Introduction: Equilibrium and non equilibrium states

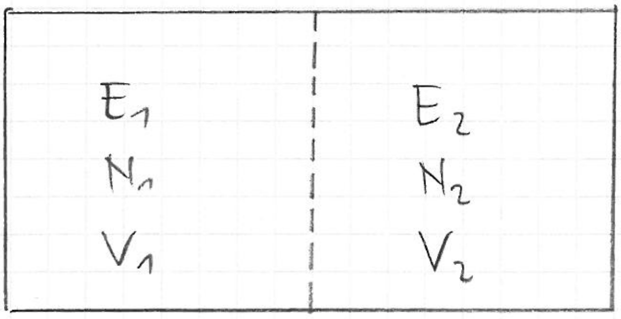
1° Thermodynamics of equilibrium states

- closed, single component system
- energy E, particle number N, volume V

t → ∞: System reaches unique macroscopic eq. state; spatially homogeneous, time-independent, no fluxes.

Eq. state is determined by maximizing the entropy $S(E,V,N)$ subject to relevant constraints.

Example: Equilibrium condition under coupling between subsystem



$$E_1 + E_2 = E$$

$$N_1 + N_2 = N$$

$$V_1 + V_2 = V$$

Maximize

$$S_{tot} = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

⇒ equality of intensive state variables defined as partial derivatives of S:

$$dS = \frac{1}{T}\, dE + \frac{p}{T}\, dV - \frac{\mu}{T}\, dN$$

$$\Rightarrow \quad T_1 = T_2, \quad p_1 = p_2, \quad \mu_1 = \mu_2 .$$

Thermodynamic stability:

For the eq. state to be a maximum of S, the matrix of second derivatives

$$(\delta S^{(2)})_{ik} = \frac{\partial^2 S}{\partial A_i \partial A_k} \qquad A_i : \text{ ext. state variables}$$

must be positive. This implies the positivity of response coefficients such as specific heat & compressibility.

Reversible and irreversible processes:

In general the entropy balance during a infinitesimal state change reads

$$dS = \underset{\nearrow}{d_e S} + \underset{\nwarrow}{d_i S}$$

$$\text{external: } \frac{dQ}{T} \qquad\qquad \text{internal}$$

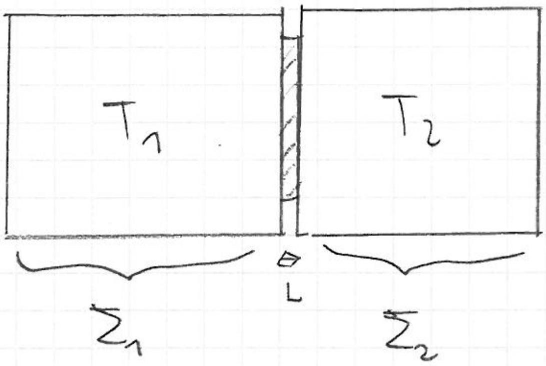
Second law: $\quad d_i S \geq 0$

For irreversible processes $\quad d_i S > 0 \quad \Rightarrow$ entropy production

2° Types of nonequilibrium processes

a) Relaxation to equilibrium

Example: Thermal contact between systems at different temperatures



Σ_1, Σ_2 : Homogeneous systems described by single state variables T_1, T_2; initially $T_2 > T_1$.

Fourier's law postulates a heat (energy) current

$$\underline{\vec{j}_Q = -\lambda \nabla T} \quad \lambda: \text{ thermal conductivity}$$

linear transport relation (phenomenological)

