Electrical Conduction, Heat Conduction, Shear Viscosity and Entropy

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We present here how to study steady linear transport phenomena by using entropy. We study the system and the environment together and identify their entropies. Concerning their interaction, quantum mechanics is considered in the study. A time parameter $\tau$ is therefore introduced to characterize the discrete nature of the quantum interactions. By combining $\tau$ and the entropy, an approach is constructed successfully to study electrical conduction, heat conduction and shear viscosity.

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INTRODUCTION

In this article, we study three linear transport phenomena: heat conduction, electrical conduction and shear viscosity. All the three phenomena are linear when the external applied forces are weak. These linear behaviours are described by empirical laws. Heat conduction is described by Fourier’s law [1–4],

$$j = -\kappa \nabla T,$$  \hspace{1cm} (1)

where $j$ is heat current density, $T$ is temperature, $\kappa$ is thermal conductivity. Electrical conduction is described by Ohm’s law

$$j = \sigma E = -\sigma \nabla U,$$  \hspace{1cm} (2)

where $\sigma$ is electrical conductivity. Shear viscosity is described by Newton’s law of viscosity

$$\tau_{zx} = \eta \frac{dv_x}{dz},$$  \hspace{1cm} (3)

where $\tau_{zx}$ is shear stress, $\eta$ is shear viscosity.

The three laws are in similar forms. So they are likely associated with entropy which is the most general concept. About a system in the equilibrium state, its entropy is well understood. But about a system in a non-equilibrium state, its entropy is even not well defined. This is because the former is static while the latter is dynamic. The three transport phenomena belong to non-equilibrium state and therefore their empirical laws have not been theoretically derived. Yet, the three phenomena are steady and linear. Their dynamical behaviour should follow a very simple principle. In this article we will use entropy to construct this principle.

The present article is organized as follows. In section 2 we review the entropy of the equilibrium state. In section 3, we try to apply the entropy to steady non-equilibrium state and identify the problem. In section 4, we solve the problem by quantum mechanics. In section 5, we study electrical conduction. In section 6, we study heat conduction. In section 7, we study shear viscosity.
OVERVIEW OF ENTROPY OF EQUILIBRIUM STATE

We consider the system and its environment as two parts. Let’s denote the total energy by \( E_0 \) and energy of the system by \( E \). The environment energy is then \( E_0 - E \). For a given \( E \), the system (environment) can be in a number of possible states. That number is denoted by \( \Omega (\Omega') \) from which the entropy is defined as \( S = k \ln \Omega \) (\( S' = k \ln \Omega' \)). Thus we have

\[
\begin{array}{ccc}
\text{energy} & \text{system + environment} & \text{system} \\
\text{number of states} & \sum_E \Omega(E)\Omega'(E_0 - E) & \Omega(E) \\
\text{entropy} & S(E) & S'(E_0 - E) \\
\end{array}
\]

(4)

The environment should be very large and therefore its entropy linearly depends on the energy fluctuations. So the temperature can be introduced by

\[
\frac{1}{T} = \left. \frac{dS'(E)}{dE} \right|_{E=E_0}
\]

(5)

to let

\[
S'(E_0 - E) = S'(E_0) - \frac{E}{T},
\]

(6)

and

\[
\Omega'(E_0 - E) \propto e^{-\frac{E}{kT}}.
\]

(7)

Thus the probability that a \( E \) occurs is

\[
P(E) \propto \Omega(E)\Omega'(E_0 - E) \propto \Omega(E)e^{-\frac{E}{kT}},
\]

(8)

which is actually the Boltzmann distribution. The average of \( E \) can be calculated through the partition function

\[
Z = \sum_E \Omega(E)e^{-\frac{E}{kT}}
\]

(9)

which leads to

\[
\overline{E} = \frac{1}{Z} \sum_E E\Omega(E)e^{-\frac{E}{kT}}.
\]

(10)

The most probable value of \( E \) can be found by maximizing Eq. (8) or maximizing its logarithm

\[
\ln \Omega(E) - \frac{E}{kT}
\]

(11)

which is equivalent to minimizing the free energy

\[
E - TS(E).
\]

(12)

