

Nonequilibrium Thermodynamics of open driven systems



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Laws of thermodynamics

Zeroth law: The definition of temperature

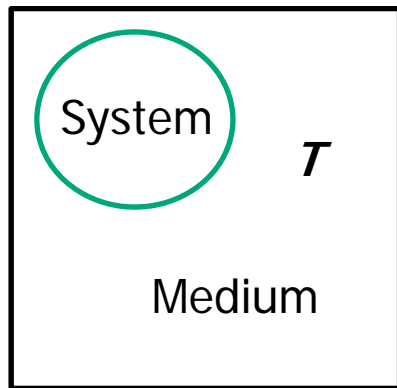
First law: Energy conservation $dU = W - Q$

Second law: the arrow of time $dS \geq -\frac{Q}{T}$ Clausius inequality

Third law: absolute zero temperature

At equilibrium  Microscopic reversibility  Detailed balance

Evolution of entropy



$$dS_{tot} = dS_{system} + dS_{medium} \geq 0$$

$$dS_{system} = dS_i - dS_e$$

Two different perspectives

$$T \cdot epr = T \cdot dS_i = T \cdot dS_{tot} = \sum_i J_i \times X_i \geq 0$$

dS_i , dS_e and dS_{tot} , rather than S_i , S_e and S_{tot} are the state functions of the internal system.

Detailed balance $\longleftrightarrow J_i = 0 \Leftrightarrow X_i = 0$

Generalized flux

Generalized force

I. Prigogine: *Introduction to thermodynamics of irreversible processes*. 3rd ed. (1967)
 T.L. Hill: *Free energy transduction in biology*. (1977)