In the present case this implies

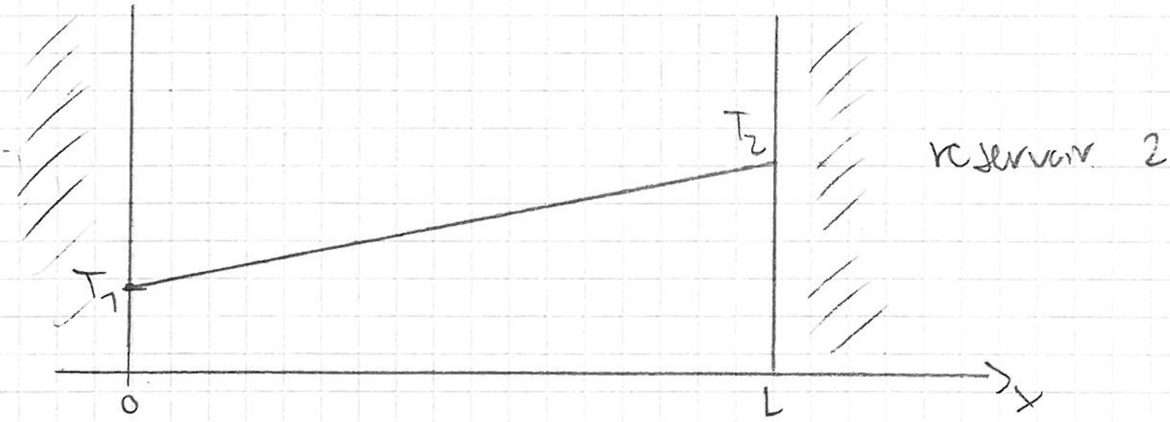
$$\left.\begin{array}{l} \dfrac{dQ_1}{dt} = \dfrac{\lambda A}{L}(T_2 - T_1), \quad \dfrac{dQ_2}{dt} = -\dfrac{dQ_1}{dt} \\ Q_1, Q_2 : \text{energy content of } \Sigma_1, \Sigma_2 \end{array}\right\}$$

Entropy production: $dS = dS_1 + dS_2 = \dfrac{dQ}{T_1} - \dfrac{dQ}{T_2} > 0$

$$\Rightarrow \sigma := \frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dQ}{dt} = \frac{\lambda A}{L}\frac{(T_2-T_1)^2}{T_1 T_2} > 0$$

provided $\lambda > 0$.

b) Nonequilibrium stationary states (NESS)



stationary heat current $j_Q = -\lambda \nabla T = -\frac{\lambda}{L}(T_2 - T_1)$

Entropy balance: $\frac{dS}{dt} = \frac{d_eS}{dt} + \underbrace{\frac{d_iS}{dt}}_{= \sigma > 0} = 0$

$\Rightarrow \quad \frac{dS_e}{dt} < 0$, the NESS exports entropy to the reservoirs.

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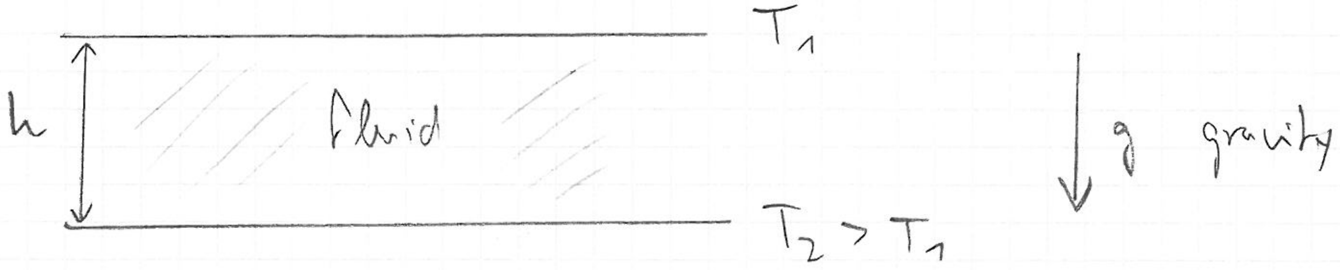
c) Close to or far from equilibrium?

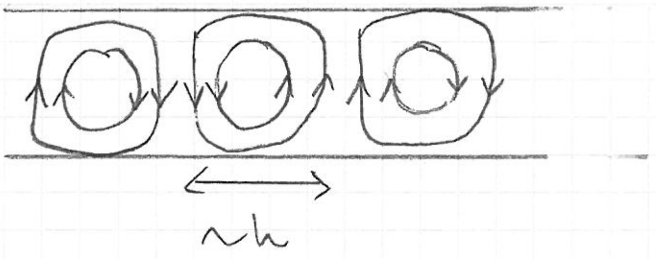
How to characterize the "distance" from thermal equilibrium?

