YITP–YSF Symposium (August 4, 2023)

Thermodynamically consistent heat engines: entropy production, efficiency, and performance

Yongjae Oh and **Yongjoo Baek**

Phys. Rev. E **108**, 024602 (2023)

* Also check Yongjae's poster @ STATPHYS28:
[PSb-19] *Efficiency at maximum power of fuel-consuming active heat en gine: a thermodynamically consistent picture*

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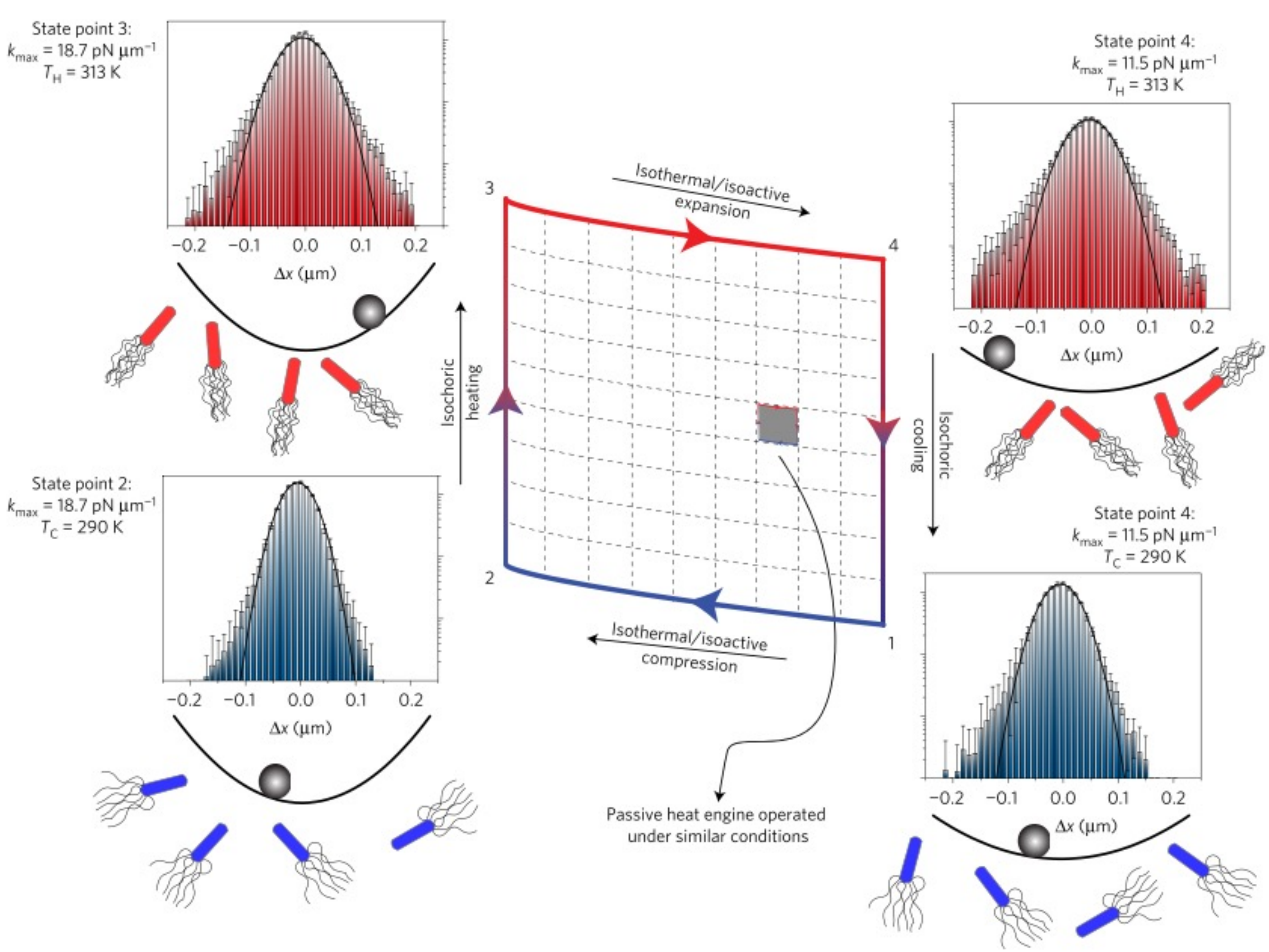
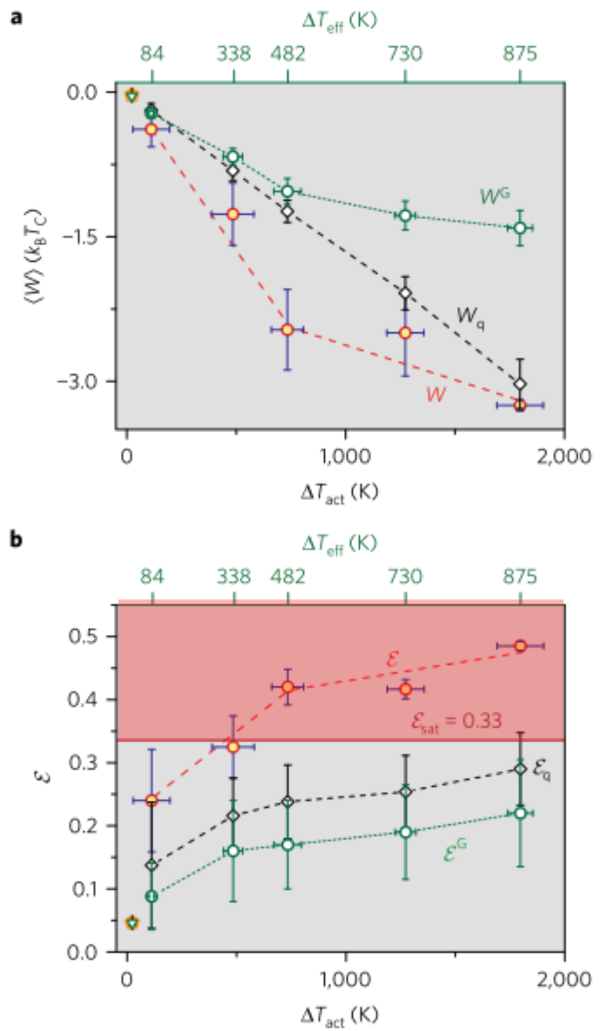
Krishnamurthy et al., Nat. Phys. (2016)

