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Basic phenomena discovered in 1820-30 by Seebeck and Peltier. Played an important role in science and technology ever since.

- Thermodynamic equilibrium: $T$, $\mu$, and $\phi$ are constant, entropy is at a maximum.

- Stationary state: charge and energy currents flow, entropy is produced at a constant rate.

- Empirically, the transport equations relate the currents to the thermodynamic forces (gradients of the driving fields, $T$, $\mu$, $\phi$).

- Thermodynamic approach explains the relationship between the entropy production and the currents, and provides the distribution of $T(x)$, $\mu(x)$, and $\phi(x)$ in the presence of these currents.

- The thermodynamic approach is based on the assumption of a local thermal equilibrium.

- The dissipative processes that drive the system towards new equilibrium and give rise to the entropy production are explained by Onsager’s statistical theory of fluctuations.
Entropy production in a stationary state

Local equilibrium: the sample is 'continuous' but every point is treated as 'a macroscopic system' in a well defined thermodynamic state. Entropy is taken as function of state $s = s(u, n)$.

First law of thermodynamics:

$$ds = \frac{\partial s}{\partial u} du + \frac{\partial s}{\partial n} dn,$$

$du(x)$ and $dn(x)$ are densities (measured relative to equilibrium)

$$\frac{\partial s}{\partial u} = \frac{1}{T(x)} \quad \frac{\partial s}{\partial n} = -\frac{\bar{\mu}(x)}{T(x)}$$

Total entropy change:

$$dS = \int_V d^3x \, ds(u, n)$$

Produced at the rate

$$\frac{dS}{dt} = \int_V d^3x \left( \frac{1}{T} \frac{\partial u}{\partial t} - \frac{\bar{\mu}}{T} \frac{\partial n}{\partial t} \right),$$
The particles and the total energy are conserved. Gauss law rigorously defines the current densities:

\[
\frac{\partial n(x, t)}{\partial t} = -\frac{1}{e} \nabla \cdot J(x),
\]

\[
\frac{\partial u(x, t)}{\partial t} = -\nabla \cdot J_u(x).
\]

Entropy produced in a steady state has to be removed. Need an entropy current through the surface of the sample.

Introduce the internal energy density

\[ \mathcal{E} = u - e\phi n \]

and define the internal energy current density

\[ J_\mathcal{E} = J_u - \phi J, \]
relating $\mathcal{E}$ and $\mathbf{J}_\mathcal{E}$ by the continuity equation

$$\frac{\partial \mathcal{E}}{\partial t} + \nabla \cdot \mathbf{J}_\mathcal{E} = \mathbf{E} \cdot \mathbf{J},$$

$\mathbf{E} = -\nabla \phi$ and $\mathbf{E} \cdot \mathbf{J}$ is the source term.

The total rate of entropy change is now

$$\frac{dS}{dt} = \int d^3x \left( \frac{1}{T} \frac{\partial \mathcal{E}}{\partial t} - \frac{\mu}{T} \frac{\partial n}{\partial t} \right)$$

$$= \int d^3x \frac{1}{T} \left( \mathbf{E} \cdot \mathbf{J} - \nabla \cdot \mathbf{J}_\mathcal{E} + \frac{\mu}{e} \nabla \cdot \mathbf{J} \right).$$

The entropy produced in the sample per unit time

$$\frac{dS}{dt} = \int d^3x \left[ \mathbf{J} \cdot \left( \frac{\mathbf{E}}{T} - \frac{1}{e} \nabla \frac{\mu}{T} \right) + \mathbf{J}_\mathcal{E} \cdot \nabla \frac{1}{T} \right] - \int d^3x \nabla \cdot \left( \frac{\mathbf{J}_\mathcal{E}}{T} - \frac{\mu \mathbf{J}}{eT} \right).$$
The second integral can be transformed into a surface integral using
\[ J_Q = J_\mathcal{E} - \frac{\mu J}{e}, \quad \text{and} \quad J_S = J_Q / T \]

This yields the surface entropy current
\[ \int d^3x \nabla \cdot \frac{J_Q}{T} = \int_{\text{surface}} dA \cdot J_S, \]

The first integral gives the entropy produced in the sample
\[ \left. \frac{dS}{dt} \right|_{\text{volume}} = \int d^3x \left[ J \cdot \left( \frac{E}{T} - \frac{1}{e} \nabla \frac{\mu}{T} \right) + J_\mathcal{E} \cdot \nabla \frac{1}{T} \right] \]

In the stationary state, the two terms compensate each other.

The integrand is a scalar product of a generalized current \( \hat{\mathbf{J}} = (\mathbf{J}, \mathbf{J}_\mathcal{E}) \) and generalized force \( \hat{\mathbf{x}} = (\mathbf{x}_\phi, \mathbf{x}_T) \)
The components of the generalized force are \( (\bar{\phi} = \phi + \mu/e) \)

\[
x_{\phi} = -\frac{\nabla(\bar{\phi})}{T} - \frac{\mu}{e} \nabla \frac{1}{T},
\]

\[
x_{T} = \nabla \frac{1}{T} = -\frac{1}{T^2} \nabla T,
\]

The entropy production per unit volume is a scalar product

\[
\frac{1}{\Delta V} \frac{dS}{dt} = \frac{ds}{dt} = \hat{\mathbf{J}} \cdot \hat{\mathbf{x}},
\]

Since \( \hat{\mathbf{J}} = 0 \) for \( \hat{\mathbf{x}} = 0 \), the currents are linear functions of the forces

\[
\hat{\mathbf{J}} = \hat{\mathbf{G}} \hat{\mathbf{x}}.
\]

Matrix \( \hat{\mathbf{G}} \), defined by transport coefficients \( G_{ab} \), describes the response of quantity \( \{a\} \) to the force conjugate to quantity \( \{b\} \).

Matrix notation is needed, since various processes can interfere.
In anisotropic media or in an external magnetic field, $G_{ab}$ is a tensor defined by its Cartesian components $G^{ij}_{ab}$.

The transport coefficients $G^{ij}_{ab}$ can either be treated as empirical constants or calculated from some model.

Examples: Ohm’s law of electrical conductance,

$$J = -\hat{\sigma} \nabla \phi(x)$$

Fourier’s law of heat conductance,

$$J_Q(x) = -\hat{\kappa} \nabla T(x)$$

Fick’s law of diffusion.

$$J_n = -D \nabla n(x)$$

Thermoelectric and thermomagnetic phenomena deal with more than one current.
Onsager’s relations

Any combination of currents and forces that preserves the scalar product \( \hat{J} \cdot \hat{x} \) yields equivalent description of the thermoelectric phenomena.

Choose those currents and forces so as to minimize the work.

For the currents and forces such that \( ds/dt = \hat{J} \cdot \hat{x} \), the transport matrix satisfies

\[
G_{ab} = \tilde{G}_{ba},
\]

\( \tilde{G}_{ba} \) is obtained from \( G_{ba} \) by transposing its Cartesian coordinates \( i, j \).