Example: Rayleigh - Bénard convection

(Bénard 1905, Rayleigh 1916)



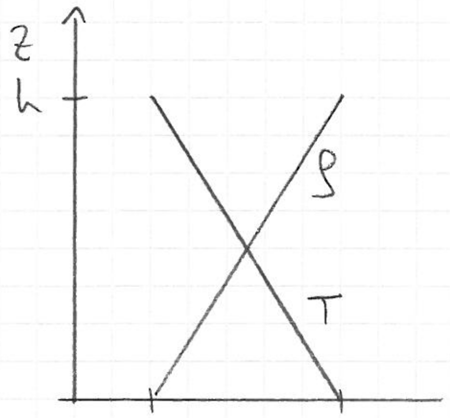
- "Small" ΔT: Heat conduction, spatially homogeneous NESS
- "Large" ΔT: Convection rolls ⇒ spatial inhomogeneity



- Further increase of ΔT leads to time-dependent periodic and eventually chaotic states.

Mechanism: Thermal expansion & buoyancy

$\Delta\rho = -\alpha \Delta T \cdot \rho$, α: thermal expansion coefficient



⇒ hot fluid elements rise subject to damping by heat conduction and viscosity (= fluid friction)

Relevant time scales:

(i) Buoyancy: Force per volume $g \alpha \rho \Delta T$

$\Rightarrow$ acceleration $a = g \alpha \Delta T$

$\Rightarrow$ time to rise to height h is

$$\tau_b \sim \sqrt{\frac{h}{g \alpha \Delta T}}$$

(ii) Heat conduction: $\vec{j}_\alpha = - \lambda \nabla T$

$\Rightarrow$ energy density q satisfies

$$\frac{\partial q}{\partial t} = - \nabla \cdot \vec{j}_\alpha = \lambda \nabla^2 T \,, \quad q = c_v T$$

$$\Rightarrow \frac{\partial T}{\partial t} = \varkappa \nabla^2 T \,, \quad \varkappa = \lambda / c_v \,, \quad [\varkappa] = \frac{\text{length}^2}{\text{time}}$$

Time scale for diffusion on scale h is then

$$\tau_\alpha \sim h^2 / \varkappa$$

(iii) Viscosity: Navier-Stokes eq. for fluid velocity $\vec{v}$:

$$\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} = \nu \nabla^2 \vec{v}$$

ν: kinematic viscosity $\Rightarrow$ $\tau_\nu \sim h^2 / \nu$

⇒ competition between buoyancy and damping is quantified by the Rayleigh number

$$R = \frac{\tau_\alpha \cdot \tau_\nu}{\tau_b^2} = \frac{\alpha g \Delta T \cdot h^3}{\varkappa \nu} \sim \Delta T$$

Onset of convection at $R = R_c \simeq 1707{,}76$.

Further reading:

- P. Manneville, Instabilities, chaos and turbulence (London, 2004)
- M. Cross, H. Greenside, Pattern formation and dynamics in nonequilibrium systems (Cambridge, 2009)

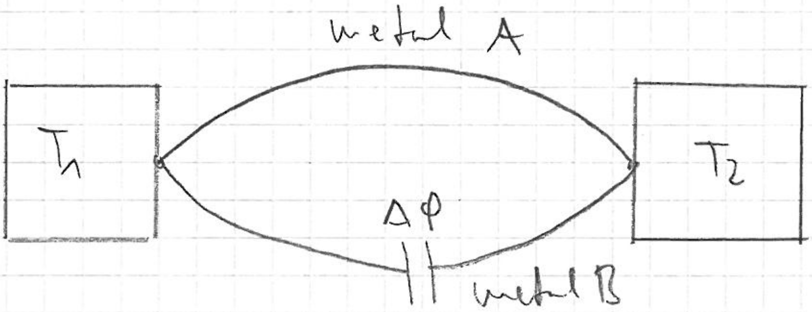
I. Classical thermodynamics of irreversible processes

1° Interference effects

A gradient in a thermodynamic variable generally gives rise to currents also in those quantities which are <u>not</u> directly associated with that variable.