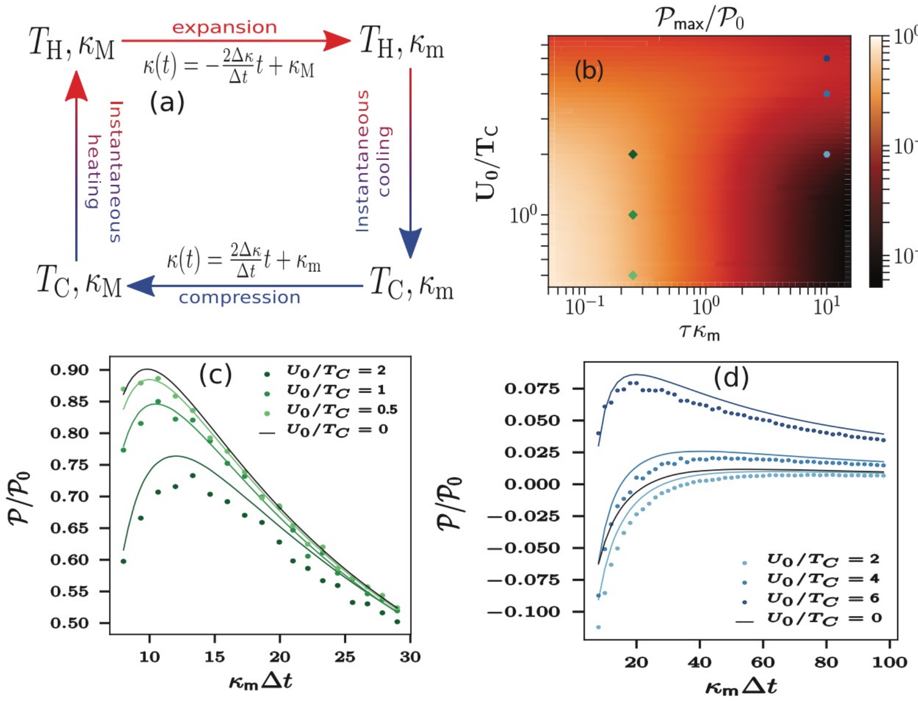
Colloidal engine powered by active particles