The most probable \( E \) and the average \( \overline{E} \) will be equal and will be actually the observed energy when the system is big. But it should be noted that when the system is small, they are not necessarily equal and also the observed energy will fluctuate explicitly [5]. The same argument applies to for example electric current.
We study here the steady non-equilibrium state by an example of an electrical conductor. Let an electric field turn on at time $t = 0$. The electric potential is $U$. Let the electric current $I$ be steady. Then at time $t$, it will generate energy $UIt$ which is absorbed by the conductor and the surroundings. We can simple take the whole conductor as a system. But we had better take only those movable electrons/ions as a system. Then the surroundings and the rest of the conductor such as the crystal lattice together form the environment. Anyway, at a time $t$ Eq. (4) becomes

$$E_0 + UIt = E_0 + UIt - E$$

and Eq. (8) becomes

$$P(E, I) \propto \Omega(E, I) \exp\left(\frac{UIt - E}{kT}\right).$$

When the conductor is big enough, the most probable current and the average of the current are approximately equal and are actually the observed steady current. We will only calculate the most probable current because the calculation is easier. The most probable current can be obtained by maximizing $P(E, I)$. To do that, we need to separate $I$ from $E$. So we assume

$$\Omega(E, I) = \Omega(E)\Omega(I).$$

Its meaning can be understood by an example. Consider a crystal lattice and two interstitial ions. The ions can jump from site to site beside vibrating. Suppose the vibrating energy is one of $\{0, \hbar\omega, 2\hbar\omega, \cdots\}$. Also suppose each ion jump once and each jump produces electric current proportional to either $qa/\tau$ or $-qa/\tau$. Then for $E = 2\hbar\omega$ and $I = 0$, we have

$$\Omega(2\hbar\omega, 0) = 3 \times 2.$$ 

Thus Eq. (14) can be factorized into two parts. One part only contains $E$, the other part only contains $I$. The $E$ part will lead us to the free energy and subsequently the most probable $E$. The $I$ part we hope can lead us to the most probable current. This part is

$$P(I) \propto \Omega(I) \exp\left(\frac{UIt}{kT}\right).$$

Let’s introduce system entropy

$$S(I) = k \ln \Omega(I).$$

Then it seems that the most probable $I$ can be obtained by maximizing

$$S(I) + \frac{UIt}{T}.\tag{19}$$

But this is impossible because $t$ is a variable. The problem arises because we have overlooked the quantum nature of the microscopic interactions.
QUANTUM MECHANICS AND $\tau$

According to quantum mechanics, a system evolves unitarily. But the unitary evolution is constantly interrupted by the interactions coming from the environment. The interaction induces the system wavefunction to collapse from time to time. Suppose this happens every $\tau$. Then during time $0 < t < \tau$, the system is in a deterministic wavefunction and the wavefunction evolves unitarily. But at time $t = \tau$, the wavefunction collapses and the result of the collapse follows a probability distribution from which the entropy emerges. Thus Eq. (13) only makes sense at time $t = \tau$ and other moments that the wavefunction collapses. So if we redo the calculation about Eq. (19), we will get

$$S(I) + \frac{UI\tau}{T}, \tag{20}$$

from which the most probable $I$ can be solely determined. To understand it better, we apply it to an example.

Let’s consider here the ionic conduction in which case the conductor is a crystalline solid conductor that is composed by a non-movable crystal lattice and some movable interstitial ions. An ion can jump from site to site. Suppose each ion jumps once every $\tau$ and each jump produces electric current proportional to $\pm qa/\tau$, where $q$ is the ion charge, $a$ is the lattice constant. Suppose the ion concentration $n$ is very low.

First, let’s consider a system that is composed by just one ion. And let the electric field $E$ turn on at time $t = 0$. Then at time $t = \tau$, the ion will either jump up $\uparrow$ or jump down $\downarrow$. So the result will be

$$\text{state} : \{ |\uparrow\rangle |\downarrow\rangle \},$$

$$\begin{align} I_V &= \{ qa/\tau - qa/\tau \}, \\
\Omega &= \{ 1 1 \} \\
P &= \{ 1 \times \exp(\frac{Eaq}{kT}) 1 \times \exp(-\frac{Eaq}{kT}) \} \tag{21} \end{align}$$

where

$$I_V = \sum_i qv_i. \tag{22}$$

But during time $0 < t < \tau$, the system is a pure wavefunction

$$|\Psi\rangle = A_1|\uparrow\rangle + A_2|\downarrow\rangle, \tag{23}$$

where $|A_1|^2 \propto \exp(\frac{Eaq}{kT}), |A_2|^2 \propto \exp(-\frac{Eaq}{kT})$. Only at time $t = \tau$, it will collapse. When it is going to collapse, it can somehow sense the number of the final states and tune $|A_1|$ and $|A_2|$ to the right amplitudes. The number of the final states for this example is the number of the environment states. But that number depends on the result of the collapse that does not happen yet. If the result is $|\uparrow\rangle$, the environment will gain an extra energy $Eaq$ and thus gain extra entropy $\frac{Eaq}{kT}$. Therefore that number will increase by a factor of $\exp(\frac{Eaq}{kT})$. If the result is $|\downarrow\rangle$, the environment will loss energy $Eaq$ and thus loss entropy $\frac{Eaq}{kT}$. Therefore that number will decrease by a factor of $\exp(-\frac{Eaq}{kT})$. Once the wavefunction has collapsed, another unitary evolution will start and the result will be Eq. (23) again just before next collapse. About how a wavefunction collapses, it is a quantum measurement problem which is studied by the decoherence theory [6, 7].
For a system that is composed by two ions, Eq. (21) becomes

