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Efficiency of chemical energy extraction using entropy growth

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Introduction

Efficiency in thermodynamics: transform one form of energy into another

Optimal for reversible transformations (importance of strong coupling)
→ however power output is zero!

At maximum power and close to equilibrium optimal efficiency is half that of a reversible transformation.

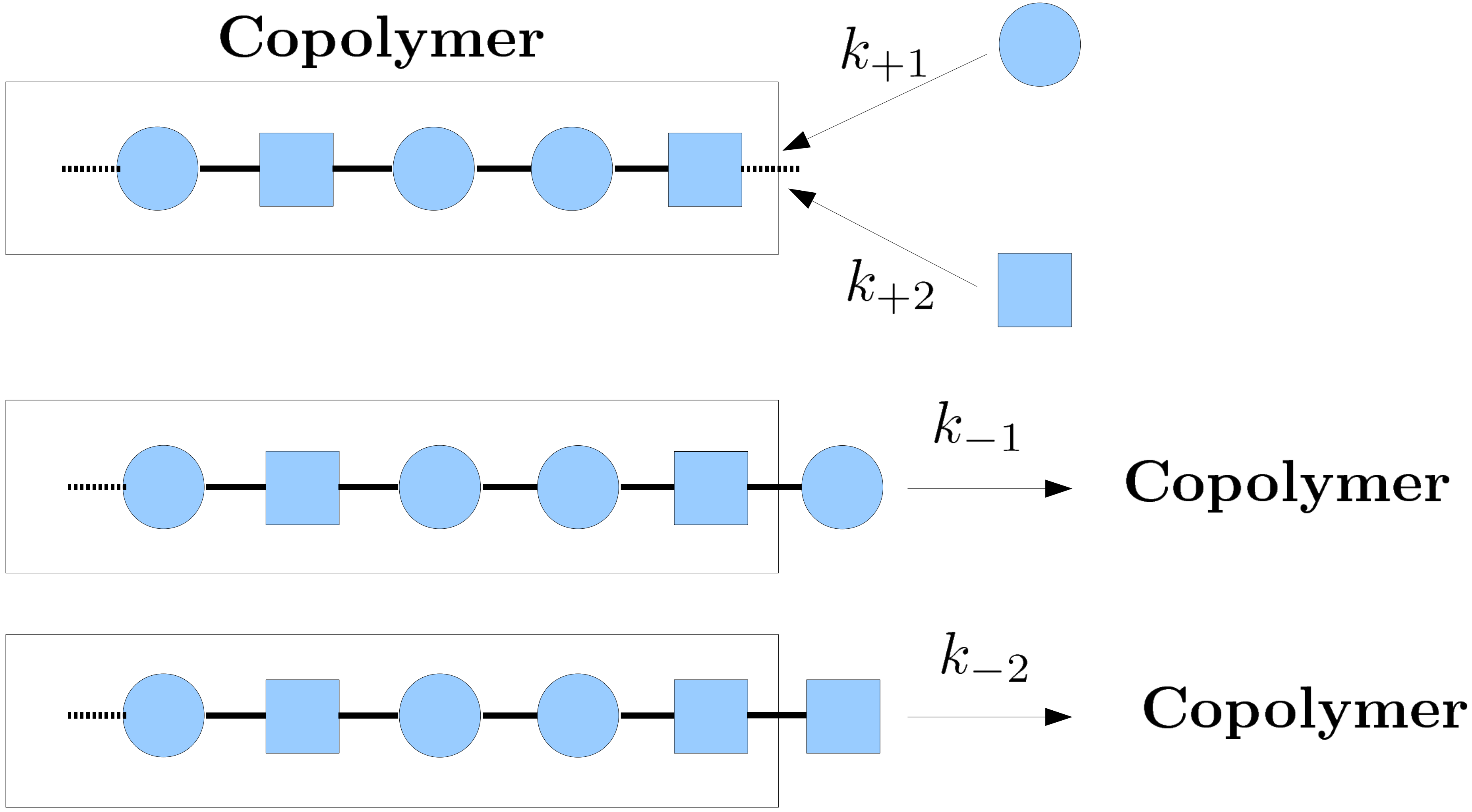
[1] C. Van den Broeck, Phys. Rev. Lett. **95**, 190602, (2005).
[2] M. Esposito, K. Lindenberg and C. Van den Broeck, PRL **102**, 130602 (2009).