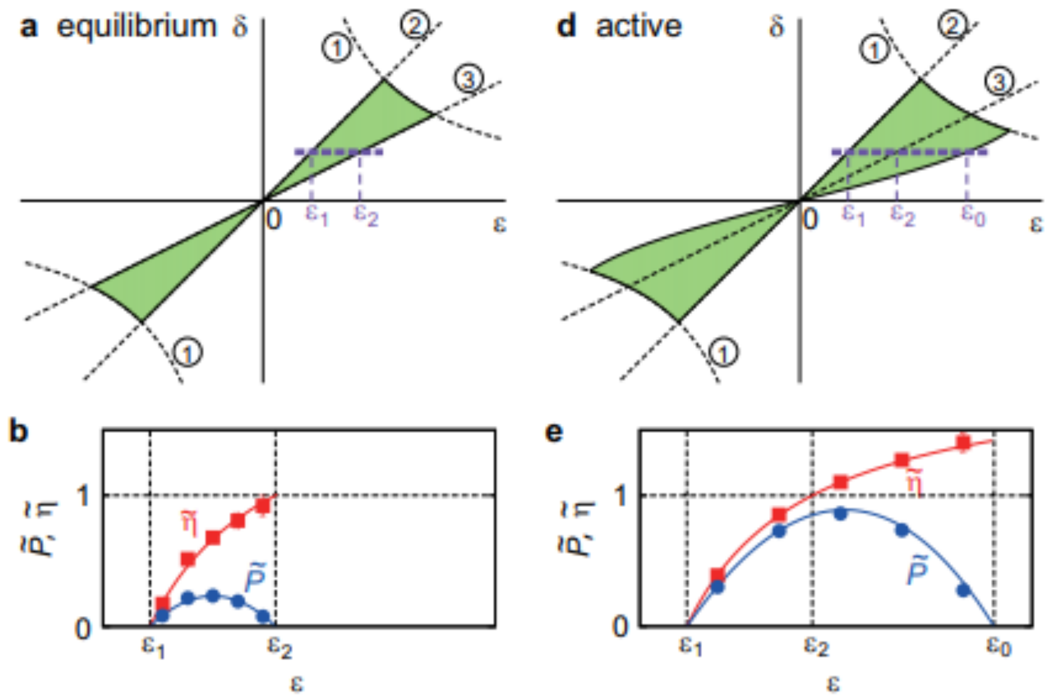


- Apparent engine efficiency can *surpass the Carnot efficiency*, but thermodynamic details are obscure.

Active-bath approaches



D. Martin *et al.*, EPL (2018)



J. S. Lee, J.-M. Park, H. Park, Phys. Rev. E (2020)

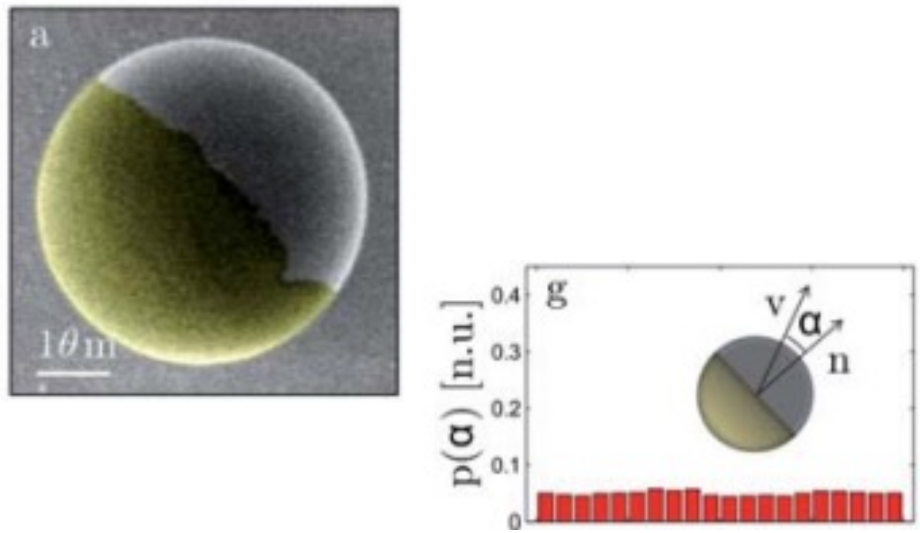
- Models often leave out thermodynamic details of self-propulsion.

$$\dot{X} = -\frac{1}{\Gamma} V'(X) + v, \quad \dot{v} = -\frac{1}{\tau} v + \eta, \quad \langle \eta(t)\eta(t')\rangle = \frac{2D}{\tau^2}\delta(t-t')$$

