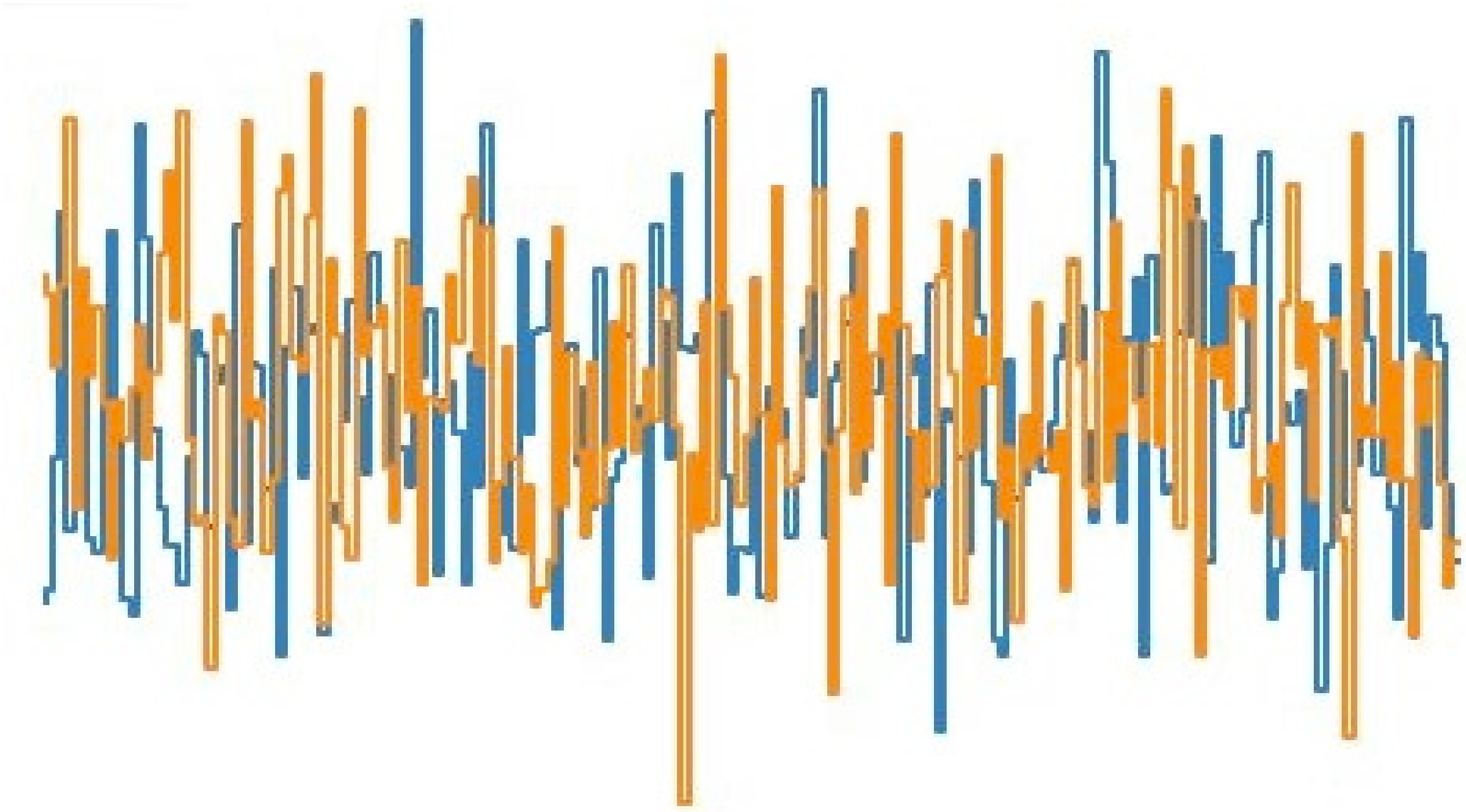
Energetic Constraints on Biological Systems

