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Master QLMN - Université Paris-Saclay

TD 6 - Non-equilibrium Statistical Physics
Irreversible Thermodynamics - CORRECTION

1 Onsager reciprocity relations

Onsager derived relations of reciprocity for the linear response coefficients. These relations can be used only if 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.

$$I_q = l_{aa}\Delta V + l_{ab}\Delta T$$

$$I_U = l_{ba}\Delta V + l_{bb}\Delta T$$

Using this formulation, the reciprocity relation $l_{ab} = l_{ba}$ 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.

Question 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 t. Write the variation of charge and energy of reservoir R_1 neglecting the heat capacity and electrical capacity of the conductor.

We consider that the system comprising R_1,the conductor and R_2 form an islated system. The conductor having neglectable heat and electrical capacity, we consider that each element of energy or particle or charge lost by R_1 is gained by R_2 and vice-versa.

$$\delta U_1 = -\delta U_2 = -\delta U$$
$$\delta Q_1 = q\delta N_1 = -q\delta N_2$$

Question 2 Derive the variation of entropy in R_1 and R_2.

We use the thermodynamical identity :

$$\begin{aligned}
dU &= TdS + \mu dN + Vdq \\
dS &= \frac{dU}{T} - \frac{\mu}{T}dN - \frac{V}{T}dq \\
\delta S_1 &= \frac{\delta U_1}{T_1} - \frac{\mu(T_1)}{T_1}dN - \frac{V_1}{T_1}dq \\
&= \frac{\delta U_1}{T_1} - \frac{\mu(T_1) - qV_1}{T_1}\delta N_1 \\
&= -\frac{\delta U_2}{T_1} + \frac{\mu(T_1) - qV_1}{T_1}\delta N_2
\end{aligned}$$

and :

$$\delta S_2 = \frac{\delta U_2}{T_2} - \frac{\mu(T_2) + qV_2}{T_2}\delta N_2$$

Question 3 Derive the total variation of entropy in during δt in the system.

$$\begin{aligned}
\delta S &= \delta S_1 + \delta S_2 \\
&= (\frac{1}{T_2} - \frac{1}{T_1})\delta U_2 + (\frac{\mu(T_1) + qV_1}{T_1} - \frac{\mu(T_2) + qV_2}{T_2})\delta N_2
\end{aligned}$$

Question 4 The rate of creation of entropy in the system is :$\frac{\delta S}{\delta t} = \sum_i J_i X_i$, where J_i is the rate of variation of the extensive variables : $J_U = \frac{\delta U}{\delta t}$ and $J_q = q\frac{\delta N}{\delta t}$. Deduce that the generalized forces associated Xi associated to the extensive quantities are : $X_U = \frac{\Delta T}{T^2}$ and $X_q = \frac{-1}{q}\Delta\left(\frac{\mu_{ec}}{T}\right)$ where $\mu ec = \mu + qV$ is the electro-chemical potential.

$$\begin{aligned}
\frac{\delta S}{\delta t} &= (\frac{1}{T_2} - \frac{1}{T_1})\underbrace{\frac{\delta U_2}{\delta t}}_{J_U} + (\frac{\mu(T_1)/q + V_1}{T_1} - \frac{\mu(T_2)/q + V_2}{T_2})\underbrace{q\frac{\delta N_2}{\delta t}}_{J_q} \\
&= \Delta(\frac{1}{T})J_U - \frac{1}{q}\Delta(\frac{\mu + qV}{T})J_q
\end{aligned}$$

We can deduce $X_U = \Delta(\frac{1}{T}) = -\frac{\Delta T}{T^2}$ and $X_q = -\frac{1}{q}\Delta(\frac{\mu_{ec}}{T})$.

Question 5 Show that the thermal conductance is given by : $\Gamma = \frac{L_{11}L_{22} - L_{12}^2}{L_11T^2}$.

The thermal conductance is given by $J_U = -\Gamma\Delta T$ with zero charge flux, i.e. $J_q = 0$. Besides, we have :

$$J_U = L_{21}X_q + L_{22}X_U = -L_{21}\frac{1}{q}\Delta(\frac{\mu_{ec}}{T}) - L_{22}\frac{\Delta T}{T^2}$$

The absence of charge flux gives us the relation $L_{11}X_q = -L_{12}X_U$ leading to $X_q = -\frac{L_{12}}{L_{11}}X_U$.

We use the previous expressions to get the thermal conductance Γ :

$$
\begin{aligned}
-\Gamma\Delta T &= -\frac{L_{21}L_{12}}{L_{11}}X_U + L_{22}X_U \\
\Gamma &= \frac{L_{21}L_{12} - L_{22}L_{11}}{L11}\frac{-1}{T^2} \\
&= \frac{L_{22}L_{11} - L12^2}{L_{11}T^2}
\end{aligned}
$$

Heat conduction constriction

$$\mathbf{J_U} = -\lambda\vec{\nabla}T = -\lambda\frac{\partial T}{\partial r}\mathbf{u_r}$$

$$\Omega = 2\pi(1-\cos\alpha)$$

$$\Sigma(r) = \Omega r^2 = 2\pi(1-\cos\alpha)r^2$$

$$
\begin{aligned}
\frac{\partial s}{\partial t} &= \vec{\nabla}(\frac{1}{T})\cdot\mathbf{J_U} \\
&= \frac{\lambda}{T^2}\vec{\nabla}T\cdot\vec{\nabla}T \\
&= \frac{\lambda}{T^2}\left(\frac{\partial T}{\partial r}\right)^2
\end{aligned}
$$

$$\mathbf{J_u}(r)\cdot\mathbf{\Sigma}(r) = \text{cste}$$

$$-\lambda\frac{\partial T}{\partial r}2\pi(1-\cos\alpha)r^2 = \text{cste}$$

$$\frac{\partial T}{\partial r} = \frac{A}{r^2}$$

$$\frac{\partial s}{\partial t} = \frac{\lambda}{T^2}\left(\frac{A}{r^2}\right)^2 \approx \frac{1}{r^4}$$