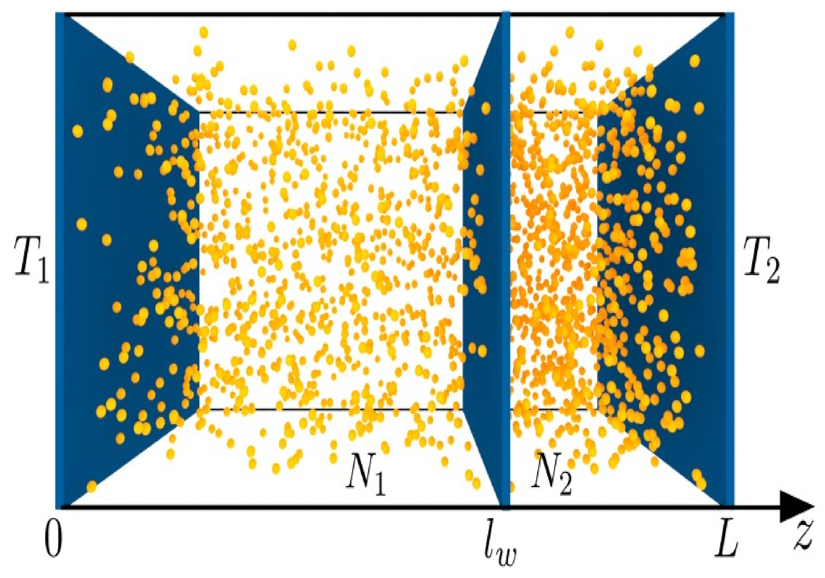
Thermodynamics of out of equilibrium steady states

Karol Makuch[1]