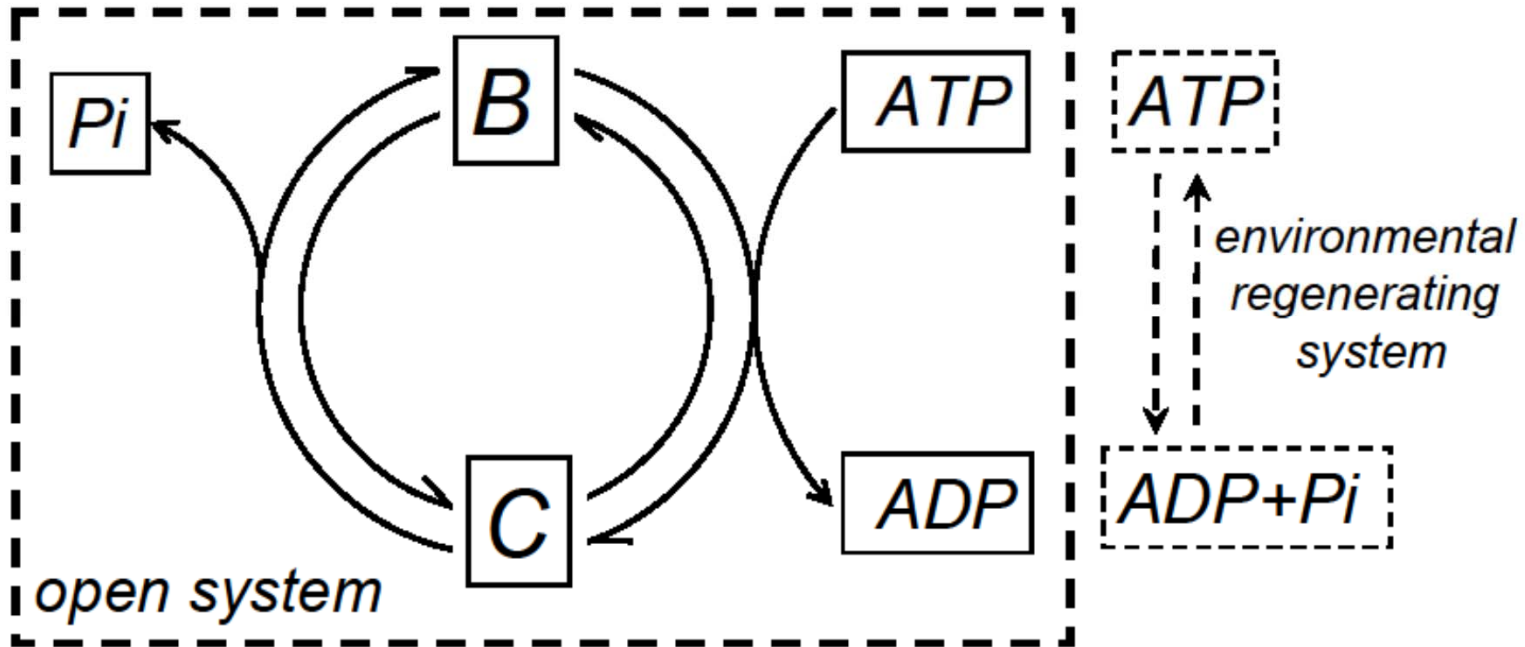
Two major questions

$$dS_{system} = epr - dS_e = epr - dS_{medium}$$

1. In steady state, what does the state function $T \cdot dS_{medium}$ mean? Total heat dissipation? Can it be used to perform work?
It requires a "real driven" perspective and a minimum work argument.
2. In the relaxation process towards steady state, how to distinguish the two origin of nonequilibrium, i.e. nonstationary and non-detailed-balance (driven) of the steady state?

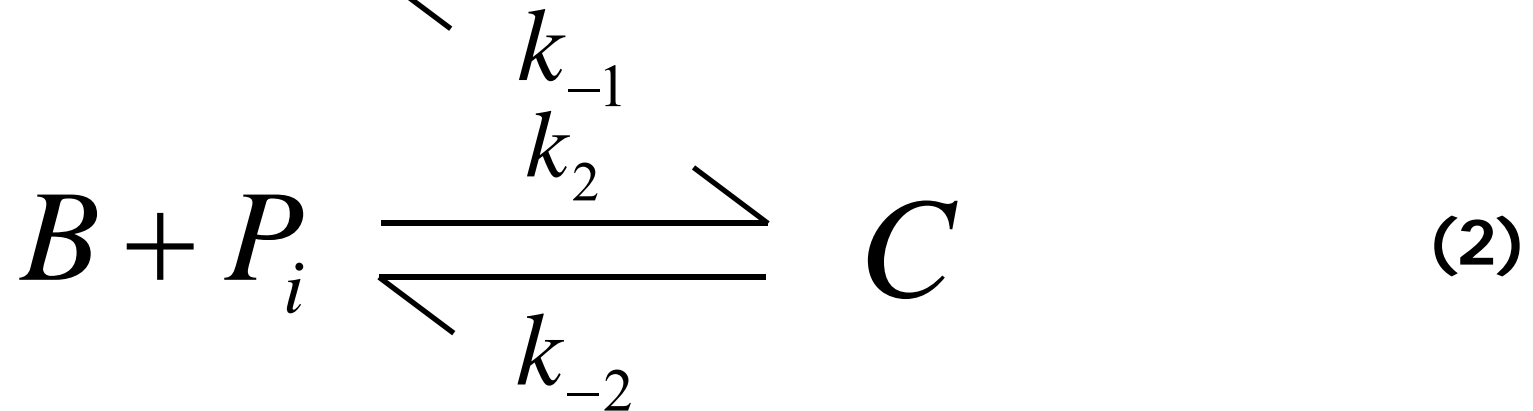
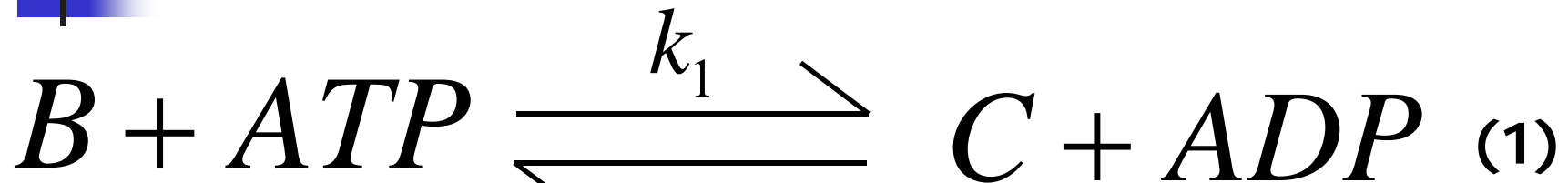
$$T \cdot epr = f_d + Q_{hk}$$

A single biochemical reaction cycle



Spontaneous ATP hydrolysis and related ATP regenerating system.