In the presence of an external magnetic field,

\[
G_{ab}(B) = \tilde{G}_{ba}(-B),
\]

This expresses the fact that if a charged particle moving in a magnetic field is to retrace its path backward upon reversal of the time axis, the direction of the magnetic field has to be reversed as well.
A complete set of thermoelectric equations

The transport and the continuity equations are not sufficient to determine the currents $\mathbf{J}$, $\mathbf{J}_\varepsilon$, and the fields $T(\mathbf{x})$, $\phi(\mathbf{x})$, $\mu(\mathbf{x})$.

The complete solution should also satisfy the Maxwell’s equations. It can be obtained by the following procedure.

- Start from an initial set $\{T(\mathbf{x}), \phi(\mathbf{x}), \mu(\mathbf{x})\}$, find the local density $n(\mathbf{x})$ from the partition function.
- Using $\nabla T(\mathbf{x})$, $\nabla \phi(\mathbf{x})$, $\nabla \mu(\mathbf{x})$ as the generalized forces find $\mathbf{J}(\mathbf{x})$ and $\mathbf{J}_u(\mathbf{x})$ from the transport equations.
- Update $\phi(\mathbf{x})$ using $n(\mathbf{x})$ and the Poisson’s equation (in the absence of time-dependent magnetic fields).
- Update $T(\mathbf{x})$ and $\mu(\mathbf{x})$ using the continuity equations.
- If the updated values do not agree with the initial set $\{T(\mathbf{x}), \phi(\mathbf{x}), \mu(\mathbf{x})\}$, iterated the procedure to the fixed point.

Transport coefficients define the physical properties of the sample. The boundary conditions describe the reservoirs.
Useful pairs of currents and forces

One set of generalized currents and forces has been found already. The same currents are obtained if we make the transformation

\[ \hat{x}^N = T \hat{x} \quad \text{and} \quad \hat{N} = \frac{\hat{G}}{T}, \quad \text{so that} \quad \hat{N} \, \hat{x}^N = \hat{G} \, \hat{x}. \]

New forces

\[ x_c^N = -\nabla \phi - \frac{T}{e} \nabla \frac{\mu}{T}, \]

\[ x_T^N = T \nabla \frac{1}{T} = -\frac{\nabla T}{T}, \]

The phenomenological transport equations can now be compared with the theoretical quantum mechanical expressions

\[ J(x) = -N_{11} \left( \nabla \phi + \frac{T}{e} \nabla \frac{\mu}{T} \right) - N_{12} \frac{\nabla T}{T}, \]

\[ J_\varepsilon(x) = -N_{21} \left( \nabla \phi + \frac{T}{e} \nabla \frac{\mu}{T} \right) - N_{22} \frac{\nabla T}{T}. \]
Another useful pair is \( \hat{J}_M = (J, J_Q) \),

\[
\begin{align*}
J \quad \text{and} \quad J_Q &= J_\epsilon - \mu \, J/e \\
\end{align*}
\]

The new forces \( \hat{x}^M = (x_c^M, x_Q^M) \) are defined by

\[
J \cdot x_c^M + J_Q \cdot x_Q^M = J \cdot x_\phi + J_\epsilon \cdot x_T,
\]

Substituting the old forces yields

\[
\begin{align*}
x_c^M &= -\frac{\nabla \bar{\phi}}{T}, \\
x_Q^M &= \nabla \frac{1}{T},
\end{align*}
\]

New transport equations

\[
\begin{align*}
J(x) &= -M_{11} \frac{\nabla \bar{\phi}}{T} + M_{12} \nabla \frac{1}{T}, \\
J_Q(x) &= -M_{21} \frac{\nabla \bar{\phi}}{T} + M_{22} \nabla \frac{1}{T}.
\end{align*}
\]
The heat current density satisfies the continuity equation

$$\frac{\partial Q}{\partial t} + \nabla \cdot J_Q = \bar{E} \cdot J,$$

with $\bar{E} = -\nabla \bar{\phi}$.

1. Prove that relation between the coefficients satisfies

$$M_{11} = G_{11}, \quad M_{12} = G_{12} - \left(\frac{\mu}{e}\right)G_{11};$$

and

$$M_{22} = G_{22} - 2\left(\frac{\mu}{e}\right)G_{12} + \left(\frac{\mu}{e}\right)^2G_{11}.$$

2. Find the conjugate forces for the pair $J(x)$ and the total energy current density $J_u(x) = J_Q(x) + \bar{\phi}J(x)$ using

$$Jx_c^P + J_u x_u^P = Jx_c^M + J_Q x_Q^M,$$

3. Prove $\nabla \cdot J_u(x) = 0$
Physical interpretation of the transport equations

User friendly transport coefficients,

\[ \sigma = L_{11}, \quad \sigma \alpha = L_{12}/T, \quad \beta = L_{21}, \quad \bar{\kappa} = L_{22}/T \]

\(\sigma\) is the electrical conductivity, \(\alpha\) is the Seebeck coefficient, \(\beta = \sigma \alpha T\).

The currents flow in response to the electrochemical and thermal gradients

\[ J(x) = -\sigma \nabla \bar{\phi} - \sigma \alpha \nabla T, \quad (4) \]

\[ J_Q(x) = -\beta \nabla \bar{\phi} - \bar{\kappa} \nabla T, \quad (5) \]

Alternative form

\[ J(x) = \sigma (\bar{E} - \alpha \nabla T), \quad (6) \]

\[ J_Q(x) = \Pi J(x) - \kappa \nabla T, \quad (7) \]

\(\Pi = \alpha T\) is the Peltier coefficient

\(\kappa = \bar{\kappa} - \sigma \alpha^2 T\) is the thermal conductivity.
Thermoelectric heats

The stationary flow leads to the entropy production, as the charge and heat currents flow down the potential and thermal gradients.

Electrons are accelerated by the field but dissipate kinetic energy.

The solution of transport equations must satisfy the energy conservation. In a stationary state, the continuity equation yields

\[ \nabla \cdot \mathbf{J}_u = \nabla \cdot (\kappa \nabla T) + \frac{J^2}{\sigma} - T \mathbf{J} \cdot \nabla \alpha = 0. \]  

(8)

The heat and charge currents produce irreversible heats at each point

1. Diffusion heat \( \dot{q}_T = -\nabla(\kappa \nabla T) \)

2. Joule heat \( \dot{q}_\phi = \frac{J^2}{\sigma} \)

But the thermoelectric heat is produced as well

3. Thompson heat \( \dot{q}_\mu = T \mathbf{J} \cdot \nabla \alpha \)

N.B. \( \dot{q}_\mu \) is linear in \( \mathbf{J} \).
Entropy production

The charge current flowing in the presence of a temperature gradient inevitably produces Thompson heat in addition to Joule heat.

In a uniform sample and constant $\nabla T$, the heat current in volume $\delta V$ is increased by the Joule and Thompson contribution.

In a non-uniform sample, there is an additional thermal diffusion heat generated at each point, $\dot{q} = -\nabla \cdot (\kappa \nabla T)$.

