Master QLMN

Nonequilibrium Statistical Physics

Irreversible Thermodynamics

1 Onsager reciprocity relations

Onsager derived relations of reciprocity for the linear response coefficients. These relations can be used provided that the generalized forces are expressed in a specific way. In this exercise we will derive linear response coefficients that do satisfy relations of reciprocity. We consider a homogeneous conductor that allows transport of charge and heat between two thermodynamic reservoirs R_1 and R_2. The reservoirs have temperature T_1 and $T_2 = T_1 + \Delta T$ and electric potential V_1 and $V_2 = V_1 + \Delta V$. We will also give an expression of the thermal conductance as a function of the linear response coefficients.

We generally use the following formulation for the flux of charge and internal energy :

$$
\begin{aligned}
I_q &= l_{11}\Delta V + l_{12}\Delta T \\
I_U &= l_{21}\Delta V + l_{22}\Delta T.
\end{aligned}
\tag{1}
$$

Using this formulation, the reciprocity relation $l_{12} = l_{21}$ is not satisfied. This is because we chose arbitrarily the formulation for the forces : ΔT and ΔV. We must define the flux of extensive quantity and identify the generalized forces starting from the rate of entropy creation. This ensures an unambiguous definition of the forces.

1. We consider that the conductor and the two reservoirs form an isolated system. q is the charge of an electron, ΔN and ΔU are the variation of number of electrons and internal energy in the reservoir R_2 during Δt. Write the variation of charge and energy of reservoir R_1 neglecting the heat capacity and electrical capacity of the conductor.

2. Derive the variation of entropy in R_1 and R_2 corresponding to a variation of charge $q\Delta N$ and energy ΔU. The chemical potential is $\mu(T)$.

3. Derive the total variation of entropy during Δt in the system.

4. The rate of creation of entropy in the system is :

$$
\frac{\Delta S}{\Delta t} = \sum_i J_i X_i, \tag{2}
$$

where J_i is the rate of variation of the extensive variables :

$$
J_U = \frac{\Delta U}{\Delta t} \quad J_q = q\frac{\Delta N}{\Delta t}.
$$

Deduce that the generalized forces associated X_i associated to the extensive quantities are :

$$\begin{aligned} X_U &= -\frac{\Delta T}{T^2} \\ X_q &= -\frac{1}{q}\Delta\left(\frac{\mu_{ec}}{T}\right), \end{aligned} \tag{3}$$

where $\mu_{ec} = \mu + qV$ is the electro-chemical potential.

5. Using this formulation, we can write coefficients that satisfy Onsager reciprocity :

$$\begin{aligned} J_q &= L_{11}X_q + L_{12}X_U \\ J_U &= L_{21}X_q + L_{22}X_U. \end{aligned} \tag{4}$$

The coefficient L_{22} cannot be immediately identified with thermal conductance. The thermal conductance Γ is defined by $J_U = -\Gamma\Delta T$ in absence of charge flux rather than for zero voltage. Derive a relation between L_{11} and L_{12} for zero charge flux. Show that the thermal conductance is given by :

$$\Gamma = \frac{L_{11}L_{22} - L_{12}^2}{L_{11}T^2}. \tag{5}$$

2 Heat conduction : production of entropy in a constriction

We consider a thermal conductor (thermal conductivity λ) occupying a volume defined in spherical coordinates. It occupies the volume comprised between R_1 and R_2. It has a cylindrical symmetry around the z axis and is comprised between $\theta = 0$ and $\theta = \alpha$. The temperatures are $T(R_1) = 300K$ and $T(R_2) = 320K$. This creates a radial heat flux in the conductor.

1. Derive the local volumic rate of creation of entropy as a function of T, $\frac{\partial T}{\partial r}$ and λ.

2. Show that the rate of creation of entropy vary as r^{-4}.

3. Where do irreversible phenomena occur in the system ?