Boulder School for Condensed Matter Physics

THE EQUATIONY BITS



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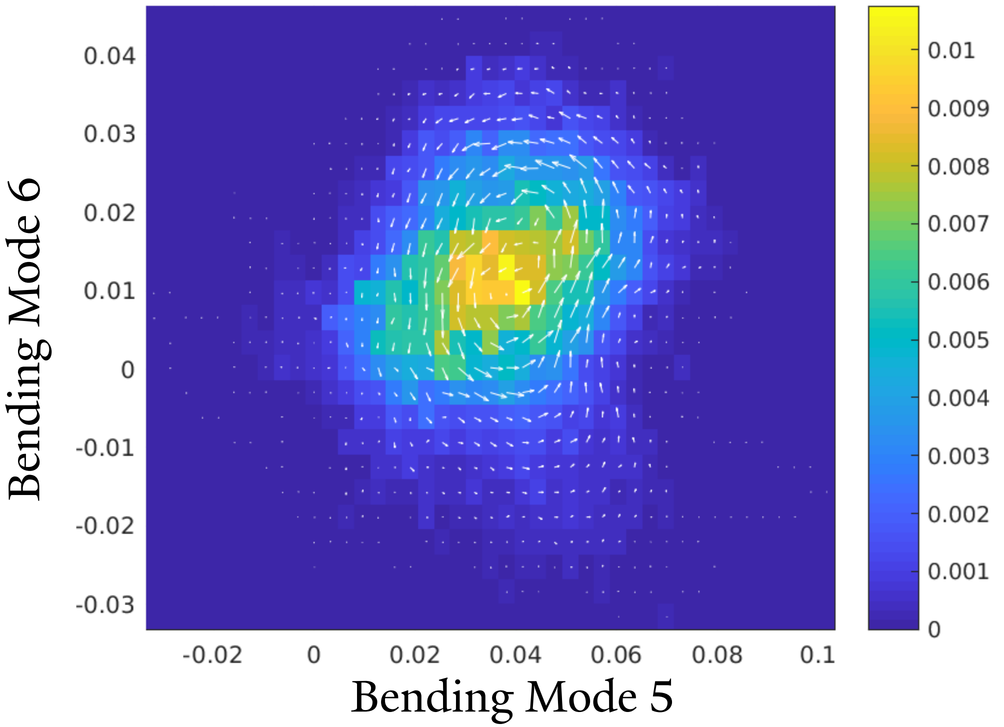
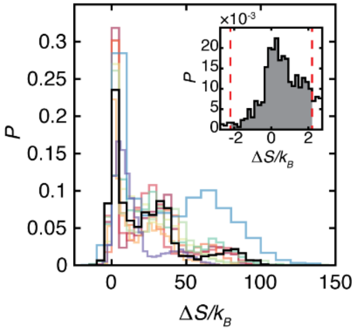
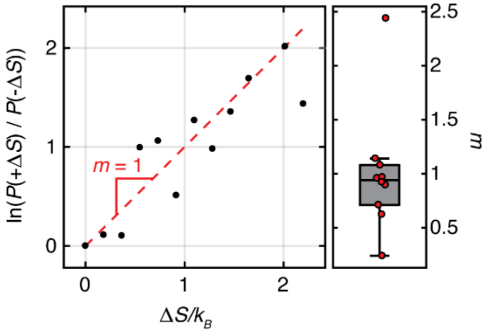
EPR on random variables

from phase space fluxes: correlating bending modes







$$\frac{P(+\Delta S)}{P(-\Delta S)} = e^{\Delta S/k_B}.$$

(1) Overdamped Langevin Equation:

$$\dot{\mathbf{a}} = \mathbf{A}\mathbf{a} + \mathbf{F}\boldsymbol{\xi}$$

(2) Fokker-Planck Equation:

$$\frac{\partial p(\mathbf{a},t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{a},t) = -\nabla \cdot (\mathbf{A}\mathbf{a}\, p(\mathbf{a},t) - \mathbf{D}\,\nabla p(\mathbf{a},t)),$$