Entropy is not changed by the thermoelectric heat

$$\frac{dS}{dt} = \int \left[ \frac{\kappa (\nabla T)^2}{T^2} + \frac{J^2}{\sigma T} \right] dV$$
Figure: The upper and the lower branch of the device have the Peltier coefficients $\Pi_A(T)$ and $\Pi_B(T)$. The two legs make contact at point $c$. At points $a$ and $b$, the device is in contact with a thermal reservoir. The battery is driving the current as indicated by the arrows. Temperature at point $c$ depends on the direction of the current.
Consider a stationary state of a two-leg device with $\alpha_A, \Pi_A, \kappa_A$ on one side and $\alpha_B, \Pi_B, \kappa_B$ on the other. The normal components of the heat and charge currents, like $T(x)$, and $\bar{\phi}(x)$, are continuous at every point.

The continuity of the heat current yields at the junction

$$\kappa_A \frac{dT}{dx} \bigg|_A = \kappa_B \frac{dT}{dx} \bigg|_B + \Pi_{AB} J,$$

(9)

$\Pi_{AB} = \Pi_A - \Pi_B$ is the relative Peltier coefficient.

The outgoing thermal current matches the incoming thermal current and the Peltier heat current $\Pi_{AB} J$ generated at the junction.

The Peltier effect arises because the energy levels in the two materials are not the same. The difference $(s_A - s_B) T$ defines the Peltier heat, which has to be added to or subtracted from the junction to ensure the continuity of the heat current.
Figure: The upper and lower branches of the device are made of different thermoelectric materials, with Seebeck coefficients $\alpha_A(T)$ and $\alpha_B(T)$. At $c$ the device is in contact with a heat source. Points $a$ and $b$ are at room temperature. The arrows indicate the direction of the heat flow. The thermoelectric voltage drives the current through an external load.
Since \( \mathbf{J} = 0 \), the electromotive force between points \( a \) and \( b \) is obtained from the transport equation as

\[
V_{ab} \equiv \bar{\phi}(a) - \bar{\phi}(b) = \int_{a}^{b} dx \, \alpha(x) \frac{dT}{dx} = \int_{T(a)}^{T(c)} dT \, \alpha_B(T) - \int_{T(b)}^{T(c)} dT \, \alpha_A(T)
\]

For small \( \Delta T = T(c) - T(a) \),

\[
V_{ab} = \int_{T}^{T+\Delta T} dT \, (\alpha_B - \alpha_A) \simeq \Delta T \left[ \alpha_B(T) - \alpha_A(T) \right],
\]

The relative Seebeck coefficient of the two materials is

\[
\alpha_A - \alpha_B = \frac{V_{ab}}{\Delta T}.
\]

Experiments provide the relative Seebeck or Peltier coefficients for a pair of different conductors. The absolute Seebeck coefficient can be obtained if the circuit is closed with a superconductor below \( T_c \), for which \( \alpha_A - \alpha_B = \alpha_A \).
The Seebeck voltage appears because particles diffuse from the hot to the cold end of the sample giving rise to an imbalance of charges which induces potential gradients in the branch $A$ and $B$ of the device.

In a stationary state, the work needed to move $\delta N_{A(B)}$ electrons against the potential $\Delta V_{A(B)}$ is provided by the heat energy.

$$e \, \delta N_{A(B)} \Delta V_{A(B)} = \Delta T \frac{\partial S_{A(B)}}{\partial N_{A(B)}} \delta N_{A(B)}$$

The Seebeck coefficient is expressed as the entropy per charge carrier:

$$\alpha(T) = \frac{\Delta V}{\Delta T} = \frac{1}{e} \frac{\partial S(T, N)}{\partial N} = \frac{1}{e} \frac{\partial s(T, n)}{\partial n},$$

Using Maxwell relation

$$\left[ \frac{\partial s(T, n)}{\partial n} \right]_{T,V} = - \left[ \frac{\partial \bar{\mu}(T, n)}{\partial T} \right]_{V,N}$$

shows $\mathbf{J} = 0$ because the thermal and electrochemical current compensate each other.
Temperature distribution in a homogeneous thermoelectrics

We now want to find the temperature distribution in the sample when the charge and heat currents are present,

\[ J = \sigma \bar{E} - \sigma \alpha \nabla T, \]  
\[ J_Q = \alpha T J - \kappa \nabla T. \]

(10) \hspace{1cm} (11)

The solutions have to satisfy the continuity equations

\[ \frac{\partial n}{\partial t} = -\frac{1}{e} \nabla \cdot J, \]  
\[ \frac{\partial u}{\partial t} = -\nabla \cdot J_u. \]

(12) \hspace{1cm} (13)

In a stationary state, this leads to the Domenicali equation for \( T(x) \):

\[ -\nabla \cdot (\kappa \nabla T) = \frac{J^2}{\sigma} - T J \cdot \nabla T \frac{d\alpha}{dT}. \]

(14)

The boundary condition is yet to be defined.
For constant coefficients, \( d\alpha/dT = 0 \), the integration yields the slope

\[
-\kappa \nabla T(x) = \frac{J^2}{\sigma} x + F.
\]  

(15)

and the next integration yields the temperature field:

\[
-\kappa T(x) = \frac{J^2 x^2}{2\sigma} + F x + G.
\]  

(16)

The boundary conditions \( T = T_0 \) at \( x_0 = 0 \) and \( T = T_1 \) at \( x_1 = L \) specify two integration constants \( F \) and \( G \).
The integration constants are:

\[ G = -\kappa T_0 = -K \frac{L}{A} T_0, \quad (17) \]

\[ F = -\frac{K}{A} (T_1 - T_0) - \frac{R I^2}{A^2}, \quad (18) \]

This yields the slope

\[ \frac{dT(x)}{dx} = \frac{1}{2} \frac{R I^2}{KL} \left( 1 - 2 \frac{x}{L} \right) + \frac{T_1 - T_0}{L}. \quad (19) \]

where

\[ K = (A/L)\kappa \quad \text{thermal conductance} \]
\[ R = L/A\sigma \quad \text{resistance} \]
\[ I = AJ \quad \text{total charge current through (one-D) sample}. \]

\[ \frac{dT(x)}{dx} \geq \frac{(T_1 - T_0)}{L} \quad \text{for} \quad 0 \leq x \leq l/2 \]
\[ \frac{dT(x)}{dx} \leq \frac{(T_1 - T_0)}{L} \quad \text{for} \quad 0 \leq l/2 \leq x \]
Heat currents at the sink and the source

$T(x)$ and $dT(x)/dx$ define the thermal current $I_Q(x) = AJ_Q(x)$ at every point. At the source:

$$I_Q|_{x=0} \equiv q_0 = \alpha T_0 I - K(T_1 - T_0) - \frac{R I^2}{2}.$$

$\alpha T_0 I$  Peltier heat generated by $I$ at the point $x = 0$

$K(T_1 - T_0)$  heat flux diffusing from the source to the sink

$R I^2/2$  one-half of the Joule heat generated $I$

For $T_0 < T_1$, the heat is pumped out of the source, as long as the Peltier heat overcomes the losses due to thermal diffusion and the Joule heat.