Active Ornstein–Uhlenbeck Process (AOUP)

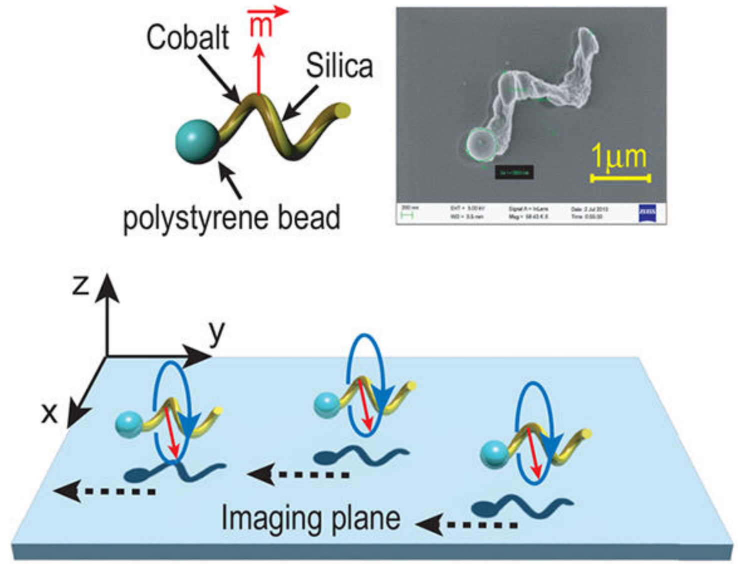
Parity issues

Janus colloidal particles (even-parity)



G. Volpe et al., Soft Matter (2011)

Helical magnetic nanoswimmers (odd-parity)

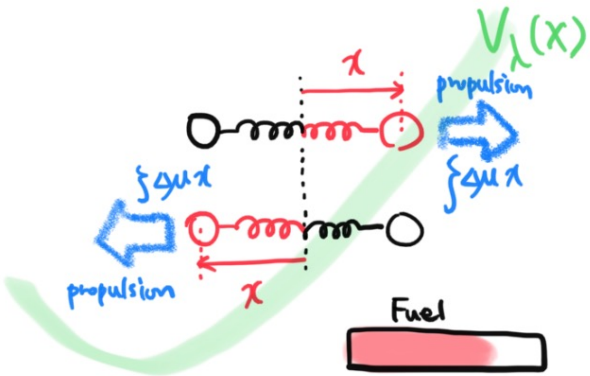


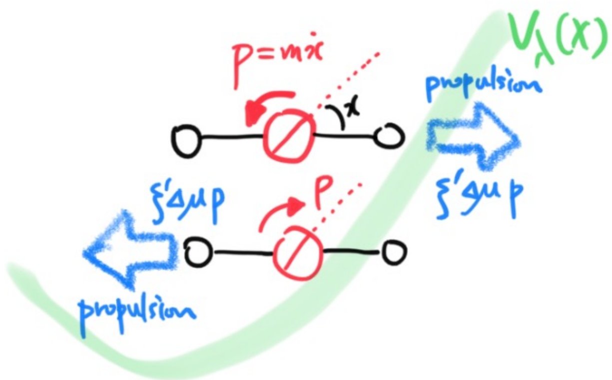
P. Mandal et al., Acc. Chem. Res. (2018)

- Self-propulsion force may keep or change its sign under time reversal, whose thermodynamic effects are yet to be addressed.

Our goals

- Construct a minimal thermodynamically consistent model of fuel-driven active engines, which reduces to the AOUP if the chemical degree of freedom is integrated out.
- Using the apparatus of stochastic thermodynamics, find a clear energetic interpretation of the engine's thermodynamic limitations.
- Explore how the parity of self-propulsion affects the engine performance, especially the efficiency at maximum power.