\[
\begin{align*}
\text{state} : & \{ | \uparrow \rangle | \uparrow \rangle \quad | \uparrow \rangle | \downarrow \rangle \quad | \downarrow \rangle | \uparrow \rangle \quad | \downarrow \rangle | \downarrow \rangle \}, \\
I_V &= \{ 2qa/\tau \quad 0 \quad -2qa/\tau \}, \\
\Omega &= \{ 1 \quad 2 \quad 1 \}, \\
P &\propto \{ 1 \times \exp(\frac{2Eaq}{kT}) \quad 2 \times 1 \quad 1 \times \exp(-\frac{2Eaq}{kT}) \}.
\end{align*}
\]

(24)

For a system that is composed by \(N\) ions, it becomes

\[
\begin{align*}
I_V &= \{ Nqa/\tau \quad \cdots \quad (2k-N)qa/\tau \quad \cdots \quad -Nqa/\tau \}, \\
\Omega &= \{ 1 \quad \cdots \quad C_N^k \quad \cdots \quad 1 \}, \\
P &\propto \{ 2 \times \exp(\frac{NEaq}{kT}) \quad \cdots \quad C_N^k \times \exp(\frac{(2k-N)Eaq}{kT}) \quad \cdots \quad 1 \times \exp(-\frac{NEaq}{kT}) \}.
\end{align*}
\]

(25)

When \(N\) is large, we can use an approximation of

\[
C_N^k \approx 2^N \frac{1}{\sqrt{\pi N/2}} \exp \left( -\frac{(k-N/2)^2}{N/2} \right).
\]

(26)

Then by writing \(k\) into \(I_V\) and by \(I = I_V/h\), we get the system entropy

\[
S(I) = S_0 - \frac{1}{2} \frac{k\tau^2 h^2}{Na^2 q^2} I^2,
\]

(27)

where \(S_0\) is the entropy of the equilibrium state, \(h\) is the height of the conductor. Thus Eq. (20) in this example becomes

\[
S(I) + \frac{UI\tau}{T} = S_0 - \frac{1}{2} \frac{k\tau^2 h^2}{Na^2 q^2} I^2 + \frac{EhI\tau}{T},
\]

(28)

by which the most probable \(I\) is obtain as

\[
I = \frac{Na^2 q^2}{k\tau hT} E.
\]

(29)

By the way, the electrical conductivity is also obtained,

\[
\sigma = \frac{na^2 q^2}{k\tau T},
\]

(30)

which is the same as the result of the kinetic theory \[8\].

One can also calculate the most probable \(I\) directly from Eq. (25). But our calculation by Eq. (20) is easier. Besides, Eq. (20) is in a general form and is ready to be applied to other studies.

We see that \(\tau\) is actually the time interval between two successive jumps of the same ion. About the time interval between two collapses of the whole system, it is much smaller especially when the system is large. For a system containing \(N\) ions, its wavefunction collapses approximately \(N\) times during \(\tau\). We also see that \(\tau\) is actually an average quantity. If we at the beginning let ions jump randomly, we will still obtain all the results the same.
ELECTRICAL CONDUCTION

We have studied a specific electrical conduction. Now we study the general electrical conduction. Thus we need to write the system entropy in a general form like

$$S(I) = S_0 - C_1 I - \frac{1}{2} C_2 I^2 - \frac{1}{3!} C_3 I^3 + \cdots.$$  \hfill (31)

$S_0$ is the entropy of the equilibrium state. $C_1$ should be zero because the point of $I = 0$ should be a stationary point. Besides, $S(I)$ should be an even function. Therefore when $I$ is small, the system entropy can be approximately written as

$$S(I) = S_0 - \frac{1}{2} C_2 I^2.$$  \hfill (32)

We have not specified the shape of the conductor. $C_2$ actually depends on it. Let’s introduce the system entropy per unit cube as

$$s(j) = s_0 - \frac{1}{2} c_2 j^2,$$  \hfill (33)

where $j$ is the current density. Then for a conductor having cross section $A$ and height $h$, there will be $S = sV$, $I = jA$, $C_2 = c_2 h/A$.

For the ionic conduction, we have $c_2 = \frac{kq^2}{na^2\tau^2}$ which is proportional to $\tau^2$. So $c_2$ is actually not independent. We had better introduce an independent parameter

$$b = \frac{c_2}{\tau^2}.$$  \hfill (34)

By $b$, we can recast $s(j)$ and we will see that it is actually independent of $\tau$. It is actually a configurational entropy which is about what the probability for a certain kind of microscopic configuration to appear.