The heat current dumped at the sink

$$I_Q|_{x=l} = \alpha T_1 I - K(T_1 - T_0) + \frac{R I^2}{2}.$$

If the current is switched on when the temperature of the source is equal to that of the sink, $T_1$, the heat current begins to flow out of the source.
Find the current that yields the maximum cooling power. Then, \(dq_0/dl = 0\), and the optimal current is

\[
I_{opt} = \frac{\alpha T_0}{R},
\]

The heat taken out of the source is

\[
q_0^{\text{max}} = \frac{\alpha^2 T_0^2}{2R} - K(T_1 - T_0).
\]

The lowest \(T_0\) is reached for \(q_0 = 0\) and \(l = l_{opt}\).

\[
(T_1 - T_0)_{\text{max}} = \frac{1}{2} z T_0^2,
\]

where

\[
z = \frac{\sigma \alpha^2}{\kappa}
\]

is the figure of merit.
Two leg device

Figure: Simple two-legged thermoelectric device.

Legs A and B conduct heat in parallel and charge in series, so $K = K_A + K_B$, $R = R_A + R_B$, and $\alpha = \alpha_A - \alpha_B$.

This converts the one-leg expressions into two-leg expressions.
In a heat pump, the battery maintains the heat flow against $\Delta T$ and compensates the losses due to the Joule and thermal diffusion.

The battery power matches the difference between the heat current dumped into the sink and the heat current leaving the source,

$$W = I_Q|_{x=l_A=l_B=l} - I_Q|_{x=0}$$

The coefficient of performance

$$\Phi = \frac{I_Q^0}{W} = \frac{\alpha T_0 l - K(T_1 - T_0) - Rl^2/2}{\alpha(T_1 - T_0)l + Rl^2}. \quad (20)$$

$d\Phi/dl = 0$ defines the current that optimizes the performance

$$I_\Phi = \frac{\alpha(T_1 - T_0)}{R(1 + ZT_M)^{1/2} - 1}, \quad (21)$$

$T_M = (T_1 + T_0)/2$ and $Z$ is the figure of merit of the device,

$$Z = \frac{(\alpha_A - \alpha_B)^2}{(K_A + K_B)(R_A + R_B)}, \quad (22)$$

Calculate the optimal coefficient of performance.
Efficiency coefficient $\eta$ of a power generator

$\eta$ is the ratio of the power delivered to the external load, $W = I^2 R_{load}$, to the heat current taken from the source.

$$\eta = \frac{W}{I_T|_{x=0}} = \frac{I^2 R_{load}}{\alpha T_0 I + K(T_0 - T_1) - RI^2/2}.$$  \quad (23)

$I = \alpha(T_0 - T_1)/(R_{load} + R)$ is the current driven by the Seebeck voltage. With $M = R_{load}/R$,

$$\eta = \frac{T_0 - T_1}{T_0} \frac{ZM}{Z(1 + M) + (1 + M)^2/T_0 - Z(1 - T_1/T_0)/2}. \quad (24)$$

Optimization with respect to $M$ yields

$$M_{opt} = (1 + ZTM)^{1/2} \quad \quad (25)$$

and

$$\eta_{max} = \frac{T_0 - T_1}{T_0} \frac{(1 + ZTM)^{1/2} - 1}{(1 + ZTM)^{1/2} + T_1/T_0}. \quad \quad (26)$$
The output power can also be written as $I\Delta V$, where $\Delta V = \alpha \Delta T - IR$
where with $\Delta T = T_0 - T_1$ (the voltage drop due to the Seebeck effect is corrected by the internal resistance of the element).

The heat taken from the source in unit time is

$I_Q = \alpha T_0 I + K\Delta T - RI^2/2$

The efficiency is

$$\eta = \frac{W}{I_Q} = \frac{(\alpha \Delta T - IR)I}{\alpha T_0 I + K\Delta T - RI^2/2}$$  \hspace{1cm} (27)

Prove that optimizing with respect to the current gives

$$\eta_{\text{max}} = \frac{T_0 - T_1}{T_0} \left( \frac{1 + ZT_M}{(1 + ZT_M)^{1/2}} - 1 \right) \frac{1}{(1 + ZT_M)^{1/2} + T_1/T_0}.$$  \hspace{1cm} (28)
The operation of a thermoelectric device with uniform and temperature independent transport coefficients has been analyzed using the transport equations

\[ \mathbf{J} = \sigma \mathbf{E} - \sigma \alpha \nabla T, \]  
(29)

\[ \mathbf{J}_Q = \alpha T \mathbf{J} - \kappa \nabla T. \]  
(30)

and the continuity equation for the total energy current

\[ -\nabla \cdot \mathbf{J}_u = 0. \]  
(31)

This provided the Domenicali equation for \( T(x) \),

\[ -\nabla \cdot (\kappa \nabla T) = \frac{\mathbf{J}^2}{\sigma} - T \mathbf{J} \cdot \nabla T \frac{d\alpha}{dT} \]  
(32)

In a device built of a uniform material the integration was straightforward.

Since \( zT \) is at the maximum at some temperature \( T_{\text{max}} \), \( zT(x) < zT_{\text{max}} \) at most points in the device.
Inhomogenous thermoelectric materials

Performance is improved if the composition changes along the length of the device, so $zT(x)$ can be at a maximum at every point.

Mahan simulated the effects of the inhomogeneous doping by making $\sigma(x)$ position-dependent and using $\kappa(x) = \kappa[\sigma(x)]$, and $\alpha(x) = \alpha[\sigma(x)]$

He replaces the second-order Domenicali differential equation by two coupled set of first-order equations:

$$\frac{dT}{dx} = J \frac{\alpha(x)}{\kappa(x)} T(x) - \frac{J_Q(x)}{\kappa(x)},$$

$$\frac{dJ_Q}{dx} = -J \frac{\alpha(x)}{\kappa(x)} J_Q(x) + \frac{J^2}{\sigma(x)} [1 + z(x) T(x)]. \quad (33)$$

The solutions depend on the conductivity profile $\sigma(x)$, which is varied to maximize the efficiency of the device as a generator, with the boundary conditions $T_0 = 300 \text{ K}$ and $T_1 = 800 \text{ K}$. 
Figure: (A) Temperature profile for a semiconductor-based thermoelectric generator with maximum efficiency; the cold end is at $x = 0$ and $T_0 = 300$ K and the hot end is at $x = L$ and $T = 800$ K. (B) Reduced conductivity $y(x) = \sigma(x)/\sigma_0$. (C) $zT(x)$ for the optimum conductivity profile (top curve) and for homogeneous doping, such that $zT$ is maximum at the average temperature in the sample. Inhomogeneous doping increase $zT$ throughout most of the device.
Segmented thermoelectrics

Divide the sample into segments with constant material parameters. By increasing the number of segments per unit length we recover Mahan’s result.