A recipe for equilibrating systems

- Consider a Langevin system with the free energy $A(\mathbf{r})$ in contact with a thermal reservoir at temperature T.
- Parity: under time reversal, $r_i \to \epsilon_i r_i$.
- Gibbsean steady-state distribution: $P_s(\mathbf{r}) \propto \mathrm{e}^{-\beta A(\mathbf{r})}$:

Dissipative response | Reactive response | Spurious drift

$$\dot{r}_i = -\sum_j (D_{ij} + R_{ij}) \frac{\partial A}{\partial r_j} + T \sum_j \frac{\partial}{\partial r_j}(D_{ij} + R_{ij}) + \eta_i$$

Flux | Force | Thermal noise

$$D_{ij}(\mathbf{r}) = \epsilon_i \epsilon_j D_{ij}(\boldsymbol{\epsilon}\mathbf{r}) = D_{ji}(\mathbf{r})$$

$$R_{ij}(\mathbf{r}) = -\epsilon_i \epsilon_j R_{ij}(\boldsymbol{\epsilon}\mathbf{r}) = -R_{ji}(\mathbf{r})$$

Dissipative/reactive | Onsager reciprocity

$$\langle \eta_i(t)\eta_j(t') \rangle = 2T D_{ij}(\mathbf{r})\delta(t - t')$$

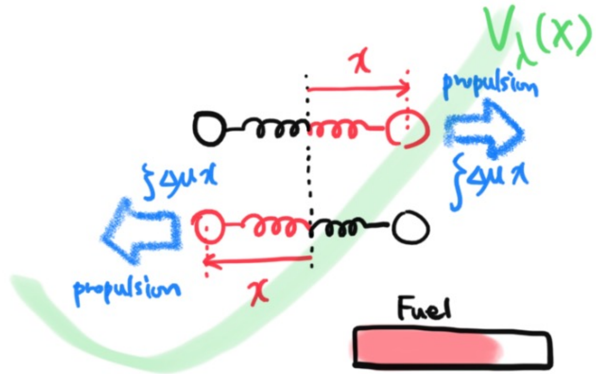
Fluctuation-dissipation relation

Even-parity dimer

Dissipative response Reactive response Force

- Free energy: $A(X, x, c) = V(X) + \frac{1}{2}kx^2 + F(c)$

Chemical free energy



- Langevin equations

$$\dot{X} = -\frac{1}{\Gamma} V'(X) + \frac{\zeta x}{\Gamma} F'(c) + \eta_X$$

$$\dot{x} = -\frac{1}{\gamma} kx + \eta_x \qquad \dot{c} = -\left(\kappa + \frac{\zeta^2 x^2}{\Gamma}\right) F'(c) + \frac{\zeta x}{\Gamma} V'(X) + \eta_c$$

Mechanochemical coupling (dissipative)

- Fluctuation-dissipation relations

$$\langle \eta_X(t)\eta_X(t')\rangle = \frac{2T}{\Gamma}\delta(t-t') \qquad \langle \eta_X(t)\eta_c(t')\rangle = -2T\frac{\zeta x}{\Gamma}\delta(t-t')$$

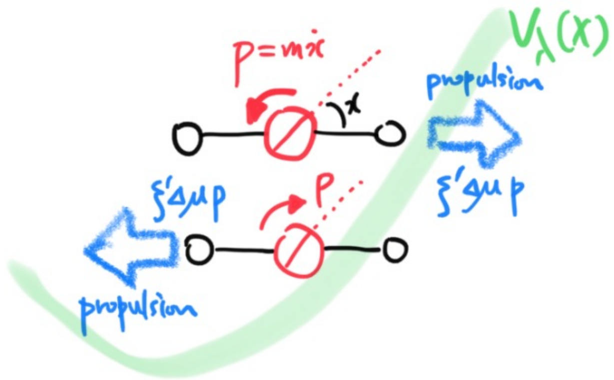
$$\langle \eta_x(t)\eta_x(t')\rangle = \frac{2T}{\gamma}\delta(t-t') \qquad \langle \eta_c(t)\eta_c(t')\rangle = 2T\left(\kappa + \frac{\zeta^2 x^2}{\Gamma}\right)\delta(t-t')$$

Odd-parity dimer

Dissipative response · Reactive response · Force

- Free energy: $A(X,x,c) = V(X) + \frac{p^2}{2m} + F(c)$

Chemical free energy



- Langevin equations

$$\dot{X} = -\frac{1}{\Gamma} V'(X) + \frac{\zeta' p}{\Gamma} F'(c) + \eta_X$$

$$\dot{p} = -\frac{\gamma'}{m} p + \eta_p \qquad \dot{c} = -\kappa F'(c) - \frac{\zeta' p}{\Gamma} V'(X) + \eta_c$$

Mechanochemical coupling (reactive)