[1]*Institute of Physical Chemistry of the Polish Academy of Sciences*

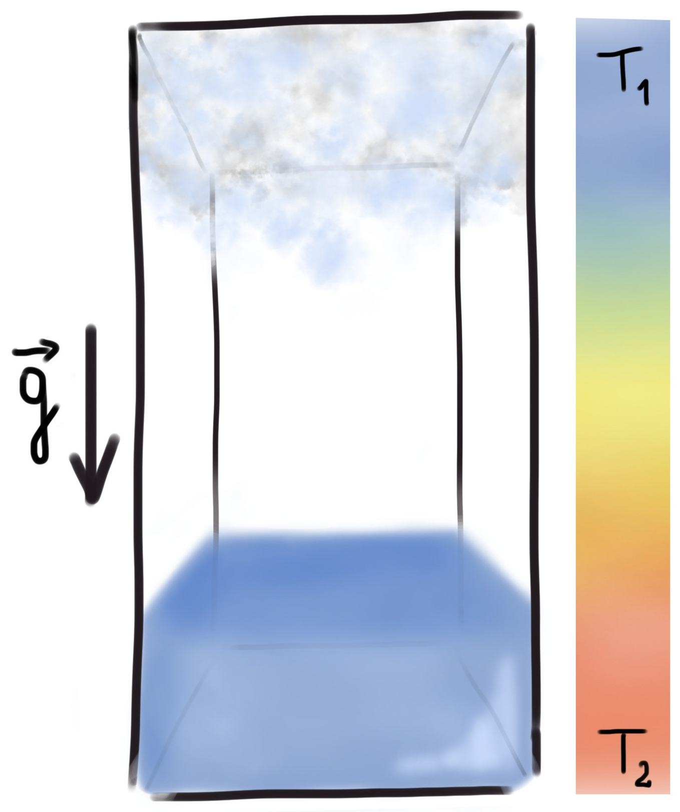
Motivation and goals

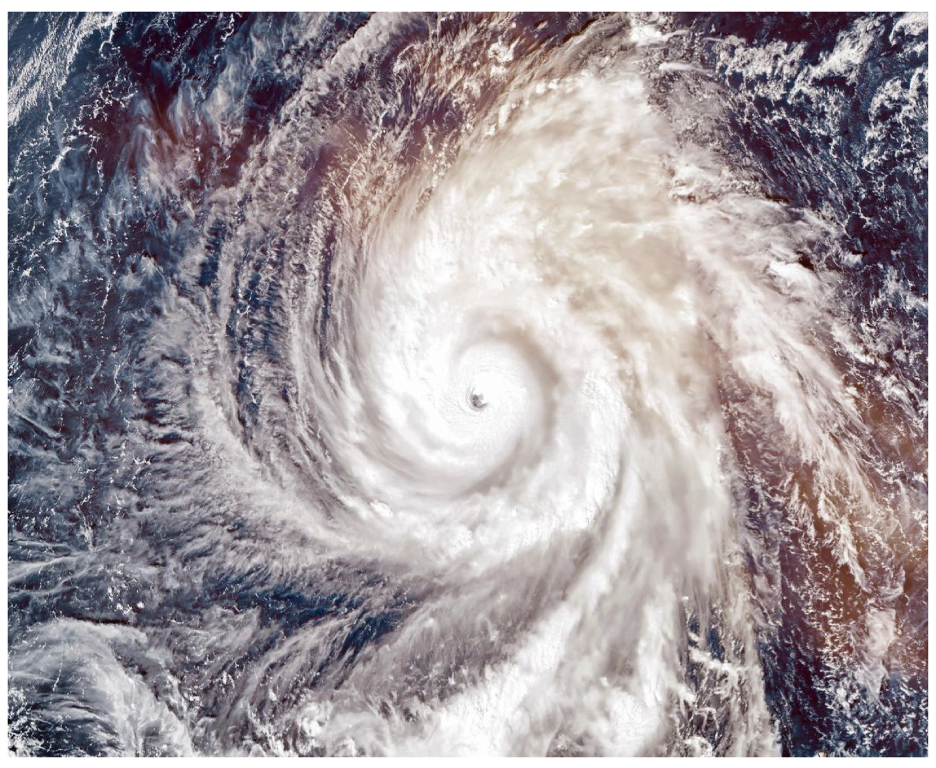
Second law of thermodynamics: after removal of the constraint (e.g. we allow the wall to move) the final state of the system minimizes the total energy of a system