We want the efficiency of a power generator, when the heat current $I_B^B$ is taken out of the source.

Let’s start with two homogeneous segments. Note, $I(x)$, $I_Q(x)$ and $T(x)$ are continuous functions of $x$ everywhere along the sample.
Efficiency of a current generator with two segments

For $T_B > T_A$, the heat is taken out from the source at rate $I_Q$,

$$I_Q^B = \alpha_B T_B I - K_B \nabla T|_{x=-b}$$

The efficiency is

$$\eta = \frac{W}{I_Q^B}$$

$W = I \Delta V$ is the power delivered to the external load. \(\Delta V\) is the total thermoelectric voltage generated by both segments, corrected for the internal resistance of the device,

$$W = I \{[\alpha_B (T_0 - T_B) + \alpha_A (T_A - T_0)] - I(R_B + R_A)\}$$

The efficiency is

$$\eta = \frac{I \alpha_{\text{eff}} (T_B - T_A) - I^2 R}{I_Q^B}$$

where

$$\alpha_{\text{eff}} = \frac{\alpha_B (T_0 - T_B) + \alpha_A (T_A - T_0)}{T_B - T_A} = \frac{\Delta V_B + \Delta V_A}{T_B - T_A}$$
Integrate Domenicali equation in A-segment and B-segment:

\[- \kappa_{A,B} \frac{dT}{dx} = \frac{J^2}{\sigma_{A,B}} x + F_{A,B}\]

and

\[- \kappa_{A,B} T(x) = \frac{J^2}{\sigma_{A,B}} \frac{x^2}{2} + F_{A,B} x + G_{A,B},\]

Integration constants are fixed by the boundary conditions.

\[T(0) = T_0 \implies G_B = -\kappa_B T_0\]
\[T(-b) = T_B \implies F_B = -\frac{K_B}{A} (T_0 - T_B) + \frac{R_B}{A} \frac{I^2}{2},\]

Similarly, in A

\[T(0) = T_0 \implies G_A = -\kappa_A T_0\]
\[T(a) = T_A \implies F_A = -\frac{K_A}{A} (T_A - T_0) - \frac{R_A}{A} \frac{I^2}{2},\]

\(K_{A,B}\) is the thermal conductance in A and B.
\(R_{A,B}\) is the electrical resistance in A and B.
\( T_0 \) follows from the continuity of the current at \( x=0 \) with

\[
\left. J^B_Q \right|_{x=0} = \alpha_B T_0 J + F_B
\]

and

\[
\left. J^A_Q \right|_{x=0} = \alpha_A T_0 J + F_A,
\]

The continuity gives

\[
\alpha_B T_0 I - K_B (T_0 - T_B) + \frac{R_B I^2}{2} = \alpha_A T_0 I - K_A (T_A - T_0) - \frac{R_A I^2}{2},
\]

Temperature \( T_0 \) is current-dependent.

Alternatively, we can choose a different boundary condition and calculate the temperature difference \( T_A - T_B \) for a given heat current \( q_0^B \) taken out of the source \( B \), when \( T_A \) is known (room temperature).
Device with N segments

Figure: Inhomogeneous thermoelectric divided into N homogeneous segments, between two reservoirs at temperatures $T_0$ and $T_1 < T_0$.

The generalization from 2 to N segments is obvious. The continuity of the heat current at any point $x_i$ of the device requires

$$
\lim_{\delta \to 0} \left[ \alpha_i \frac{I}{A} - \kappa_i \frac{dT}{dx} \right]_{x_i-\delta} = \lim_{\delta \to 0} \left[ \alpha_{i+1} \frac{I}{A} - \kappa_{i+1} \frac{dT}{dx} \right]_{x_i+\delta}
$$
Temperature profile for $N$ segments

Matching the currents yields $N$ equations for temperatures $T_1, \ldots, T_N$

Given $T_0$, $I_Q^0$, and the parameters of each segment, $R_i, \alpha_i, \kappa_i$, \{ $T_1, \ldots, T_N$ \} follow from the recursion.

$$T_1 = \left[ K_1 T_0 + \alpha_1 T_0 I - (I_Q^0 + \frac{I^2}{2} R_1) \right] / K_1,$$

$$T_2 = \left( 1 + \frac{K_1}{K_2} + I \frac{\alpha_2 - \alpha_1}{K_2} \right) T_1 - \frac{K_1}{K_2} T_0 - \frac{I^2}{2K_1} (R_1 + R_2).$$

\ldots \ldots

$$T_i = \left( 1 + \frac{K_{i-1}}{K_i} + I \frac{\alpha_i - \alpha_{i-1}}{K_i} \right) T_{i-1} - \frac{K_{i-1}}{K_i} T_{i-2} - \frac{I^2}{2K_i} (R_{i-1} + R_i).$$

\ldots \ldots

The boundary condition is $T_{i=0} = T_B$ and $T_{i=N}(I, I_Q^0) = T_A$.

We can choose some $I_Q^0$ and generate $T_N$ recursively.

If $T_N \neq T_A$ we change $I_Q^0$ and start again.

The temperature profile depends on the current.
The efficiency of a segmented generator is, as before,

\[ \eta_{\text{eff}} = \frac{I \alpha_{\text{eff}} (T_0 - T_N) - I^2 R}{I_0} \]

but

\[ \alpha_{\text{eff}} = \frac{\sum_{i=1}^{N} \alpha_i (T_i - T_{i-1})}{T_N - T_0} \rightarrow \int_{x_0}^{x_N} dx \frac{\alpha(x) \nabla T(x)}{T_N - T_0} \]

and

\[ R = \sum_{i=1}^{N} R_i \rightarrow \int_{x_0}^{x_N} dx \ R(x) \]

The efficiency has now an implicit current-dependence via the temperature profile. The optimization can bring surprises.

The actual efficiency of the device might be smaller than the estimate based on the average transport coefficients. (Mahan)
The figure of merit of the device is

$$Z_{\text{eff}} = \frac{\alpha_{\text{eff}}^2}{KR}$$

$K$ is the thermal conductance of the device obtained from the thermal resistance $1/K$. Since all segments are connected into series, $1/K$ is the sum

$$\frac{1}{K} = \sum_{i=1}^{N} \frac{1}{K_i}$$

$Z_{\text{eff}}$, like $\eta_{\text{eff}}$, depends on the current and the temperature distribution in the sample. Choosing optimal doping can increase the efficiency.
None of the results discussed so far would be possible without the reciprocity relation between the Seebeck and the Peltier coefficients.

The proof of the symmetry of the thermoelectric coefficients was provided by Onsager in his study of the interference between various irreversible processes. Following Onsager, we shall do the following.

