Recent reading

Theory

Allocating dissipation across a molecular machine cycle to maximize flux

Brown and Sivak [1] conclude that minimizing the depth (and number, I think) of intermediate metastable states maximizes the flux.

Their model defines forward and reverse rate constants similar to our model, although they deal with the input energy in a somewhat different manner. In our case, nonequilibrium populations drive the system. Here, the energy difference between the initial and final state of the system (E1E_1) drive the flux (see Figure 1).

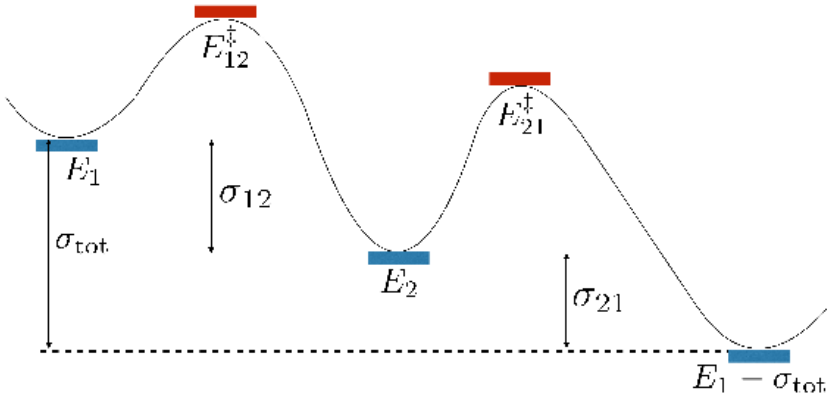

FIG. 2. **Free energy landscape** representing a two-state molecular machine. The left-most state (at free energy E_1) and the right-most state ($E_1 - \sigma_{\text{tot}}$) represent the same stage of molecular machine operation, separated by one complete cycle. The middle state (E_2) represents an intermediate state, while $E_{12}^{\ddagger}$ and $E_{21}^{\ddagger}$ are the free energies of barriers between the states. σ_{12} and σ_{21} are the dissipations for each transition, which sum to σ_{tot}, the dissipation budget for one cycle.

Figure 1: The two state model from Brown and Sivak.

Raising the barrier (E2E_2), decreases the flux. Each barrier is associate with some energy "dissipation" between the initial and

final energy states (I think this is just a free energy difference ΔE\Delta E but there is probably some reason why they chose σ\sigma for these). It turns out that maximum flux does not occur when there is an even dissipation of energy at each barrier. Rather, there is an optimal distribution of these energy dissipation terms that depends on the rate constants for each barrier. There may be a way to use this information to look at the evolved surface splines, although the evolved splines have varying number of peaks and troughs.

> We find an unequal optimal dissipation allocation occurs when: the nonequilibrium steady-state flux is maximized, rather than an efficiency or power; optimization is subject to fixed total dissipation budget per cycle, rather than fixed flux or entropy production rate; cycle transitions have different bare rate constants, corresponding to different barrier heights; and the ratio of forward and reverse rate constants varies exponentially, not linearly, with dissipation ((2)).

This article interprets the results of Wagoner and Dill [2] that flux is affected differently by changing the individual rate constants for barrier crossing.

Locked synchronous rotor motion in a molecular motor A new synchronous

rotary molecular motor from Feringa's group [3]. Štacko, et al. demonstrate controlled rotary and translational motion in a geared, unidirectional molecular motor. This motor is based off their 2nd generation ones that was discussed at ACS 2017; there is a photochemical isomerization and then a thermal helix inversion. Now, by introducing a new chemical substituent

(napthalene or biaryl here),

Random, thermal motions of the napthalene are suppressed.

A computational study was undertaken...

Helix inversion takes a reasonable 5.4 ±\pm 1.8 seconds.

Experiments

Cyclodextrin Rotaxanes and Polyrotaxanes

[4] Hydrophobic and van der Waals interactions drive the formation of rotaxane with cyclodextrins. For polar guests, dipole-dipole interactions may also play a role. In channel inclusions, many CD rings may be stacked like columns.

References

1. Brown AI, Sivak DA. 2017 Allocating dissipation across a molecular machine cycle to maximize flux. See https://arxiv.org/abs/1703.05283v3.

2. Wagoner JA, Dill KA. 2016 Molecular Motors: Power Strokes Outperform Brownian Ratchets. *The Journal of Physical Chemistry B* **120**, 6327–6336. See https://doi.org/10.1021/acs.jpcb.6b02776.

3. Štacko P, Kistemaker JCM, van Leeuwen T, Chang M-C, Otten E, Feringa BL. 2017 Locked synchronous rotor motion in a molecular motor. *Science*. See http://science.sciencemag.org/content/sci/356/6341/964.

4. Wenz G, Han B-H, Müller A. 2006 Cyclodextrin rotaxanes and polyrotaxanes. *Chemical Reviews* See http://pubs.acs.org/doi/full/10.1021/cr970027%2B.