$$V_1, V_2 : \min_{V_1+V_2=V} U(S_{12}, V_1, V_2, N)$$

$$S_{12} = S_1 + S_2$$



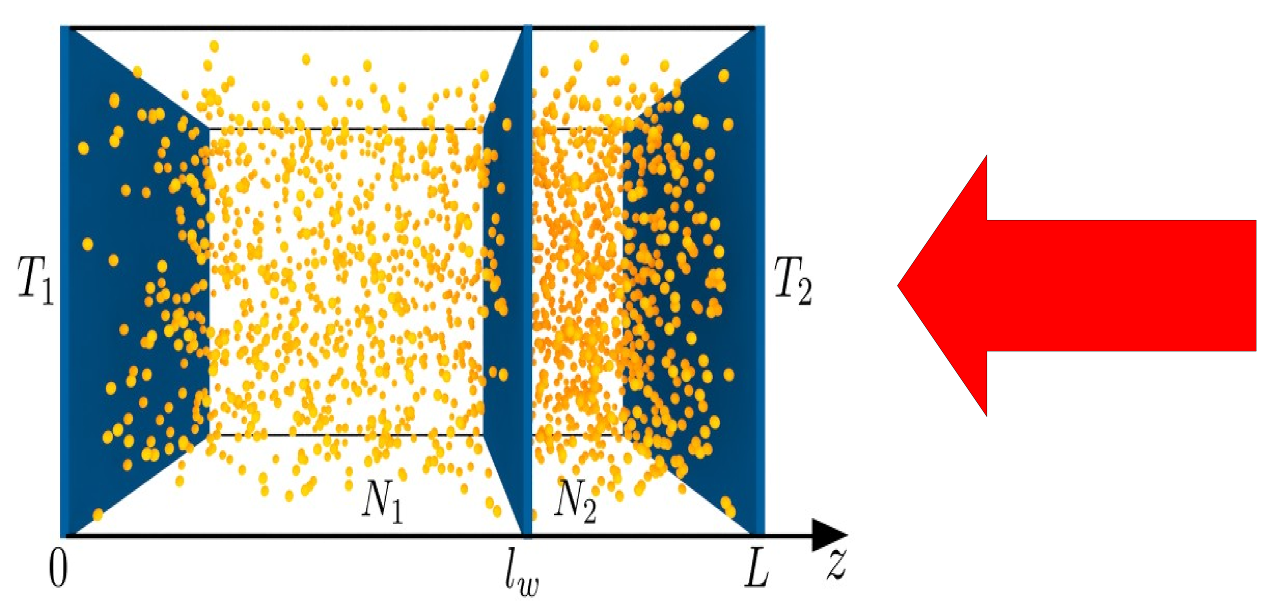


Is there a generalization of the second law to steady states?
Does the nonequlibrium entropy exist and is it useful?
Does steady state thermodynamics exist?

State of the art

Prigogine (1967), Oono and Paniconi (1998), Hatano and Sasa (2001), Komatsu, Nakagawa, Tasaki, Netz, Speck, Seifert, Mandal, Jarzynski, ...

higher temperature differences?

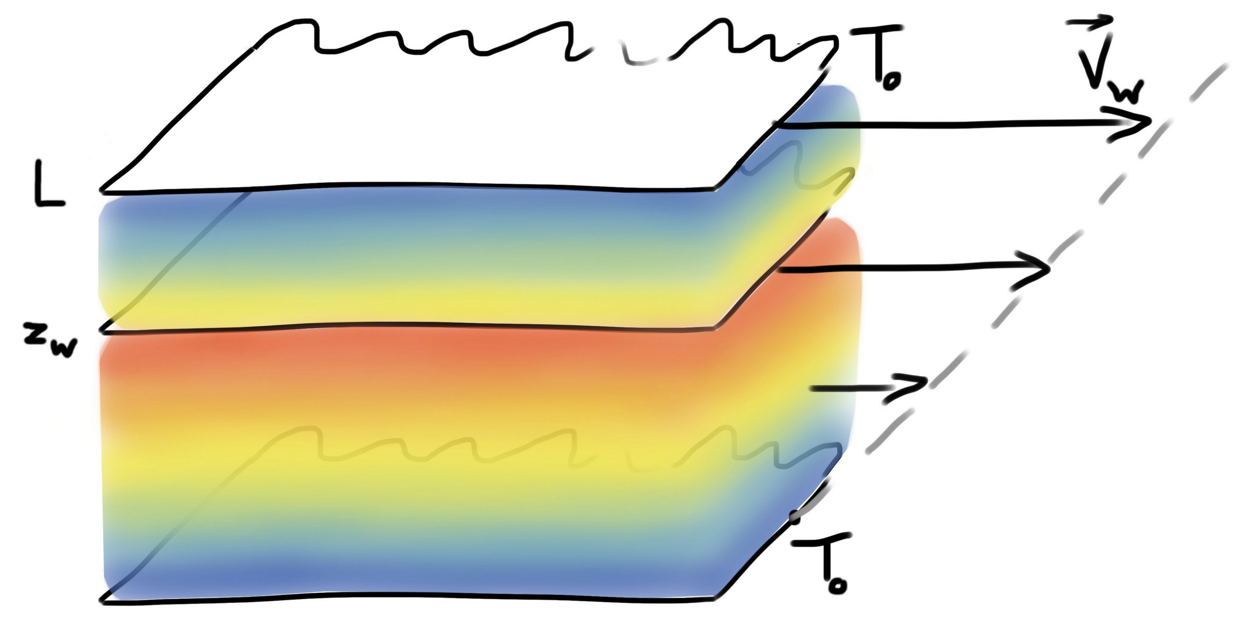


heat flow

$$V_1, V_2 : \min_{V_1+V_2=V} U(S_{12}^*, V_1, V_2, N)$$

Hołyst *et al.* J. Chem. Phys. 157, 194108 (2022)