- Introduce the thermodynamic description of fluctuations in a system with a small temperature and potential gradients.
- Introduce statistical theory using Boltzmann relation between the entropy and the probability of a given thermodynamic state.
- Assume that the decay of thermodynamic fluctuations is due to the same dissipative processes that occur in stationary state with finite currents.
- Show that the reciprocity relation between the Seebeck and Peltier coefficients follows from the time-reversal symmetry of the quantum mechanical laws that govern the electron dynamics.
First moments of thermodynamic variables

To discuss the fluctuations of a thermodynamic variable $\rho_{\alpha}$ it is useful to introduce its first moment

$$p_{\alpha} = \frac{1}{\Delta V} \int_{\Delta V} d^3x \, x \, \rho_{\alpha}(x),$$

$\Delta V$ is the volume around $x$ in which the local system is in thermodynamic equilibrium. Typical examples are the moments of $\rho_u(x) = u(x), \rho_e(x) = en(x), \rho_m(x) = mn(x)$

The fluctuating state is characterized by $p_{\alpha} \neq 0$.

For each moment one can define the ’center of fluctuation’ $X$, e.g., for an inhomogeneous sample, $X$ is the center of mass.

$$p_{\alpha} = \frac{M_{\alpha}}{\Delta V} X_{\alpha} \quad \text{where} \quad M_{\alpha} = \int_{\Delta V} d^3x \, \rho_{\alpha}(x)$$

The bigger the fluctuation, the bigger $|X|$. 

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The rate of change of $p_\alpha(x)$ defines the corresponding current density,

$$\frac{\delta p_\alpha}{dt} = \frac{1}{\Delta V} \int d^3x \frac{\partial \rho_\alpha(x, t)}{\partial t} x = -\frac{1}{\Delta V} \int d^3x \nabla \cdot J_\alpha(x) x = J^0_\alpha$$

$J_\alpha(x)$ is the current density defined by the continuity equation for the conserved physical quantity $\rho_\alpha(x)$

$$\frac{\partial \rho_\alpha(x)}{\partial t} = -\nabla \cdot J_\alpha(x)$$

$J^0_\alpha$ is the uniform current density that describes the decay of fluctuations

$$J^0_\alpha = \frac{1}{\Delta V} \int d^3x J_\alpha(x),$$

We have applied the periodic boundary conditions to eliminate the surface term.
The system is fluctuating in the presence of temperature and potential gradients but we are assuming that each small part is locally in thermal equilibrium.

Entropy of the fluctuating state is

\[ S = S(\mathbf{p}_\alpha, \mathbf{p}_\beta, \ldots) \]

It has a maximum in the equilibrium state, where all the moments vanish.

Assuming the local thermal equilibrium we can relate the change in entropy to the change in the heat, the work and the particle number.

\[ dS = \frac{1}{T}(dU - dW) - \frac{e\phi + \mu}{T} dN \]

The system can be pushed out of equilibrium by adding an amount of energy \( dU \) without changing the volume or the number of particles. This defines the heat fluctuation, \( \delta Q = dU \) and its "center of heat" \( \mathbf{p}_q/\delta Q \) at point \( x \). The additional entropy is \( dS = \delta Q / T(x) \).
Heat and energy fluctuations

If the fluctuation decays by shifting its “center of heat” to $x + \Delta x$, where temperature is $T(x + \Delta x)$, the change in the entropy density is

$$ds = \frac{1}{\Delta V} \left[ \frac{\delta Q}{T(x + \Delta x)} - \frac{\delta Q}{T(x)} \right] \approx \frac{\Delta x \delta Q}{\Delta V} \frac{\partial}{\partial x} \frac{1}{T} = \delta p^x \nabla_x \frac{1}{T}.$$

$ds = \delta p_q \cdot \nabla (1/T)$ is the entropy change per unit volume due to the decay of fluctuation in an arbitrary direction and

$$\frac{ds}{dt} = \delta p_q \cdot \nabla \frac{1}{T}.$$

The entropy production is the product of the uniform heat current density and the “thermodynamic force” that drives the current

$$\frac{ds}{dt} = J_q^0 \cdot f_q,$$

where the conjugate force is

$$f_q = \nabla \frac{1}{T} = \frac{ds}{\delta p_q}.$$
Particle fluctuations

When $\delta N$ electrons are displaced by $\Delta x$, the entropy density changes by

$$ds = -\frac{\delta N}{\Delta V} \frac{\mu(x + \Delta x) + e\phi(x + \Delta x)}{T(x + \Delta x)} + \frac{\delta N}{\Delta V} \frac{\mu(x) + e\phi(x)}{T(x)}$$

$$\simeq -\frac{\delta N \Delta x}{\Delta V} \nabla_x \frac{\bar{\mu}}{T} = -\delta p_n \cdot \nabla \frac{\bar{\mu}}{T}.$$ 

The rate of change of the entropy density due to the decay of the density fluctuation is again a scalar product

$$\frac{\delta s}{dt} = J_n \cdot f_n,$$

$J_n = \delta p_n/\Delta t$ is the uniform number current and the conjugate force is

$$f_n = -\nabla \frac{\bar{\mu}}{T} = \frac{ds}{\delta p_n}.$$

Again, the entropy production due to the decay of a fluctuation is the product of the uniform current density and the thermodynamic force.
Energy fluctuation in a gravitational field

For the charge transport we choose the moment \( \mathbf{p}_e = e \mathbf{p}_n \), with the charge current \( \mathbf{J}_e = \frac{\delta \mathbf{p}_e}{\delta t} \). The entropy production is \( \frac{\delta s}{\delta t} = \mathbf{J}_e \cdot \mathbf{f}_e \) with

\[
\mathbf{f}_e = -\nabla \frac{\mu/e + \phi}{T} = -\nabla \frac{\phi}{T} = \frac{ds}{\delta p_e}.
\]

In all the cases, the entropy production accompanying the spontaneous decay of fluctuations is the product of the uniform current density and the conjugated thermodynamic force.

When the system is placed in a “small gravitational potential” \( \psi(x) \) that couples to the internal energy density \( \mathcal{E}(x) \), there is additional contribution to the entropy change given by

\[
-\frac{\psi}{T} d\mathcal{E}
\]

The decay of an energy fluctuation that preserves the volume and the number of particles introduces an extra contribution to the change in entropy density,

\[
ds = -\frac{\delta Q \Delta x}{\Delta V} \nabla_x \frac{\psi}{T} = -\delta \mathbf{p}_q \cdot \nabla \frac{\psi}{T} \approx -\delta \mathbf{p}_q \cdot \frac{\nabla \psi}{T},
\] (34)
The total thermal force conjugate to the uniform heat current density of a system in a gravitational field is therefore

\[ f_q = \nabla \frac{1}{T} - \frac{\nabla \psi}{T}. \]

In thermal equilibrium there are neither currents nor forces. This condition is expressed by the equations

\[ \nabla \psi - T \nabla \frac{1}{T} = 0, \]

\[ \nabla \phi + \frac{T}{e} \nabla \frac{\mu}{T} = 0. \]

We shall use these relations when analyzing the response of nonmagnetic systems to static but spatially inhomogeneous fields.
When several types of fluctuations are simultaneously present, the additional entropy is affected by their interference.

