Onsager Relations
An advancement towards non-equilibrium thermodynamics

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Outline

Foreword

Debye's mysterious visitor

"One day in 1925 Pieter Debye was sitting in his office at the Eidgenossische Technische Hochschule in Zurich when a visitor from Norway was announced. In came a tall young man, who walked silently across the room, bent over the desk, and said solemnly : 'Professor Debye, your theory of electrolytes is incorrect.'

Whereopon Debye, after begging the stranger to sit down and inviting him to discuss his objections, offered him an assistantship for the following year. The young man's name was Lars Onsager."

Who was Lars Onsager ?

Lars Onsager
(1903-1976)
Norwegian-American
chemist and physicist.
Born

About Onsager
"Nobody outside of physics and
chemistry has ever heard of
Onsager, even though this is
[Onsager relations] one of at least
four fundamental contributions he
made to statistical physics."

- ► solution of the Ising model
- ► nematic model for liquid crystals
- ► theory of turbulance
  (independent discovery)

On the discovery

Discovery

"[Onsager made the breakthrough] in 1920s, and published in 1931 in that obscure journal to which unacceptable ideas are condemned by the scientific establishment, The Physical Review. This work was recognized as being absolutely brilliant, and when Onsager was decently aged he got the 1968 Nobel Prize in chemistry for initiating non-equilibrium thermodynamics."

Context : Why is it useful ?

The Onsager relations give foundations to a wide family of effects :

- Peltier effect (heat on electric connectors)
- Seebeck effect (voltage on heat connectors)
- Thermoelectric effect (two above)
- Magnetocaloric Effect
- Spin Seebect effect
- any other effects considering coupling of currents
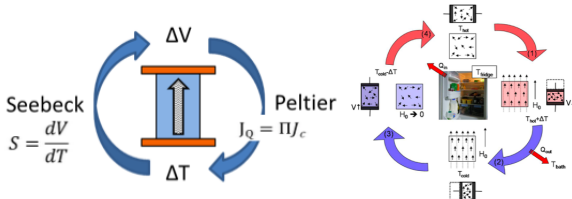
Local equilibrium and linear response

We'd like to consider near, but non-equilibrium states and for this we will assume that we **can** define equilibrium properties, for at least part of the system.

Moreover, describing our system by $x_1, x_2, ..., x_N$ macroscopic variables, we'll assume that their variation is small and we postulate (neglecting noises) that their values tend towards equilibrium.

$$\dot{x}_i = - \sum_j \lambda_{ij} x_j$$

Energy and Entropy representations

Energy representation

$$dU = \left(\frac{\partial U}{\partial S}\right)dS + \left(\frac{\partial U}{\partial V}\right)dV + \left(\frac{\partial U}{\partial N_i}\right)dN_i + \left(\frac{\partial U}{\partial x_j}\right)dx_j$$

$$dU = TdS - pdV + \mu_i dN_i + P_j dx_j$$

Entropy representation

$$dS = \left(\frac{\partial S}{\partial U}\right)dS + \left(\frac{\partial S}{\partial V}\right)dV + \left(\frac{\partial S}{\partial N_i}\right)dN_i + \left(\frac{\partial S}{\partial x_j}\right)dx_j$$

$$dS = \frac{1}{T}dS + \frac{p}{T}dV - \frac{\mu_i}{T}dN_i - F_j dx_j$$

The quantity F_j is now the generalized force associated with x_j, and is related to the generalized force P_j. In the approach to equilibrium these generalized forces drive changes in the extensive variables to equilibrate a system.

Entropy expansion

Let's consider a set of extensive variables, A_i, with equilibrium values of A_i^{eq}. Their deviation from equilibrium is given by

$$\alpha_i = A_i - A_i^{eq}$$

If we are close to equilibrium then the entropy can be expanded in terms of α

$$S(\alpha) = S(0) + \frac{\partial S}{\partial \alpha_i}\alpha_i + \frac{1}{2}\frac{\partial^2 S}{\partial \alpha_i \partial \alpha_j}\alpha_i\alpha_j + ...$$

$$\beta_{ij} = -\frac{1}{2}\frac{\partial^2 S}{\partial \alpha_i \partial \alpha_j}$$

$$S(\alpha) - S_0 = -\frac{1}{2}\beta_{ij}\alpha_i\alpha_j$$

The driving forces

$$S(\alpha) - S_0 = -\frac{1}{2}\beta_{ij}\alpha_i\alpha_j$$

We can identify this term with generalized forces
(thermodynamic forces) introduced before