We will consider chemical energy extraction using the configuration entropy of a growing copolymer.

This model has been studied in:

[3] C. H. Bennett, BioSystems **11**, 85 (1979)
[4] D. Andrieux and P. Gaspard, PNAS **105**, 9516 (2008) & J. Chem. Phys. **130**, 014901 (2009)

Copolymerization model



$$\frac{k_{+1}}{k_{-1}} = \frac{k_{+2}}{k_{-2}} = \mathrm{e}^{-\epsilon}$$

$T\epsilon$ Free enthalpy per monomer

Thermodynamic description

Isothermal and isobaric open system:

$$G = U + PV - TS = H - TS = \sum_i \mu_i N_i$$

$$d_i S = -\frac{dG}{T} = -\frac{dH}{T} + dS = -\frac{\sum_j \mu_j dN_j}{T} \geq 0$$

Entropy production $\dot{S}_i \equiv \frac{d_i S}{dt} = A_1 J_1 + A_2 J_2$

Affinities $A_{1,2} = (\mu_{1f,2f} - \mu_{1c,2c})$

Fluxes $J_{1,2} = \dot{N}_{1c,2c}$

Kinetic description

Configuration entropy per monomer

$$D = -\lim_{l\to\infty} \frac{1}{l} \sum_{\omega} P_\omega \ln P_\omega$$
$$= -p\ln p - (1-p)\ln(1-p)$$

Free enthalpy per monomer $T\epsilon$

$$\frac{k_{+1}}{k_{-1}} = \frac{k_{+2}}{k_{-2}} = \exp\{-\epsilon\}$$

Entropy production $\boxed{\dot{S}_i = (D-\epsilon)v = Av \geq 0}$

Velocity of polymer growth $v = J_1 + J_2 = k_{+1} - k_{-1}p + k_{+2} - k_{-2}(1-p)$

Probability to
insert monomer 1:

$$p = (a - \sqrt{a^2 - 4(k_{-1} - k_{-2})k_{+1}})/(2(k_{-1} - k_{-2})$$

where $a = k_{+1} + k_{+2} + k_{-1} - k_{-2}$

$$\boxed{\dot{S}_i = (D - \epsilon)v = Av \geq 0}$$

The model has two variables: ϵ and k_{+2}

Time rescaling
$(k_{+1} = 1)$

$$A, v > 0 \quad if \quad \epsilon < \ln 2$$

Equilibrium: $$A, v = 0 \quad if \quad \epsilon = \ln 2$$

$$A, v < 0 \quad if \quad \epsilon > \ln 2$$

$0 < \epsilon < \ln 2$ Entropy driven growth

$\epsilon < 0$ Enthalpy driven growth

$$A = D - \epsilon$$

$$\boxed{\dot{S}_i = (D - \epsilon)v = Av \geq 0}$$

Power

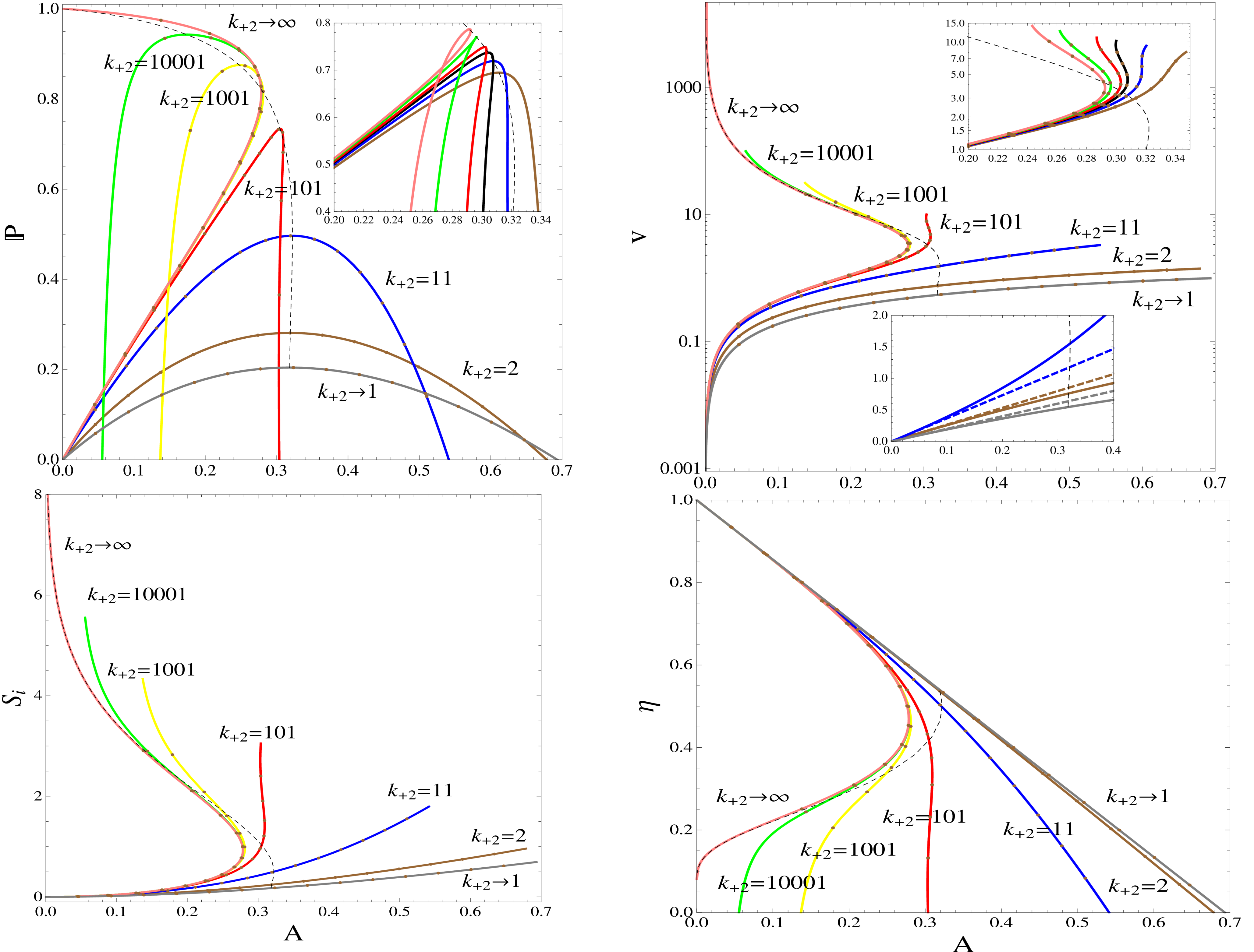
Efficiency

$$\mathbb{P} = \epsilon v = (D - A)v \qquad \eta = \frac{\epsilon v}{Dv} = \frac{D - A}{D}$$

Linear regime: $v = LA + \mathcal{O}(A^2)$

Equilibrium: $A \longrightarrow 0$ ⟹ $\eta \longrightarrow 1 \quad \mathbb{P} \longrightarrow 0$

Efficiency at maximum power: $\partial_A \mathbb{P} = 0$ ⟹ $\eta \longrightarrow 1/2$


ℙ
A
$k_{+2}\to\infty$
$k_{+2}=10001$
$k_{+2}=1001$
$k_{+2}=101$
$k_{+2}=11$
$k_{+2}=2$
$k_{+2}\to1$
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
1.0
0.20
0.22
0.24
0.26
0.28
0.30
0.32
0.34
v
0.001
0.1
10
1000
1.0
1.5
2.0
3.0
5.0
7.0
10.0
15.0
$\dot{S}_i$
0
2
4
6
8
η

Conclusions

Our model illustrates how chemical energy can be extracted from the environment using configuration entropy

A regime of linear response exists but fails to accurately describe the efficiency at max power (no universality close to equilibrium)

A nonlinear branch occurs far from equilibrium along which entropy production increases while affinity decreases. Power, velocity, efficiency, entropy production become bi-valued functions of the affinity.