A single biochemical reaction cycle

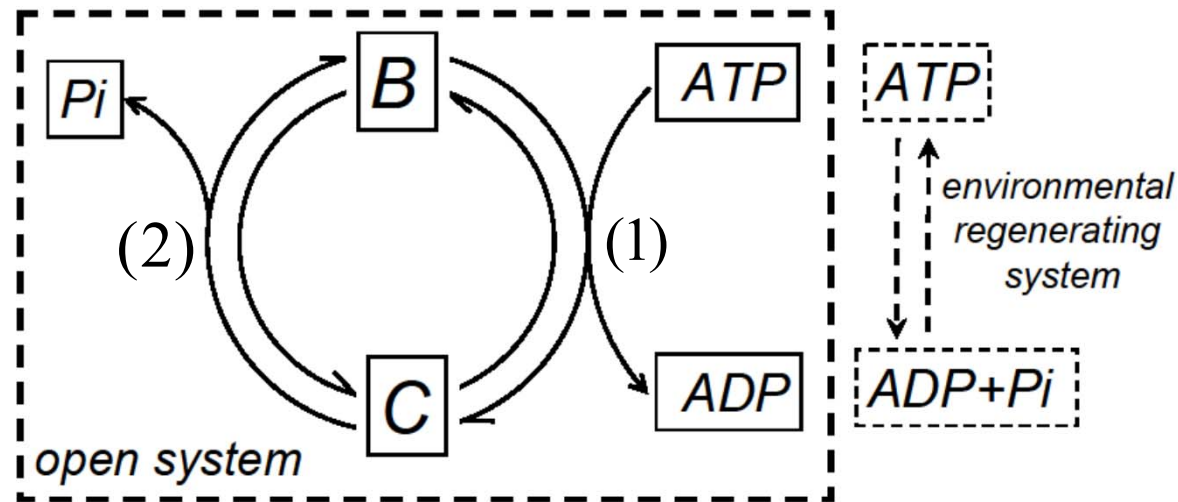


Equilibrium condition: $\frac{[ATP]^{eq}}{[ADP]^{eq}[P_i]^{eq}} = \frac{k_{-1}k_{-2}}{k_1k_2}$

Open driven system: regenerating system
keeping the concentrations of ATP, ADP and P_i

$$\gamma = \frac{k_1k_2[ATP]^{ss}}{k_{-1}k_{-2}[ADP]^{ss}[P_i]^{ss}} \neq 1$$

Heat dissipation



After an internal clockwise cycle, the traditional heat dissipation during ATP hydrolysis

$$\begin{aligned}
 h_d &= (h_B^0 + h_{ATP}^0 - h_C^0 - h_{ADP}^0) + (h_C^0 - h_{Pi}^0 - h_B^0) \\
 &= h_{ATP}^0 - h_{ADP}^0 - h_{Pi}^0 \neq T \cdot \Delta S_e = T \cdot \Delta S_{medium}.
 \end{aligned}$$

Could not be calculated only from the dynamics of the internal system.



Heat dissipation

There is an external step for the regenerating system converting $ADP + P_i$ back to ATP after each completion of a cycle. The **minimum work** (non-PV) it has to do is just the free energy difference between $ADP + P_i$ and ATP, i.e.

$$W_{\min} = \mu_{ATP} - \mu_{ADP} - \mu_{P_i}$$

Driven energy of the internal system

The extra heat dissipation $h_d^{ext} = W_{\min} - (h_{ATP}^0 - h_{ADP}^0 - h_{P_i}^0)$

The total heat dissipation of such a reaction cycle is

$$h_d + h_d^{ext} = W_{\min} = k_B T \log \gamma = T \cdot \Delta S_e = T \cdot \Delta S_{medium}$$



Master equation model

Consider a motor protein with N different conformations R_1, R_2, \dots, R_N . k_{ij} is the first-order or pseudo-first-order rate constants for the reaction $R_i \rightarrow R_j$.

$$\frac{dc_i(t)}{dt} = \sum_j (c_j k_{ji} - c_i k_{ij})$$

No matter starting from any initial distribution, it will finally approach its stationary distribution satisfying

$$\sum_{j=1}^N (c_j^{ss} k_{ji} - c_i^{ss} k_{ij}) = 0 \qquad c_j^{eq} k_{ji} = c_i^{eq} k_{ij}$$