Examples:

a) Thermoelectricity



$T_2 - T_1 = \Delta T$

Seebeck-effect: ΔT fixed, no electric current

$\Rightarrow$ potential $\Delta\phi = -K_S \cdot \Delta T$ }
Seebeck coefficient

Peltier-effect: $T_1 = T_2$, impose $\Delta\phi$ & current I

$\Rightarrow$ heat current $J_Q = \Pi \cdot I$

The two effects are found to be related through the Thomson relation

$$\Pi = K_S \cdot T$$

b) Thermodiffusion

Soret-effect: Diffusion current driven by a temperature gradient

Dufour-effect: Energy flux driven by a concentration gradient

c) Heat conduction in crystals

Fourier's law in anisotropic materials reads

$$J_Q^{(i)} = - \sum_{j=1}^{3} \lambda_{ij} \frac{\partial T}{\partial x_j} \, , \qquad i = 1, 2, 3 \mathrel{\hat{=}} x, y, z$$

Experimentally, the matrix λ_{ij} is found to be symmetric even when this is *not* required by the symmetry of the crystal.

2° Canonical form of the entropy production

General situation:

- thermodynamic state variables $A_1, \dots, A_n$
- equilibrium values $A_1^{(0)}, \dots, A_n^{(0)}$
- deviations from equilibrium $\alpha_i = A_i - A_i^{(0)}$

$\Rightarrow$ corresponding entropy change ΔS is a negative quadratic form

$$\left.\begin{array}{l} \Delta S = -\frac{1}{2}\sum_{i,k} g_{ik}\cdot\alpha_i\alpha_k \\ \\ g_{ik} \text{ positive, symmetric matrix} \end{array}\right\}$$

The generalized thermodynamic force associated to α_i is

$$\underline{X_i = \frac{\partial}{\partial\alpha_i}\Delta S = -\sum_{k=1}^{n} g_{ik}\alpha_k}$$

A stationary nonequilibrium state is characterized by fluxes

$$J_i = \frac{d\alpha_i}{dt}$$

(<u>Ex</u>: Heat flux through a surface)

$\Rightarrow$ entropy production is

$$\sigma = \frac{d}{dt}\Delta S = -\sum_{i,k} g_{ik}\dot{\alpha}_i\alpha_k = \underline{\sum_i J_i X_i}$$

<u>Example:</u> For heat conduction we have shown

$$\sigma = \underbrace{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}_{\substack{\text{driving force,} \\ X = \frac{1}{T}}} \underset{\nwarrow\ \text{flux}}{\frac{d\alpha}{dt}}$$

Combining this with the most general linear transport law

$$\underline{J_i = \sum_k L_{ik} X_k} \qquad L_{ij}: \text{Onsager coefficients}$$

we find

$$\underline{\sigma = \sum_{ik} L_{ik} X_i X_k} = \langle X | \hat{L} | X \rangle$$

<u>Remarks:</u>

- $\sigma > 0$ for any choice of forces requires the matrix $\hat{L}$ to be positive definite.
- This implies in particular $L_{ii} > 0$, but does not determine the sign of off-diagonal coefficients describing interference effects.
- Positivity of $\hat{L}$ does however constrain the magnitude of off-diagonal terms.

<u>Example:</u> For $n=2$ positivity requires

$$\left. (L_{12} + L_{21})^2 < 4 L_{11} L_{22} \quad \right\}$$

3° Onsager's reciprocity relations

Onsager (1931, Nobel prize in chemistry 1968) derived the reciprocity relations

$$L_{ij} = L_{ji}$$

from the condition of microscopic time reversal invariance. The basic idea is to link microscopic fluctuations to macroscopic transport laws, similar to Einstein's theory of Brownian motion.

a) Fluctuation theory

Let $\Omega(A_1,..,A_n)$ denote the number of microstates consistent with the macroscopic state variables $A_1,..,A_n$, which is related to the entropy through the Boltzmann relation

$$S = k_B \ln \Omega \quad , \quad \Omega = e^{S/k_B}$$

Then the probability of observing a fluctuation $(\alpha_1,..,\alpha_n)$ in equilibrium is

$$P(\alpha_1,..,\alpha_n) = \frac{\Omega(A_1^{(0)}+\alpha_1,..,A_n^{(0)}+\alpha_n)}{\Omega(A_1^{(0)},..,A_n^{(0)})} =$$

$$= \frac{1}{W} e^{\frac{1}{k_B}\Delta S(\alpha_1,..,\alpha_n)} = \frac{1}{W} e^{-\frac{1}{2k_B}\sum_{ik} g_{ik}\alpha_i\alpha_k}$$

W: Normalization