(3) The phase space velocity, $\dot{\boldsymbol{a}}$, in terms phase space current $\boldsymbol{j}(\boldsymbol{a},t)$[11]

$$\dot{\mathbf{a}} = \frac{\mathbf{j}(\mathbf{a},t)}{p(\mathbf{a},t)} = \mathbf{A}\mathbf{a} - \mathbf{D}\nabla \ln\big(p(\mathbf{a},t)\big)$$

$$S_{sys}(t) \equiv -\ln(p(\mathbf{a},t),t)$$

$$\Delta S(t) = \int_0^t \mathrm{d}\tau\, \dot{\mathbf{a}}^T(\tau)\, \mathbf{D}^{-1}\, \mathbf{v}^{ss}[\mathbf{a}(\tau)]$$

11. Seifert 2012 Rep. Prog. Phys. 75 126001

EPR on fields

High cost to oscillate, low cost to synchronize

$$\langle\frac{dS}{dt}\rangle = \lim_{T\to\infty}\frac{1}{T}\sum_{\mathbf{x}(t)} P[\mathbf{x}]\ln\frac{P[\mathbf{x}]}{\tilde{P}[\mathbf{x}]}$$

Dissipation: The Phase-Space Perspective
R. Kawai, J. M. R. Parrondo, and C. Van den Broeck
Phys. Rev. Lett. 98, 080602 – Published 22 February 2007

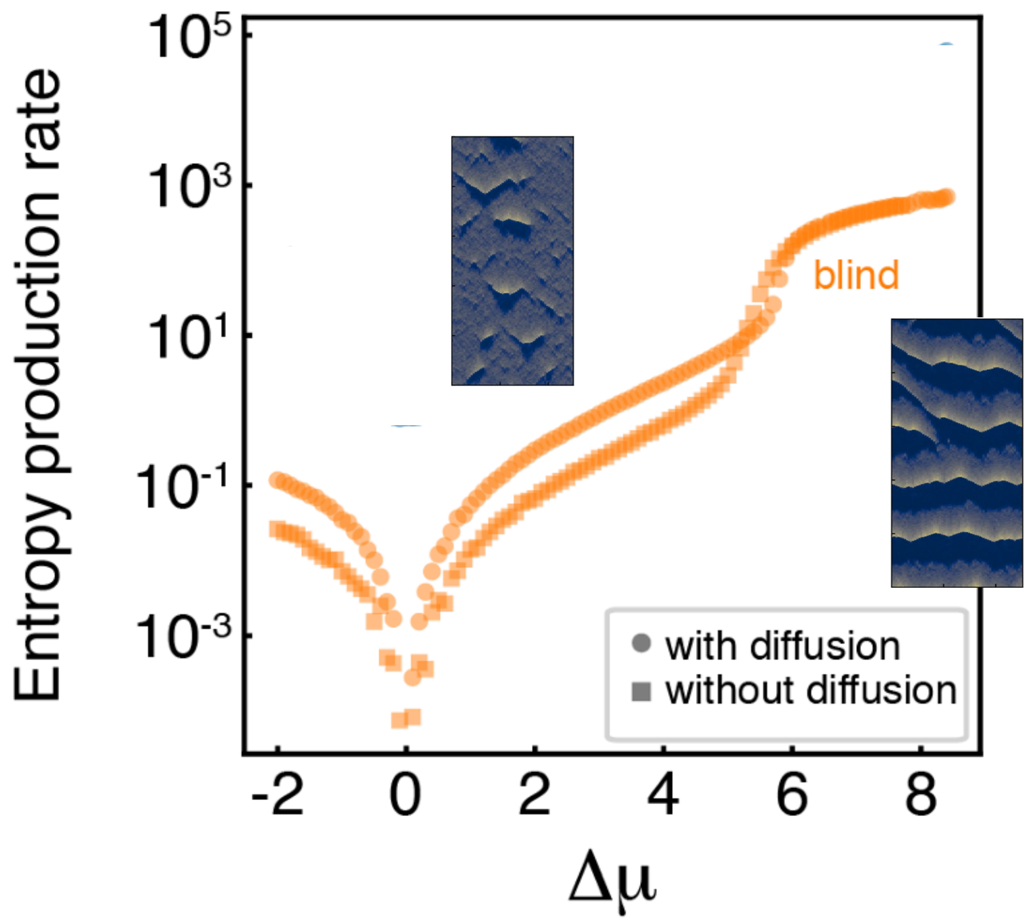
$$P[\mathbf{x}(\omega)] \propto \exp\left(-\frac{1}{2}\int\frac{d\omega}{2\pi}C^{-1}_{\mu\nu}(\omega)x^{\mu}(-\omega)x^{\nu}(\omega)\right)$$