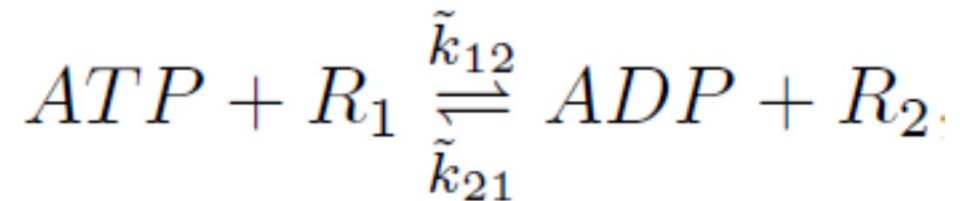
Self-assembly or self-organization

Detailed balance



Coupled with energy source

Assume only one of the transition is involved in the energy source, i.e. ATP and ADP.



$$k_{12} = \tilde{k}_{12}[ATP], k_{21} = \tilde{k}_{21}[ADP]$$

If there is no external mechanism to keep the concentrations of ATP and ADP, then

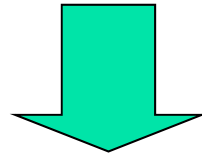
$$\frac{dc_T}{dt} = -\frac{dc_D}{dt} = -\tilde{k}_{12}c_Tc_1 + \tilde{k}_{21}c_Dc_2.$$



Thermodynamic constraints

$$\mu_i^0 \propto -k_B T \log c_i^{eq} \quad \text{Boltzmann's law}$$

$$\mu_i(c_i^{eq}) = \mu_j(c_j^{eq}), \mu_T(c_T^{eq}) = \mu_D(c_D^{eq})$$



$$\mu_i^0 - \mu_j^0 = k_B T \log \frac{k_{ij}}{k_{ji}}; \mu_T^0 - \mu_D^0 = k_B T \log \frac{c_D^{eq}}{c_T^{eq}},$$

$$\mu_1^0 + \mu_T^0 - \mu_2^0 - \mu_D^0 = k_B T \log \frac{\tilde{k}_{12}}{\tilde{k}_{21}}.$$



Heat dissipation

$$\begin{aligned} \tilde{h}_d^{open}(t) &= k_B T \sum_{i>j} (c_i(t)k_{ij} - c_j(t)k_{ji}) (h_i^0 - h_j^0) \\ &\quad + k_B T (c_1(t)k_{12} - c_2(t)k_{21}) (\mu_T - \mu_D) \end{aligned}$$

In an NESS, its kinetics and thermodynamics can be decomposed into different cycles (Kirchhoff's law, Beijing school). The minimum amount of total heat dissipation for each internal cycle

$$Q_{\min}^c = k_B T \log \frac{k_{i_0 i_1} k_{i_1 i_2} \dots k_{i_n i_0}}{k_{i_0 i_n} k_{i_n i_{n-1}} \dots k_{i_1 i_0}};$$

$$c = \{i_0 \rightarrow i_1 \rightarrow i_2 \dots \rightarrow i_n \rightarrow i_0\}$$

$$\tilde{h}_d^{ness} = k_B T \sum_{i>j} (c_i^{ss} k_{ij} - c_j^{ss} k_{ji}) \log \frac{k_{ij}}{k_{ji}} = T \cdot dS_e = T \cdot dS_{medium}.$$



Energy transduction efficiency

A mechanical system coupled fully reversibly to a chemical reactions, with a constant force resisting the mechanical movement driven by the chemical gradient.

$$W_{\min} \cdot J_{c \rightarrow m} = \tilde{h}_d^{ness} + P_{mech} = T e_p^{ness} + P_{mech}$$

Transduction from chemical energy to mechanical energy

$$W_{\min} > 0, J_{c \rightarrow m} > 0, e_p^{ness} > 0, P_{mech} > 0 \quad \eta = \frac{P_{mech}}{W_{\min} \cdot J_{c \rightarrow m}} = \frac{P_{mech}}{T e_p^{ness} + P_{mech}} < 1$$

Transduction from mechanical energy to chemical energy

$$W_{\min} > 0, J_{c \rightarrow m} < 0, e_p^{ness} > 0, P_{mech} < 0$$

$$\eta = \frac{-W_{\min} \cdot J_{c \rightarrow m}}{-P_{mech}} = \frac{-W_{\min} \cdot J_{c \rightarrow m}}{T e_p^{ness} - W_{\min} \cdot J_{c \rightarrow m}} < 1$$