- Fluctuation-dissipation relations

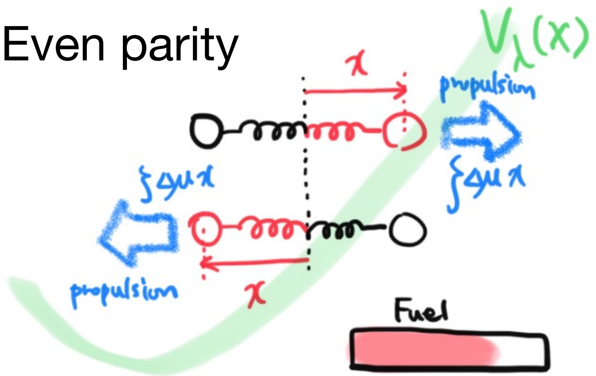
$$\langle \eta_X(t)\eta_X(t') \rangle = \frac{2T}{\Gamma}\delta(t-t') \qquad \langle \eta_X(t)\eta_c(t') \rangle = 0$$

$$\langle \eta_p(t)\eta_p(t') \rangle = 2T\gamma'\delta(t-t') \qquad \langle \eta_c(t)\eta_c(t') \rangle = 2T\kappa\delta(t-t')$$

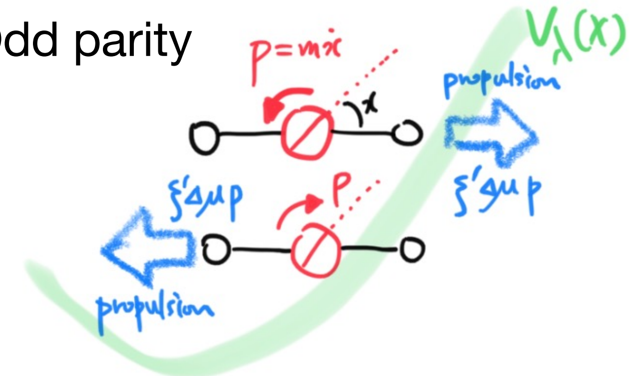
Active dimers

- Replacing $F'(c)$ with a constant chemical driving $\Delta\mu$, the engine becomes *active*.

Even parity



Odd parity



$$\dot{X} = -\frac{1}{\Gamma} V'(X) + \frac{\zeta x}{\Gamma}\Delta\mu + \eta_X$$

$$\dot{x} = -\frac{1}{\gamma} kx + \eta_x$$

AOUP-like dynamics

$$\dot{X} = -\frac{1}{\Gamma} V'(X) + \frac{\zeta' p}{\Gamma}\Delta\mu + \eta_X$$

$$\dot{p} = -\frac{\gamma'}{m} p + \eta_p$$

$$\dot{c} = -\left(\kappa + \frac{\zeta^2 x^2}{\Gamma}\right)\Delta\mu + \frac{\zeta x}{\Gamma} V'(X) + \eta_c$$

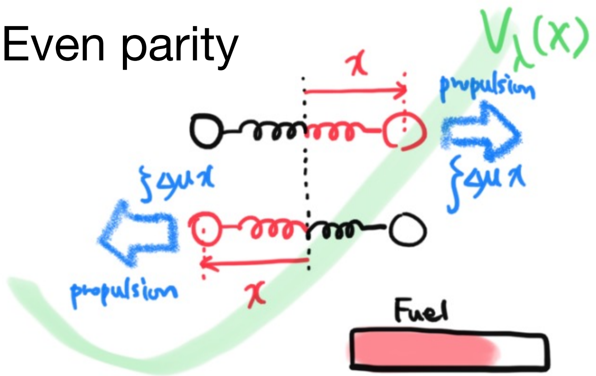
$$\dot{c} = -\kappa\Delta\mu - \frac{\zeta' p}{\Gamma} V'(X) + \eta_c$$

These signs contain the parity information

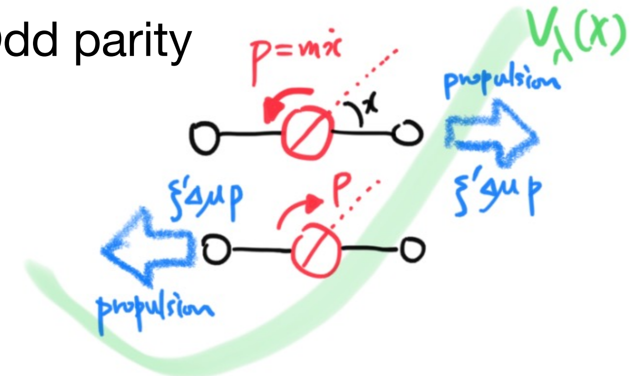
Assumption of tight coupling

- By setting $\kappa = 0$, we remove background chemical reactions which do not contribute to the dimer propulsion.