$$C^{\mu\nu}(\omega) = \langle x^{\mu}(\omega)x^{\nu}(-\omega)\rangle$$

$$E(\omega) = \frac{1}{2}\mathrm{Tr}[\mathbf{C}(\mathbf{C}^{-1}(-\omega)-\mathbf{C}^{-1}(\omega))]$$

$$E(\mathbf{q},\omega) = \frac{1}{2}\mathrm{Tr}[\mathbf{C}(\mathbf{C}^{-1}(\mathbf{q},-\omega)-\mathbf{C}^{-1}(\mathbf{q},\omega))]$$

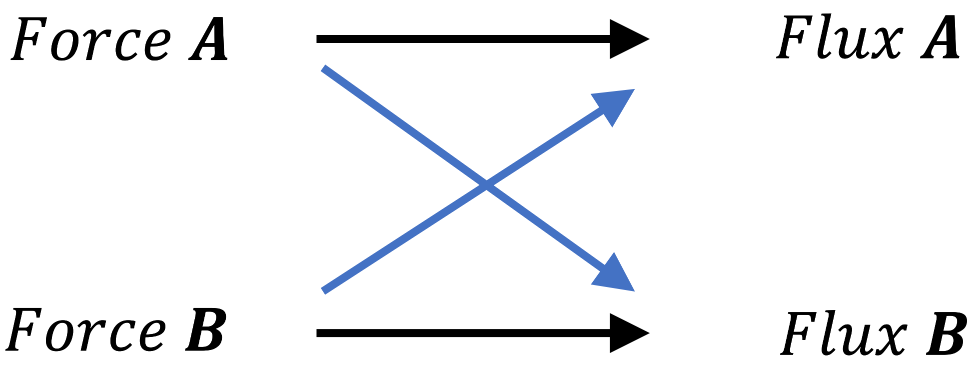
$$\langle\frac{dS}{dt}\rangle = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}E(\omega)$$