For small moments, \( \{p_\alpha, p_\beta, \ldots \} \), the entropy can be expanded as

\[
s(p_\alpha, p_\beta, \ldots) = s_0 - \frac{1}{2} \sum_{\gamma \delta, ij} \eta_{ij}^{\gamma \delta} p_\gamma^i p_\delta^j ,
\]

Greek indices label the different moments and Latin indices specify the Cartesian coordinates of a given moment. By definition,

\[
\eta_{ij}^{\gamma \delta} = \left[ \frac{\partial s(p_\alpha, \ldots, p_\beta, \ldots)}{\partial p_\gamma^i \partial p_\delta^j} \right]_0 = \eta_{ij}^{\delta \gamma} ,
\]

The first-order terms are absent from the expansion, because the entropy has its maximum in the equilibrium state and the forces vanish.
The rate of entropy production per unit volume is

\[ \frac{d\Delta s^{(2)}}{dt} = \frac{d\hat{p}}{dt} \cdot \hat{f}. \]

where \( \hat{f} = (f_\alpha, \ldots, f_\kappa) \) is the generalized force vector, \( f^i_\alpha \) is the thermodynamic force driving the fluctuation \( p_\alpha \),

\[ f^i_\alpha = \frac{\partial \Delta s^{(2)}}{\partial p^i_\alpha} = -\sum_{\delta j} \eta^{ij}_\alpha \delta p^j_\delta. \]

and \( d\hat{p}/dt = (dp_\alpha/dt, \ldots, dp_\kappa/dt) \) is the generalized current density.

If the regression of fluctuations is due to the same irreversible processes that occur in the presence of externally applied forces, then, for small moments, the currents are described by the same empirical equations

\[ \frac{d\hat{p}}{dt} = \hat{G}\hat{f}, \]

and the matrix elements \( G^{ij}_{\alpha\beta} \) are the same phenomenological constants. The microscopic reversibility makes the transport matrix \( \hat{G} \) symmetric.
Statistical description of fluctuations

If $W$ is the "thermodynamic probability" of a particular macroscopic state with $m$ fluctuation $\{p_\alpha, p_\beta, \ldots, p_\kappa\}$ ($W$ gives the number of occurrences of such a state in the statistical ensemble), its entropy is defined as

$$S(p_\alpha, p_\beta, \ldots, p_\kappa) = k_B \log W + \text{const},$$

The distribution function of the fluctuation $\{p_\alpha, p_\beta, \ldots, p_\kappa\}$ is

$$P(p_\alpha, p_\beta, \ldots, p_\kappa) = \frac{1}{Z} e^{\Delta V \Delta s^{(2)}/k_B} = \frac{1}{Z} \exp \left[ -\frac{1}{2k_B} \sum_{\gamma\delta,ij} (\Delta V \eta^{ij}) p^i_\gamma p^j_\delta \right],$$

$Z$ is the partition function $Z = \sqrt{\frac{(2\pi k_B/\Delta V)^m}{\det \hat{\eta}}}$

and $P$ is normalized

$$\int d^3p_\alpha \ldots d^3p_\kappa \ P(p_\alpha \ldots p_\kappa) = 1.$$
Probability distribution \( P(p_\alpha, \ldots, p_\kappa) \times (\Delta p)^m \) is the probability of finding the thermodynamic state with the moments \( p_\alpha, p_\beta, \ldots, p_\kappa \) within the intervals \( p'_\alpha \leq p_\alpha \leq p'_\alpha + \Delta p_\alpha, \ldots, p'_\kappa \leq p_\kappa \leq p'_\kappa + \Delta p_\kappa \).

The average value of any function \( g(p_\alpha, \ldots, p_\kappa) \) is given by the integral

\[
\langle g \rangle = \int d^3 p_\alpha \ldots d^3 p_\kappa \, g(p_\alpha, \ldots, p_\kappa) \, P(p_\alpha, \ldots, p_\kappa)
\]

The correlation between two functions \( g \) and \( h \) is defined as

\[
\langle gh \rangle = \int d^3 p_\alpha \ldots d^3 p_\kappa \, g(p_\alpha, \ldots, p_\kappa) \, h(p_\alpha, \ldots, p_\kappa) \, P(p_\alpha, \ldots, p_\kappa)
\]

Expressing the forces as

\[
f^i_\alpha = \frac{k_B}{\Delta V} \frac{\partial \ln P}{\partial p^i_\alpha}, \tag{35}
\]

shows that the moments and the forces are correlated in the following way

\[
\langle p^i_\alpha f^j_\beta \rangle = -\frac{k_B}{\Delta V} \delta_{ij} \delta^\alpha_\beta.
\]
Equal time correlation functions of currents and forces

By definition, the correlation function $\langle p^i_\alpha f^j_\beta \rangle$ is given by

$$\langle p^i_\alpha f^j_\beta \rangle = \frac{k_B}{\Delta V} \int d^3 p_\alpha \ldots d^3 p_\kappa \ p^i_\alpha \frac{\partial \ln P}{\partial p^j_\beta} P = \frac{k_B}{\Delta V} \int d^3 p_\alpha \ldots d^3 p_\kappa \ p^i_\alpha \frac{\partial P}{\partial p^j_\beta}.$$ 

Partial integration then yields

$$\langle p^i_\alpha f^j_\beta \rangle = \frac{k_B}{\Delta V} P p^i_\alpha|_{-\infty}^{\infty} - \frac{k_B}{\Delta V} \int d^3 p_\alpha \ldots d^3 p_\kappa \ p^i_\alpha \frac{\partial p^i_\alpha}{\partial p^j_\beta} P,$$

where the first term vanishes and $\frac{\partial p^i_\alpha}{\partial p^j_\beta} = \delta_{ij} \delta_{\alpha \beta}$.

The system of linear equations for the simultaneous averages of the mean squares and the product of fluctuations $\langle p^i_\alpha p^j_\beta \rangle$ is obtained by inverting the matrix $\hat{\eta}$,

$$\langle p^i_\alpha f^j_\beta \rangle = - \sum_{\delta, k} \eta^{ik}_\beta \delta \langle p^i_\alpha p^k_\delta \rangle = - \frac{k_B}{\Delta V} \delta_{\alpha \beta} \delta_{ij},$$
To prove the symmetry of the transport matrix, Onsager calculates

\[ A^{ij}_{\alpha\beta}(\tau) = \langle p^i_\alpha(t)p^j_\beta(t + \tau) \rangle. \]

\( \langle \ldots \rangle \) was defined by the equal-time distribution function, \( P(p_\alpha, p_\beta, \ldots) \), so it has to be generalized. By the ergodic hypothesis, the ensemble average is equivalent to the time average, defined as

\[ A^{ij}_{\alpha\beta}(\tau) = \lim_{t'' \to \infty} \frac{1}{t'' - t'} \int_{t'}^{t''} dt \ p^i_\alpha(t)p^j_\beta(t + \tau) = p^i_\alpha(t)p^j_\beta(t + \tau), \]

This time average can be calculated if one knew the regression of a fluctuation \( p^j_\beta \) from \( t \) to \( t + \tau \).

