A GENERALIZED DETAILED BALANCE RELATION

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References:

J.R. England "Statistical physics of self-replication."
[J. Chem. Phys. **139**, 121923 (2013)].

D. Ruelle "A generalized detailed balance relation."
[arXiv:1510.08357]

(Usual) detailed balance

System M immersed in bath at inverse temperature β, pressure p

$\pi_\tau(K \to J)$: conditional probability that macrostate J of M evolves in time τ to macrostate K

$$\frac{\pi_\tau(K \to J)}{\pi_\tau(J \to K)} = \exp[\beta(G(K) - G(J))]$$

(G denotes the Gibbs Free Energy)

"Proof" based on deterministic dynamics, and:

- equilibrium statistical mechanics
  (extended)

- definition of metastable states
  (long lifetime compared with local equilibration)

- time reversal symmetry
  (microscopic reversibility)

Remarks:

- Detailed balance applies to systems far from equilibrium,
  no need to approximate deterministic by stochastic dynamics
  (only mixing implicit in local equilibration)

- Difference from other theories for nonequilibrium:
  conditions on dynamics are weak
  but no predictions on reaction rates

Outline of 'proof'

$$\pi(J \to K) = \frac{\rho(\chi_J.(\chi_K \circ f^\tau))}{\rho(\chi_J)}$$

$$\rho(\chi_J.(\chi_K \circ f^\tau)) = \rho(\chi_K.(\chi_J \circ f^\tau))$$

$\Rightarrow$ $$\frac{\pi(K \to J)}{\pi(J \to K)} = \frac{\rho(\chi_J)}{\rho(\chi_K)}$$

and $$\rho \sim \exp(-\beta G)$$

$\Rightarrow$ detailed balance

Application to biology (England)

- Large system M (bacterium)
- Active bath (metastable solutes)

$$\frac{\pi(K \to J)}{\pi(J \to K)} \geq \exp[-\langle \Delta S \rangle - \beta \langle \Delta Q \rangle] \qquad (*)$$

where

$\Delta Q =$ heat (enthalpy) transferred to bath in transition $J \to K$

Interpretation

Channels $\qquad \alpha : (J, \alpha^{\mathrm{in}}) \to (K, \alpha^{\mathrm{out}})$

$$\pi(J \to K) = \sum_\alpha \pi^\alpha(J \to K) \quad , \quad \pi(K \to J) = \sum_\alpha \pi^{-\alpha}(K \to J)$$

$$\frac{\pi^{-\alpha}(K \to J)}{\pi^\alpha(J \to K)} = \exp[\beta \Delta^\alpha \mu] . \exp[\beta(\Delta G + \Delta^\alpha G)] \qquad (\dagger)$$

Define probabilities

$$p^\alpha = \frac{\pi^\alpha(J \to K)}{\pi(J \to K)}$$

then

$$\frac{\pi(K \to J)}{\pi(J \to K)} = \exp[\beta \Delta G] \sum_\alpha p^\alpha \exp[\beta(\Delta^\alpha G + \Delta^\alpha \mu)]$$

i.e.,

$$\frac{\pi(K \to J)}{\pi(J \to K)}$$
$$= \exp[-\Delta S + \beta \Delta H] \sum_{\alpha} p^{\alpha} \exp[-\Delta^{\alpha} S + \beta \Delta^{\alpha} H] \qquad (**)$$

and by convexity of the exponential we obtain $(*)$

with

$$\langle \Delta S \rangle = \Delta S + \sum_{\alpha} p^{\alpha} \Delta^{\alpha} S \quad , \quad \langle \Delta Q \rangle = -\Delta H - \sum_{\alpha} p^{\alpha} \Delta^{\alpha} H$$

Remarks

- Probabilities $\bar{p}^\alpha : (K, \alpha^{\mathrm{out}}) \to (J, \alpha^{\mathrm{in}})$ given by

$$\bar{p}^\alpha = \frac{p^\alpha \exp[\beta(\Delta^\alpha G + \Delta^\alpha \mu)]}{\sum_\gamma p^\gamma \exp[\beta(\Delta^\gamma G + \Delta^\gamma \mu)]}$$

- Application of $(**)$ to self-replication:

  More efficient replication corresponds to greater transfer $-\Delta^\alpha Q$ of energy (enthalpy) to the bath

Towards a proof

Hamiltonian H_Λ defines f^τ and $\rho(d\Omega)$

Macrostates J, K defined by acceptable subsets of phase space for:

- $\Omega|$ neighborhood V of M in Λ
- metastability

(local equilibration includes thermalization and diffusion of solutes)

Central point: to prove (†) we use the fact that time τ is large w.r.t. local equilibration (diffusion) time

$$\frac{\pi^{-\alpha}(K \to J)}{\pi^{\alpha}(J \to K)} = \frac{\rho(\chi_J^\alpha)}{\rho(\chi_K^{-\alpha})} = \frac{\rho(\chi_J^\alpha)}{\rho(\chi_K^\alpha)} \cdot \frac{\rho(\chi_K^\alpha)}{\rho(\chi_K^{-\alpha})}$$

$$\approx \frac{\rho(\chi_J)}{\rho(\chi_K)} \cdot \exp[\beta(\Delta^\alpha G + \Delta^\alpha \mu)]$$