Collaboration with ***Ben Macha*** *(Yale)*

Onsager reciprocal relation

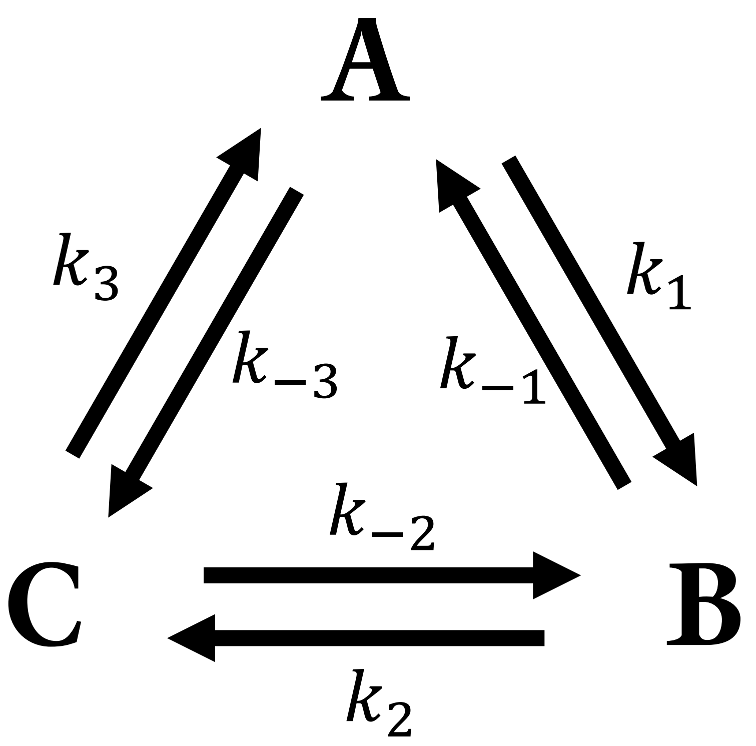
Linear force-flux relation:
When a system is near equilibrium with time-reversal-symmetry (TRS), the "fluxes" in each of its sub-processes are linearly related to the "forces"



$$\boldsymbol{L_{BA} = L_{AB}}$$
(Onsager reciprocal relation)

$$\begin{pmatrix} Flux\ \boldsymbol{A} \\ Flux\ \boldsymbol{B} \end{pmatrix} = \begin{bmatrix} L_{AA} & L_{AB} \\ L_{BA} & L_{BB} \end{bmatrix} \begin{pmatrix} Force\ \boldsymbol{A} \\ Force\ \boldsymbol{B} \end{pmatrix}$$

Onsager reciprocal relation: reversible cyclic reaction



ABC cyclic network:

- Species A, B, C

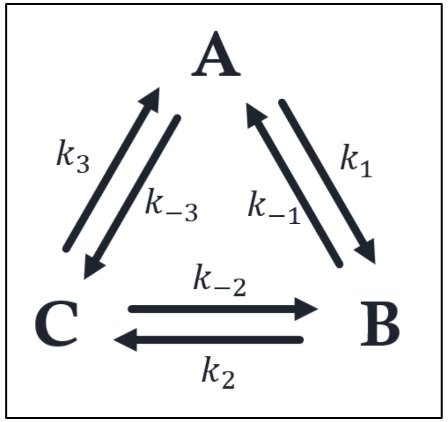
forward reaction coefficients:

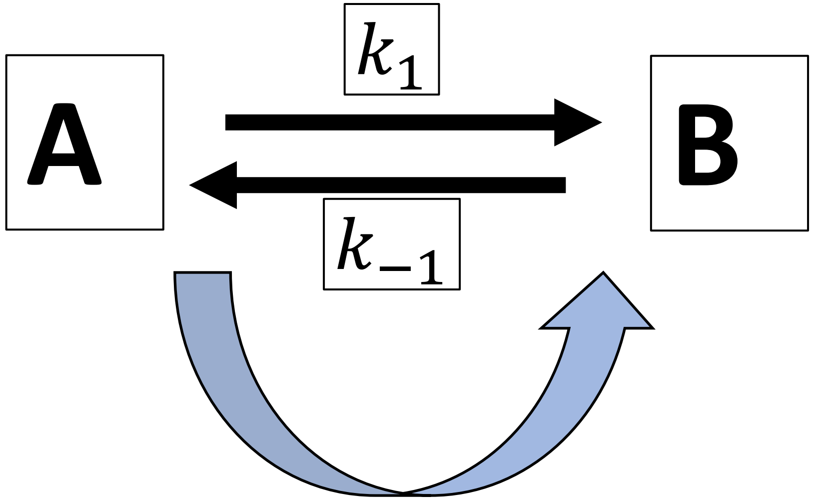
k_1, k_2, k_3

backward reaction coefficients:

k_{-1}, k_{-2}, k_{-3}

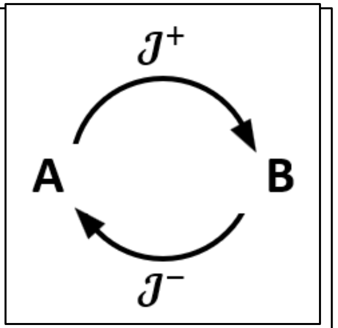
Onsager reciprocal relation: reversible cyclic reaction





net chemical flux:

$$\mathcal{J}_1 = \mathcal{J}_1^{+} - \mathcal{J}_1^{-}$$
$$= k_1 A - k_{-1} B$$

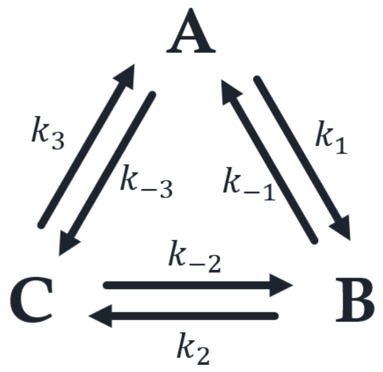


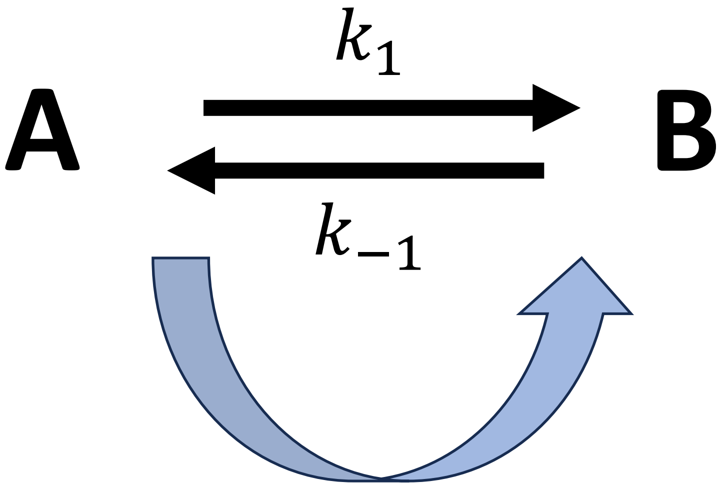
chemical affinity ("force"):

$$\mathcal{F}_1 = \mu_A - \mu_B$$
$$= k_B ln(k_1 A / k_{-1} B)$$

μ_A, μ_B: **chemical potential**
k_B: **Boltzmann constant**

Onsager reciprocal relation: reversible cyclic reaction





net chemical flux:

$$\mathcal{J}_1 = \mathcal{J}_1^+ - \mathcal{J}_1^- = k_1 A - k_{-1} B$$
$$\mathcal{J}_2 = \mathcal{J}_2^+ - \mathcal{J}_2^- = k_2 B - k_{-2} C$$
$$\mathcal{J}_3 = \mathcal{J}_3^+ - \mathcal{J}_3^- = k_3 C - k_{-3} A$$

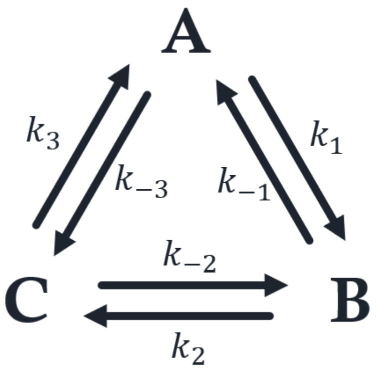
chemical affinity ("force"):

$$\mathcal{F}_1 = \mu_A - \mu_B = k_B ln(k_1 A / k_{-1} B)$$
$$\mathcal{F}_2 = \mu_B - \mu_C = k_B ln(k_2 B / k_{-2} C)$$
$$\mathcal{F}_3 = \mu_C - \mu_A = k_B ln(k_3 C / k_{-3} A)$$

$$\mathcal{F}_1 + \mathcal{F}_2 + \mathcal{F}_3 = 0$$

(two independent forces)