Even parity



Odd parity



$$\dot{X} = -\frac{1}{\Gamma} V'(X) + \frac{\zeta x}{\Gamma} \Delta\mu + \eta_X$$

$$\dot{x} = -\frac{1}{\gamma} kx + \eta_x$$

AOUP-like dynamics

$$\dot{X} = -\frac{1}{\Gamma} V'(X) + \frac{\zeta' p}{\Gamma} \Delta\mu + \eta_X$$

$$\dot{p} = -\frac{\gamma'}{m} p + \eta_p$$

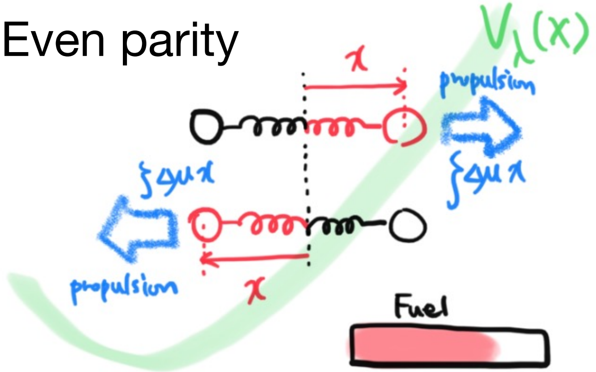
$$\dot{c} = -\left(\cancel{\kappa} + \frac{\zeta^2 x^2}{\Gamma}\right) \Delta\mu + \frac{\zeta x}{\Gamma} V'(X) + \cancel{\eta_c}\ \ \zeta x \eta_X$$

$$\dot{c} = \cancel{\kappa\Delta\mu} - \frac{\zeta' p}{\Gamma} V'(X) + \cancel{\eta_c}$$

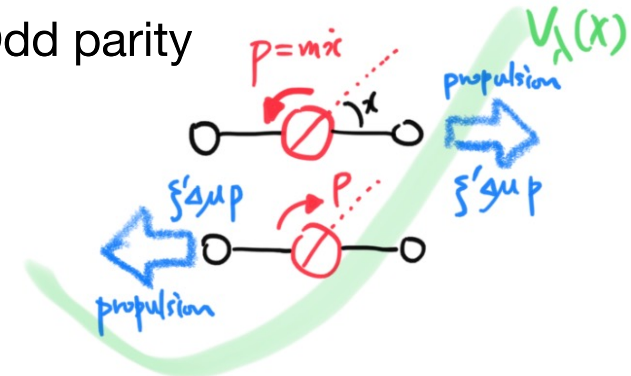
Final model

- By setting $\kappa = 0$, we only consider the chemical reactions directly driving the dimer.

Even parity



Odd parity



$$\dot{X} = -\frac{1}{\Gamma} V'(X) + \frac{\zeta x}{\Gamma} \Delta\mu + \eta_X$$

$$\dot{x} = -\frac{1}{\gamma} kx + \eta_x$$

$$\dot{c} = -\zeta x \dot{X}$$

Fuel is consumed when the dimer moves

AOUP-like dynamics

$$\dot{X} = -\frac{1}{\Gamma} V'(X) + \frac{\zeta' p}{\Gamma} \Delta\mu + \eta_X$$

$$\dot{p} = -\frac{\gamma'}{m} p + \eta_p$$

$$\dot{c} = -\frac{\zeta' p}{\Gamma}\left(-\Gamma\dot{X} + \zeta' p \Delta\mu + \Gamma\eta_X\right)$$

Fuel is consumed through dissipative interaction with the surrounding

1st law of thermodynamics

- Even-parity case: from $H_\lambda(X,x) = V_\lambda(X) + \frac{1}{2}kx^2$,

$$\frac{dH_\lambda}{dt} = \frac{\partial V_\lambda}{\partial \lambda}\dot{\lambda} + V_\lambda' \circ \dot{X} + kx \circ \dot{x}$$

$$= \underbrace{\frac{\partial V_\lambda}{\partial \lambda}\dot{\lambda}}_{\equiv -\dot{W}_{\mathrm{out}}} + \underbrace{(-\Gamma\dot{X} + \Gamma\eta_X) \circ \dot{X} + (-\gamma\dot{x} + \gamma\eta_x) \circ \dot{x}}_{\equiv \dot{Q}} \underbrace{- \Delta\mu\dot{c}}_{\equiv \dot{W}_{\mathrm{chem}}}$$