The steady-state entropy production is always the total dissipation, which is nonnegative

The evolution of entropy

$$S^0 = \sum_i s_i^0 c_i; S^{open} = -k_B \sum_i c_i \log c_i.$$

$$\tilde{S}^{open} = S^0 + S^{open}$$

$$\frac{d\tilde{S}^{open}}{dt} = e_p^{open} - \frac{\tilde{h}_d^{open}}{T};$$

$$\frac{dS^{open}}{dt} = e_p^{open} - \frac{h_d^{open}}{T}$$

$$\begin{aligned} \tilde{F}^{open} &= H^0 - T\tilde{S}^{open} \\ &= \mu^0 - TS^{open} \end{aligned}$$

$$H^0 = \sum_i h_i^0 c_i, \mu^0 = \sum_i \mu_i^0 c_i$$

Enthalpy-entropy compensation

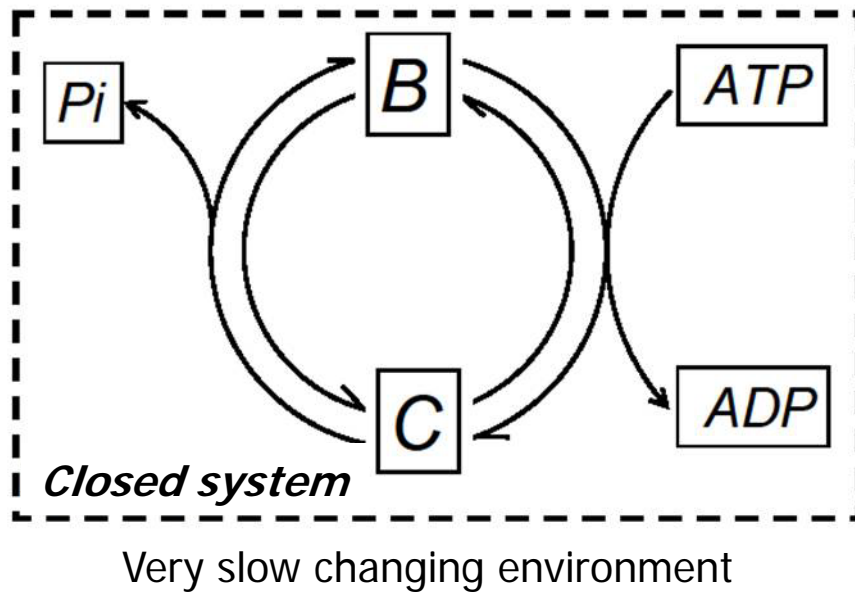
Operationally defined heat if we do not know the temperature dependence of $\Delta\mu^0$

$$h_d^{ness} = \tilde{h}_d^{ness}$$

$$h_d^{open}(t) = k_B T \sum_{i>j} (c_i(t)k_{ij} - c_j(t)k_{ji}) \log \frac{k_{ij}}{k_{ji}};$$

$$e_p^{open}(t) = k_B \sum_{i>j} (c_i(t)k_{ij} - c_j(t)k_{ji}) \log \frac{c_i k_{ij}}{c_j k_{ji}}.$$

QSS v.s. NESS



$$\frac{dF^{close}}{dt} = -f_d^{close};$$

$$\frac{dS^{close}}{dt} = e_p^{close} - \frac{h_d^{close}}{T};$$

$$Te_p^{open} = Te_p^{close} = f_d^{close} \geq 0.$$

This reflects the different perspective of Boltzmann/Gibbs and Prigogine: Gibbs states free energy never increase in a closed, isothermal system; while Prigogine states that the entropy production is non-negative in an open system. They are equivalent.