Onsager reciprocal relation: reversible cyclic reaction



Entropy production rate (Onsager's form):

$$\dot{S} = \sum_i \mathcal{J}_i \mathcal{F}_i = \mathcal{J}_1 \mathcal{F}_1 + \mathcal{J}_2 \mathcal{F}_2 + \mathcal{J}_3 \mathcal{F}_3$$

$$= \mathcal{J}_1 \mathcal{F}_1 + \mathcal{J}_2 \mathcal{F}_2 + \mathcal{J}_3 (-\mathcal{F}_1 - \mathcal{F}_2)$$

$$= (\mathcal{J}_1 - \mathcal{J}_3)\mathcal{F}_1 + (\mathcal{J}_2 - \mathcal{J}_3)\mathcal{F}_2$$

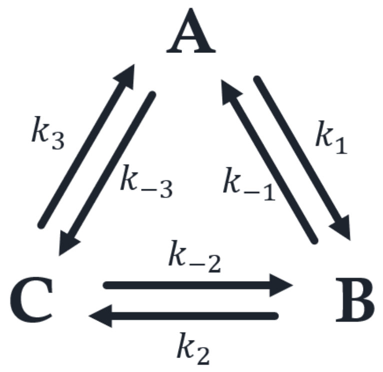
$$= \mathcal{J}_{n1} \mathcal{F}_1 + \mathcal{J}_{n2} \mathcal{F}_2$$

two independent forces:
$\mathcal{F}_1, \mathcal{F}_2$

corresponding chemical flux:
$\mathcal{J}_{n1}, \mathcal{J}_{n2}$

$$\begin{pmatrix} \mathcal{J}_{n1} \\ \mathcal{J}_{n2} \end{pmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{pmatrix} \mathcal{F}_1 \\ \mathcal{F}_2 \end{pmatrix}$$

Onsager reciprocal relation: reversible cyclic reaction



Entropy production rate (Onsager's form):

$$\dot{S} = \sum_i \mathcal{J}_i \mathcal{F}_i = \mathcal{J}_1\mathcal{F}_1 + \mathcal{J}_2\mathcal{F}_2 + \mathcal{J}_3\mathcal{F}_3$$

$$= \mathcal{J}_1\mathcal{F}_1 + \mathcal{J}_2\mathcal{F}_2 + \mathcal{J}_3(-\mathcal{F}_1 - \mathcal{F}_2)$$

$$=(\mathcal{J}_1 - \mathcal{J}_3)\mathcal{F}_1 + (\mathcal{J}_2 - \mathcal{J}_3)\mathcal{F}_2$$

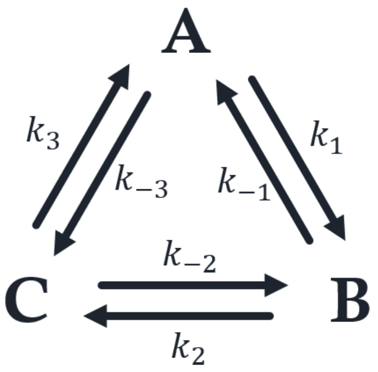
$$= \mathcal{J}_{n1}\mathcal{F}_1 + \mathcal{J}_{n2}\mathcal{F}_2$$

two independent force:
$\mathcal{F}_1, \mathcal{F}_2$

corresponding chemical flux:
$\mathcal{J}_{n1}, \mathcal{J}_{n2}$

$$\begin{pmatrix} \mathcal{J}_{n1} \\ \mathcal{J}_{n2} \end{pmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{pmatrix} \mathcal{F}_1 \\ \mathcal{F}_2 \end{pmatrix}$$