Concerning $j$, Eq. (20) becomes

$$- \frac{1}{2} c_2 j^2 + \frac{j E \tau}{T},$$  \hfill (35)

which leads to

$$j = \frac{1}{b\tau T} E.$$  \hfill (36)

This formula is the same as Ohm’s law (2). In addition, the electrical conductivity is obtained,

$$\sigma = \frac{1}{b\tau T}.$$  \hfill (37)

HEAT CONDUCTION

The heat conduction can be studied similarly. Let’s take a system and fix it in between two thermal baths. One bath has temperature $T_1$, the other $T_2$. Let $T_1 < T_2$ and let a steady heat current $J$ flow through the system. As an analog of Eq. (33), we have

$$s(j) = s_0 - \frac{1}{2} c_2 j^2.$$  \hfill (38)
And as an analog of Eq. (32), we have

\[ S(J) = S_0 - \frac{1}{2} C_2 J^2. \]  

Thus about heat conduction, Eq. (20) becomes

\[ -\frac{1}{2} C_2 J^2 + J \tau \left( \frac{1}{T_1} - \frac{1}{T_2} \right), \]  

which leads to

\[ J = \frac{\tau}{C_2} \left( \frac{1}{T_1} - \frac{1}{T_2} \right). \]  

Let the system have height \( h \). In the limit of \( h \to 0 \), the above equation becomes

\[ J = -\frac{\tau h}{C_2 T^2} \frac{dT}{dh}, \]  

which can be recast as

\[ j = -\frac{1}{b \tau T^2} \frac{dT}{dh}. \]  

where \( b = c_2 / \tau^2 \) which is introduced as an analog of Eq. (34). This is the same as Fourier’s law (11). In addition, the thermal conductivity is obtained,

\[ \kappa = \frac{1}{b \tau T^2}. \]  

For dilute gas, \( C_2 \) has been calculated in a paper [9]. By using Eq. (41), the paper has also calculated the thermal conductivity and the result is the same as the kinetic theory. In that paper, Eq. (41) is obtained by an analysis of the entropy production.

**SHEAR VISCOSITY**

The previous analysis can be applied to shear viscosity too. Think two \( z \)-axis perpendicular plates between which it is filled with a fluid with cross section \( A \) and height \( h \). Let the bottom plate keep still, the top plate move along \( x \)-axis at a steady speed \( v_x \). Each molecule of the fluid takes part in two kinds of movements. One is the heat movement. The other is the macroscopic movement associated with \( \frac{dv_x}{dz} \). The former contributes entropy to the environment. The latter contributes entropy to the system.

Let the velocity gradient \( \frac{dv_x}{dz} \) be the same everywhere. Then as an analog of Eq. (33), the system entropy per unit cube is

\[ s \left( \frac{dv_x}{dz} \right) = s_0 - \frac{1}{2} c_2 \left( \frac{dv_x}{dz} \right)^2. \]  

During \( \tau \), the force \( F \) applied to the top plate will generate heat \( F v_x \tau \) which subsequently brings an extra entropy \( F v_x \tau / T \). Then as an analog of Eq. (35), the steady velocity gradient can be obtained by maximizing

\[ -\frac{1}{2} c_2 \left( \frac{dv_x}{dz} \right)^2 + \frac{\tau \tau \tau}{T} \frac{dv_x}{dz} \]  

during \( \tau \).
which leads to
\[
\frac{dv_x}{dz} = \tau_{xx} \frac{\tau}{c_2 T}, \tag{47}
\]
where $\tau_{xx} = F/A$. It can be transformed to the form of
\[
\tau_{xx} = b \tau T \frac{dv_x}{dz}, \tag{48}
\]
where $b = c_2 / \tau^2$ which is introduced as an analog of Eq. (34). It is the same as Newton’s law of viscosity (3). In addition, the shear viscosity is obtained,
\[
\eta = b \tau T. \tag{49}
\]

CONCLUSION

We have studied electrical conduction, thermal conduction and shear viscosity by the same approach. In the approach, we have used the entropy as a central concept. We have also considered quantum mechanics explicitly and introduced a parameter $\tau$ to characterize the time interval between two successive interactions of a microscopic particle. This allows us to analyze the system/environment interactions as a series of discrete quantum processes from which entropy emerges to characterize the probability for a microscopic configuration to appear. We have taken the steady electric current as the most probable current and established an equation to find it. The found current follows Ohm’s law. In the same way, we have reproduced Fourier’s law and Newton’s law of viscosity.

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