Real driven: Housekeeping heat

Housekeeping heat $Q_{hk}(t) = k_B T \sum_{i>j} (c_i(t)k_{ij} - c_j(t)k_{ji}) \log \frac{c_i^{ss} k_{ij}}{c_j^{ss} k_{ji}}.$

The minimum heat dissipation for each cycle could be distributed to each $i \rightarrow j$ as

$$Q_{ij} = k_B T \log \frac{k_{ij}}{k_{ji}} + T(s_i^0 - s_j^0)$$

The steady-state entropy difference $\Delta S_{ij}^{ss} = k_B \log \frac{c_i^{ss}}{c_j^{ss}} + s_j^0 - s_i^0$

$$Q_{ij} + T\Delta S_{ij}^{ss} = k_B T \log \frac{c_i^{ss} k_{ij}}{c_j^{ss} k_{ji}}$$

$$Q_{hk}(t) = \langle Q_{ij} + T\Delta S_{ij}^{ss} \rangle \geq 0. \quad Q_{hk}(t) = 0 \Leftrightarrow \text{No driven (approaching equilibrium state with detailed balance)}$$



Time-independent systems

Relative entropy

$$\frac{dF}{dt} = -f_d; \quad \mathbf{f}_d: \text{ free energy dissipation rate}$$

$$\frac{dE}{dt} = Q_{hk} - h_d; \quad \mathbf{h}_d: \text{ heat dissipation/work out}$$

$$\mathbf{Q}_{hk}: \text{ house keeping heat/work in}$$

$$Q_{hk}(t) = k_B T \sum_{i>j} (c_i(t)k_{ij} - c_j(t)k_{ji}) \log \frac{c_i^{ss} k_{ij}}{c_j^{ss} k_{ji}}.$$

$$\frac{dS}{dt} = e_p - \frac{h_d}{T}; \quad \mathbf{e}_p: \text{ entropy production rate}$$

$$e_p(t) = k_B \sum_{i>j} (c_i(t)k_{ij} - c_j(t)k_{ji}) \log \frac{c_i k_{ij}}{c_j k_{ji}}; \quad h_d(t) = k_B T \sum_{i>j} (c_i(t)k_{ij} - c_j(t)k_{ji}) \log \frac{k_{ij}}{k_{ji}};$$



Two origins of irreversibility

$$f_d \geq 0, \quad Q_{hk} \geq 0,$$

$$T e_p = f_d + Q_{hk} \geq 0.$$

e_p characterizes total time irreversibility in a Markov process.

When system reaches stationary, $f_d = 0$.

When system is closed (i.e., no active energy drive, detailed balanced) $Q_{hk} = 0$.

Boltzmann: $f_d = T \cdot e_p > 0$ but $Q_{hk} = 0$;

Prigogine (Brussel school, NESS): $Q_{hk} = T \cdot e_p > 0$ but $f_d = 0$.

$f_d \geq 0$ in driven systems is “self-organization”.



Time-dependent systems

$$\frac{dc_i(t)}{dt} = \sum_j (c_j k_{ji}(t) - c_i k_{ij}(t))$$

Entropy in Hatano-Sasa equality. We would like to call it intrinsic entropy, which could be defined at individual level.

$$\frac{dS(t)}{dt} = e_p(t) - \frac{h_d(t)}{T}$$

$$\frac{dF(t)}{dt} = W^{ext}(t) - f_d(t)$$

Dissipative work in Jarzynski equality

$$\frac{dU(t)}{dt} = W^{ext}(t) - Q_{ex}(t)$$

$$Q_{hk}(t) = T e_p(t) - f_d(t) = h_d(t) - Q_{ex}(t)$$



Two kinds of Second Law

$$\frac{dS}{dt} \geq -\frac{h_d}{T} \left(e_p \geq 0 \right) \quad \frac{dF}{dt} \leq W^{ext} \left(f_d \geq 0 \right)$$

In detailed-balance case, they are equivalent.

$$T e_p = f_d, \quad Q_{hk} \equiv 0$$

In non-detailed balance case, the new one is stronger than the traditional one.

$$\begin{aligned} \frac{dF}{dt} \leq W^{ext} &= \frac{dU}{dt} + Q_{ex} \\ \Rightarrow \frac{dS}{dt} &\geq -\frac{Q_{ex}}{T} \geq -\frac{h_d}{T} \end{aligned}$$



Summary

- Regenerating system approach would distinguish quasi-steady-state and nonequilibrium-steady-state, and supply an equilibrium thermodynamic foundation for the expression of heat dissipation in nonequilibrium steady state of subsystems, without the need to know “environment”;
- Thermodynamic superstructure would explicitly distinguish Boltzmann and Prigogine’s thesis, and further clarify the two kinds of the Second Law;
- So far, a comprehensive framework for both equilibrium and nonequilibrium statistical mechanics is proposed.



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Thanks for your attention!
