m \frac{(2N)!}{m!(2N-m)!}(-1+\frac{m}{N})^s \tag{.173}$$

To get the first time that the system return, we need to do something more. We define the quantity $Q(s)$ as the probability of the first time return. $Q(s)$ and $P(s)$ have the following relation:

$$P(s) = Q(s) + \sum_{k=1}^{s-1} Q(k)P(s-k) \to h(z) = g(z) + g(z)h(z) \tag{.174}$$

$$h(z) = \sum_{s=1}^{\infty} P(s)z^s, g(z) = \sum_{s=1}^{\infty} Q(s)z^s \tag{.175}$$

And $\frac{dg}{dz}|_{z=1} = \sum_s sQ(s)$ is the period of the return time. $g'(z)$ can be related to $h(z)$ by

$$h(z) = g(z) + g(z)h(z) \to g' = \frac{1}{(1+h)^2}h' \tag{.176}$$

and

$$h(z) = \sum_{s=1}^{\infty} P(s)z^s = \sum_{s=1}^{\infty} \frac{1}{2^{2N}} \sum_{m=0}^{2N} \frac{(2N)!}{m!(2N-m)!}(-1+\frac{m}{N})^s z^s \tag{.177}$$

$$= \frac{1}{2^{2N}} \sum_{m=0}^{2N} \frac{(2N)!}{m!(2N-m)!} \frac{(-1+\frac{m}{N})z}{1-(-1+\frac{m}{N})z} \tag{.178}$$

For the discussion of $z = 1$, only when $m = 2N$, $h(z)$ has singularity, i.e.

$$h(z)|_{z=1} \to \frac{1}{2^{2N}} \frac{z}{1-z} + regularterms \tag{.179}$$

$$\Rightarrow h'(z) = \frac{1}{2^{2N}}[\frac{1}{1-z} + \frac{z}{(1-z)^2}] \tag{.180}$$

$$h'(z)|_{z\to 1} \approx \frac{1}{2^{2N}} \frac{1}{(1-z)^2}, h(z) \approx \frac{1}{2^{2N}} \frac{1}{1-z} \tag{.181}$$

$$\Rightarrow g'(z)|_{z\to 1} \approx \frac{1}{(1+h)^2} h'|_{z\to 1} = 2^{2N} \tag{.182}$$

$$\sum_s sQ(s) = 2^{2N} \tag{.183}$$

This time is much larger than the lifetime of universe, if we choose $2N \sim 10^{23}$. So the irreversible process is not likely to occur.