Heat and mass flow



Makuch et al. J. Chem. Phys. 159, 194113 (2023)

Change of a steady state:

$T_0 \to T_0 + dT \qquad V_w \to V_w + dV_w \qquad L \to L + dL$

First law

Energy balance $E = E_k + U$
when passing to another (nearby) steady state

$$dE = \text{đ}Q - pdV + \text{đ}W_w$$

excess heat

$$\text{đ}Q = -\int_{t_i}^{t_f} dt \int_{\partial V(t)} d^2r\, \hat{n} \cdot (J_q(t) - J_{q,st}(t))$$

excess work of the wall (parallel motion)

$$\text{đ}W_w = \int_{t_i}^{t_f} dt \int_{\partial V(t)} d^2r\, \hat{n} \cdot (\Pi \cdot \mathbf{v} - \Pi_{st}(t) \cdot \mathbf{v}_{st}(t))$$

Second law

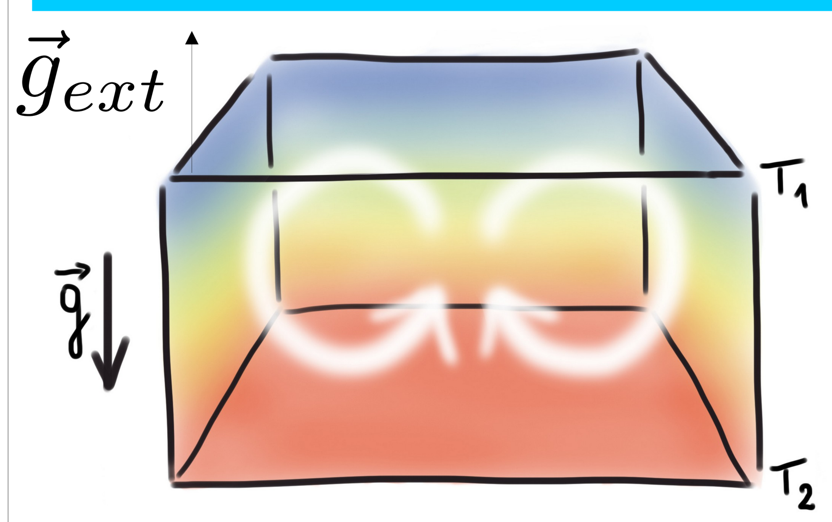
$$S^*(U,V) = Nk_B \left\{ \frac{5}{2} + \frac{3}{2} \log \left[\frac{2}{3} \frac{\varphi_0 U}{N} \left(\frac{V}{N} \right)^{2/3} \right] \right\}$$

$$V_1, V_2 : \min_{V_1+V_2=V} U(S_{12}^*, V_1, V_2, N)$$

$$S_{12}^* = S_1^* + r S_2^*$$

Position of the wall determined by: $dE - \text{đ}Q - \text{đ}W_w \leq 0$

Rayleigh-Benard convection



$$\frac{\partial Z_{cm}}{\partial g_{ext}} > 0$$

$T_2 \to T_2'$
$g \to g'$

times: $t_i \quad t_f$

$$\Delta E_{t_f t_i} = \text{đ}Q + \text{đ}M_S + \text{đ}W_{dt\varphi}$$

total energy:
-internal,
-macroscopic kinetic,
-gravitational potential

net heat

work due to motion of surface

change of the potential energy

Makuch, Phys. Fluids 36, 111701 (2024)

Outlook

Steady state thermodynamics

- including chemical reactions in collaboration with:

Robert Hołyst, Anna Maciołek, Konrad Giżyński, Paweł J. Żuk, Jakub Wróbel