From the statistical point of view, the laws describing the time-evolution of the fluctuating state apply to the averages taken over very many cases of irreversible processes starting from the same thermodynamic state. This suggests how to find the time dependent averages.
Calculating the time-dependent averages by Onsager’s prescription

Follow the evolution of the system over a very great length of time and, whenever the variables \( p_\alpha, \ldots, p_\kappa \) assume the values \( p'_\alpha, \ldots, p'_\kappa \), record the value of these variables \( \tau \) seconds later.

The average of all these records defines the functions \( \bar{p}_\alpha(\tau; p'_\alpha, \ldots, p'_\kappa), \ldots, \bar{p}_\kappa(\tau; p'_\alpha, \ldots, p'_\kappa) \), which describe the average regression of the fluctuation \( \{p'_\alpha, \ldots, p'_\kappa\} \) in the time interval \( \tau \).

Since we assume that the irreversible processes starting from any of the states \( p'_{i\alpha}, \ldots, p'_{j\kappa} \) at time \( t \) evolve according to well-known (linear) empirical laws, the time dependence of function \( \bar{p}^j_\alpha \) is described by the same rate equation as that of the fluctuation \( p^j_\beta \):

\[
\frac{d\bar{p}^j_\beta}{dt} = \sum_{\delta k} G^{jk}_{\beta\delta} \frac{\partial s(p_\alpha, \ldots, p_\kappa)}{\partial p^k_\delta}.
\]

The average \( A_{\alpha\beta}^{ij}(\tau) \) describes the particular case where, at time \( t \), the fluctuating state is characterized by a single variable \( p^i_\alpha \), with value \( p'^i_\alpha \).
Since all the moments except $p^i_\alpha$ are zero at time $t$, the corresponding forces vanish, and we have

$$f^k_\delta = \frac{\partial s(p^\alpha, \ldots, p^\kappa)}{\partial p^k_\delta} = 0 \quad \text{for} \quad \delta \neq \alpha, \ k \neq i \quad (36)$$

$$f^i_\alpha = \frac{\partial s(p^\alpha, \ldots, p^\kappa)}{\partial p^i_\alpha} = \left[ \frac{ds(p^i_\alpha)}{dp^i_\alpha} \right]_{p^i_\alpha = p^{i'}_\alpha},$$

Thus, we can calculate $A^{ij}_{\alpha \beta}(\tau)$ using

$$\frac{d\bar{p}^j_\beta}{dt} = G^{ji}_{\beta \alpha} f^i_\alpha.$$

The rate $d\bar{p}^j_\beta / dt$ gives the macroscopic average $\bar{p}^j_\beta(t + \tau, p^{i'}_\alpha)$ for small $\tau$. Expanding $\bar{p}^j_\beta(t + \Delta t, p^{i'}_\alpha)$ for small $\Delta t$ yields

$$\bar{p}^j_\beta(t + \Delta t, p^{i'}_\alpha) = \bar{p}^j_\beta(t, p^{i'}_\alpha) + \frac{d\bar{p}^j_\beta}{dt} \Delta t = \bar{p}^j_\beta(t, p^{i'}_\alpha) + G^{ji}_{\beta \alpha} f^i_\alpha \Delta t.$$
We now recall that the deterministic laws of mechanics or quantum mechanics do not depend on the direction of time. If the fluctuating variables of a macroscopic system depend only on the position of the particles, the event in which at time $t$ the moment $p^i_\alpha$ has the value $p^{i'}_\alpha$ and the moment $p^j_\beta$ assumes the value $p^{j'}_\beta$ after $\tau$ seconds occurs just as many times as the event in which $p^j_\beta = p^{j'}_\beta$ is followed $\tau$ seconds later by $p^i_\alpha = p^{i'}_\alpha$. The same is true if the fluctuating variables depend on the energy of the particles.

Because of micro-reversibility, the statistical average must satisfy the condition

$$A^{ij}_{\alpha\beta}(\tau) = \langle p^i_\alpha(t)p^j_\beta(t+\tau) \rangle = \langle p^j_\beta(t)p^i_\alpha(t+\tau) \rangle = A^{ji}_{\beta\alpha}(\tau).$$
Calculating $A^i_j(\tau)$

For small $\tau = \Delta t$ the ensemble average can be calculated:

$$A^i_j(\Delta t) = \langle p^i_\alpha(t) p^j_\beta(t + \Delta t) \rangle = \frac{p^{i'}_\alpha \bar{p}^j_\beta(t + \Delta t, p^{i'}_\alpha)}{p^{i'}_\alpha \bar{p}^j_\beta(t, p^{i'}_\alpha) + G^{ji}_{\beta\alpha} \Delta t p^{i'}_\alpha f^i_\alpha}$$

$$= A^i_j(0) - \frac{k_B}{\Delta V} G^{ji}_{\beta\alpha} \Delta t .$$

In the first line, we have replaced the ensemble average by the time average and used the fact that the value of the macroscopic variable $p^j_\beta$ at time $t + \tau$ is given by the function $\bar{p}^j_\beta(t + \tau; p^{i'}_\alpha)$, with $p^{i'}_\alpha = p^i_\alpha(t)$.

The second line is obtained by expanding $\bar{p}^j_\beta(t + \Delta t, p^{i'}_\alpha)$ for small $\Delta t$.

The third line follows from the orthogonality relation $\langle p^i_\alpha f^j_\beta \rangle \simeq \delta_\alpha \beta \delta_{ij}$.
Onsager’s relations

Similar calculation gives

\[ A_{\beta \alpha}^{ji} (\Delta t) = A_{\beta \alpha}^{ji} (0) - \frac{k_B}{\Delta V} G_{\alpha \beta}^{ij} \Delta t \]

and because of microreversibility we must have \( A_{\alpha \beta}^{ij} (\tau) = A_{\beta \alpha}^{ji} (\tau) \). Thus, the transport matrix \( \hat{G} \) must be symmetric and the transport coefficients satisfy Onsager’s reciprocal relation

\[ G_{\beta \alpha}^{ji} = G_{\alpha \beta}^{ij}. \]

Even though the irreversible changes of a macro-state are governed by the laws of statistical mechanics, which are probabilistic, the underlying time evolution follows the deterministic laws of mechanics, which satisfy time-reversal symmetry.
As an example, consider an anisotropic crystal to which an electrical force is applied in the $i$-direction and a thermal force in the $j$-direction. Then, the heat current in the $j$-direction has an additional component proportional to the electrical force, and the charge current in the $i$-direction has an additional component proportional to the thermal force. Microscopic reversibility ensures that these constants of proportionality are equal, provided we use the correct forces.

Diagonal components $G_{ij}^{\alpha\alpha}$, say, conductivity or thermal conductivity, satisfy $G_{ij}^{ji} = G_{ij}^{ij}$.

If we consider a system in the presence of a magnetic field $B \neq 0$, the particles would retrace their paths if the sign of all velocities and the sign of the magnetic field were reversed. Thus, the reciprocal relations should read

$$G_{\beta\alpha}^{ji}(B) = G_{\alpha\beta}^{ij}(-B).$$