Onsager reciprocal relation: reversible cyclic reaction

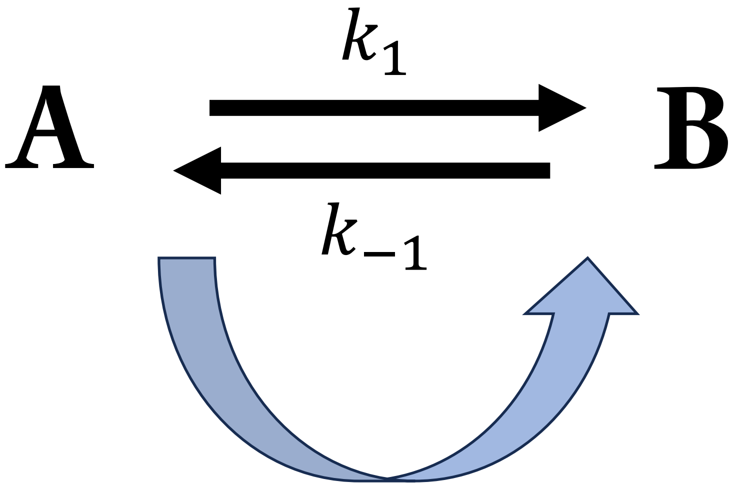


$$\begin{pmatrix} \mathcal{J}_{n1} \\ \mathcal{J}_{n2} \end{pmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{pmatrix} \mathcal{F}_1 \\ \mathcal{F}_2 \end{pmatrix}$$

(near equilibrium)

chemical flux:

$\mathcal{J}_1^+ \approx \mathcal{J}_1^- \Rightarrow k_1 A \approx k_{-1} B$



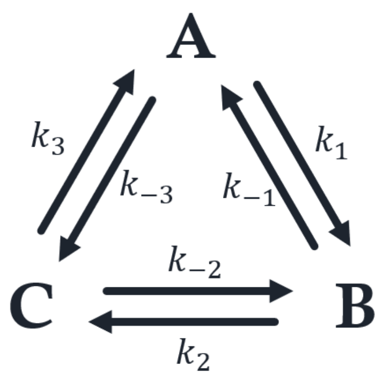
chemical affinity ("force"):

$\mathcal{F}_1 = k_B ln(k_1 A / k_{-1} B)$

$\approx k_B \cdot \frac{k_1 A - k_{-1} B}{k_{-1} B_0} = k_B \cdot \frac{k_1 A - k_{-1} B}{k_1 A_0}$

$= \frac{k_B}{k_1 A_0} \mathcal{J}_1$

Onsager reciprocal relation: reversible cyclic reaction



$$\begin{pmatrix} \mathcal{J}_{n1} \\ \mathcal{J}_{n2} \end{pmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{pmatrix} \mathcal{F}_1 \\ \mathcal{F}_2 \end{pmatrix}$$

(near equilibrium)

$$\mathcal{F}_1 \approx \frac{k_B}{k_1 A_0}\mathcal{J}_1, \mathcal{F}_2 \approx \frac{k_B}{k_2 B_0}\mathcal{J}_2, \mathcal{F}_3 \approx \frac{k_B}{k_3 C_0}\mathcal{J}_3$$

$$\mathcal{J}_{n1} = \mathcal{J}_1 - \mathcal{J}_3 = \frac{k_1 A_0}{k_B}\mathcal{F}_1 - \frac{k_3 C_0}{k_B}\mathcal{F}_3 = \left(\frac{k_1 A_0}{k_B} + \frac{k_3 C_0}{k_B}\right)\mathcal{F}_1 + \frac{k_3 C_0}{k_B}\mathcal{F}_2$$

$$\mathcal{J}_{n2} = \mathcal{J}_2 - \mathcal{J}_3 = \frac{k_2 B_0}{k_B}\mathcal{F}_2 - \frac{k_3 C_0}{k_B}\mathcal{F}_3 = \frac{k_3 C_0}{k_B}\mathcal{F}_1 + \left(\frac{k_2 B_0}{k_B} + \frac{k_3 C_0}{k_B}\right)\mathcal{F}_2$$

$L_{12} = L_{21}$