$$F_i = -\frac{\partial S}{\partial x_i} = \sum_j \beta_{ij}x_j$$

Using this we can rewrite the linear response equation

$$\dot{x}_i = -\sum_j \gamma_{ij}F_j$$

We'll show that the matrix γ_{ij} is symmetric

Expectation values

$$\langle F_i x_j \rangle = -\int d^N x e^{S[x]} \frac{\partial S}{\partial x_i} x_j = -\int d^N x \left(\frac{\partial}{\partial x_i} e^{S[x]} \right) x_j = \delta_{ij}$$

$$\langle F_i F_j \rangle = \langle F_i \sum_k \beta_{jk} x_k \rangle = \beta_{ij}$$

$$\langle x_i x_j \rangle = \langle x_i \sum_j (\beta^{-1})_{jk} F_k \rangle = (\beta^{-1})_{ij}$$

Reversability in time

On the microscopic level the equations need to be time reversible, and time-shift invariant. This is why fluctuations must obey

$$\langle x_i(t+\tau)x_j(t)\rangle \ = \langle x_i(t-\tau)x_j(t)\rangle \ = \langle x_i(t)x_j(t+\tau)\rangle$$

$$\frac{1}{\tau}(\langle x_i(t+\tau)x_j(t)\rangle - \langle x_i(t)x_j(t)\rangle) = \frac{1}{\tau}(\langle x_i(t)x_j(t+\tau)\rangle - \langle x_i(t)x_j(t)\rangle)$$

$$\langle \dot{x}_i(t)x_j(t)\rangle \ = \langle x_i(t)\dot{x}_j(t)\rangle$$

Onsager relations

Onsager assumed that the fluctuations obey the same law as the deterministic values (Onsager hypothesis)

$$\langle \dot{x}_i(t) x_j(t) \rangle = \langle \sum_k \gamma_{ik} F_k(t) x_j(t) \rangle = \gamma_{ij}$$

$$\langle x_i(t) \dot{x}_j(t) \rangle = \langle x_i(t) \sum_k \gamma_{jk} F_k(t) \rangle = \gamma_{ji}$$

Which gives

$$\gamma_{ij} = \gamma_{ji}$$

That's it.

Leading you astray

Say we'd like to find the relation between the electric current I and the heat current W, caused by the temperature difference ΔT and the potential difference $\Delta \phi$. Naivly we could think that the relations look this way :

$$W = I_{11} \Delta T + I_{12} \Delta \phi$$

$$I = I_{21} \Delta T + I_{22} \Delta \phi$$

and that the Onsager relations tell us $I_{12} = I_{21}$, but this is wrong. Where's the catch ? We need to formulate the currents in the **entropy representation**.

Correct formulation

As we've learned the entropic forces are minus derivatives of entropy, so we need to consider how entropy changes

Let's assume we've got 2 containers, both with heat and charged particles like electrons. Let them be related by ΔT and $\Delta \phi$ and assume there's a flow of energy dU and particles dn from the first to the second container.

Calculating entropy changes

The change of entropy in first container will be

$$dS_1 = -\frac{1}{T}dU + \frac{\mu(T)}{T}dn$$

And the second

$$dS_2 = \frac{1}{T + \Delta T}dU - \frac{\mu(T + \Delta T) + e\Delta\phi}{T + \Delta T}dn$$

Therefore the total entropy change equals

$$dS = dS_1 + dS_2 \simeq \left(-\frac{\Delta T}{T^2}dU\right) + \left(-\frac{\Delta T}{e}\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) - \frac{\Delta\phi}{T}\right)edn$$

Calculating entropy changes

If we now identify $dx_1 = dU$, $dx_2 = edn$ and recall that the thermodynamic forces had the form

$$F_i = -\frac{\partial S}{\partial x_1}$$

We easily notice that the forces we've been looking for, have the form :

$$F_1 = \frac{\Delta T}{T^2}$$

$$F_2 = \left(\frac{\Delta T}{e} \frac{\partial}{\partial T} \left(\frac{\mu}{T} \right) + \frac{\Delta \phi}{T} \right) edn$$

Calculating entropy changes

Now the relations between the currents $W = dx_1/dt = dU/dt$ and $I = dx_2/dt = edn/dt$ have the following form :

$$W = \gamma_{11}\frac{\Delta T}{T^2} + \gamma_{12}\left(\frac{\Delta T}{e}\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) + \frac{\Delta\phi}{T}\right)$$

$$I = \gamma_{21}\frac{\Delta T}{T^2} + \gamma_{22}\left(\frac{\Delta T}{e}\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right) + \frac{\Delta\phi}{T}\right)$$

And the Onsager relations state that $\gamma_{12} = \gamma_{21}$.

Closing words

Thank you for your attention !

Literature

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