- Odd-parity case: from $H_\lambda(X,p,c) = V_\lambda(X) + \frac{p^2}{2m}$,

$$\frac{dH_\lambda}{dt} = \frac{\partial V_\lambda}{\partial \lambda}\dot{\lambda} + V_\lambda' \circ \dot{X} + \frac{p}{m} \circ \dot{p}$$

$$= \underbrace{\frac{\partial V_\lambda}{\partial \lambda}\dot{\lambda}}_{\equiv -\dot{W}_{\mathrm{out}}} + \underbrace{(-\Gamma\dot{X} + \zeta' p\Delta\mu + \Gamma\eta_X) \circ \left(\dot{X} - \frac{\zeta' p}{\Gamma}\Delta\mu\right) + \left(-\frac{\gamma' p}{m} + \eta_p\right) \circ \frac{p}{m}}_{\equiv \dot{Q}} \underbrace{- \Delta\mu\dot{c}}_{\equiv \dot{W}_{\mathrm{chem}}}$$

2nd law of thermodynamics

- Even-parity case: the reservoir entropy production is given by

$$\Delta S_{\mathrm{res}} = \ln \frac{\mathcal{P}_{\lambda}[X, x]}{\mathcal{P}_{\lambda^R}[X^R, x^R]} = -\int \mathrm{dt}\left[\frac{V'(X) - \zeta x \Delta\mu}{T} \circ \dot{X} + \frac{kx}{T} \circ \dot{x}\right] = -\frac{Q}{T}$$

- Odd-parity case: the reservoir entropy production is given by

$$\Delta S_{\mathrm{res}} = \ln \frac{\mathcal{P}_{\lambda}[X, p]}{\mathcal{P}_{\lambda^R}[X^R, p^R]} = -\int \mathrm{dt}\left[\frac{V'(X)}{T} \circ \left(\dot{X} - \frac{\zeta' p}{\Gamma}\Delta\mu\right) + \frac{\dot{p}}{T} \circ \frac{p}{m}\right] = -\frac{Q}{T}$$

- In both cases, the entropy production satisfies the Clausius formula.
- For the periodic/steady state, the 2nd law of thermodynamics is obtained as the Clausius inequality $\langle \Delta S_{\mathrm{res}} \rangle = -\int \mathrm{dt}\, \dot{Q}/T \geq 0$.

Energetically interpretable efficiency

- Consider a cyclic engine which operates between two reservoirs at temperatures $T_1 > T_2$. For convenience, we leave out the notation $\langle \cdots \rangle$ for the ensemble average. Then, in the periodic state,

$$-\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = -\frac{Q_1}{T_1} - \frac{W_{\text{out}} - Q_1 - W_{\text{chem}}}{T_2}$$

$$= -\frac{1}{T_2}\left[W_{\text{out}} - \left(1 - \frac{T_2}{T_1}\right) Q_1 - W_{\text{chem}}\right] \geq 0$$

- Thus, we identify the efficiency bounded from above:

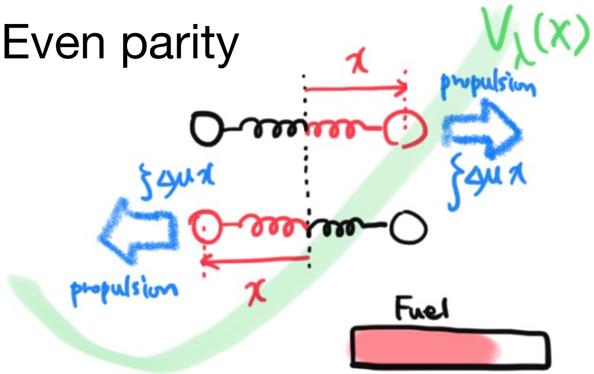
$$\eta \equiv \frac{W_{\text{out}}}{\left(1 - \frac{T_2}{T_1}\right) Q_1 + W_{\text{chem}}} \equiv \frac{W_{\text{out}}}{\eta_C Q_1 + W_{\text{chem}}} \leq 1$$

Carnot efficiency

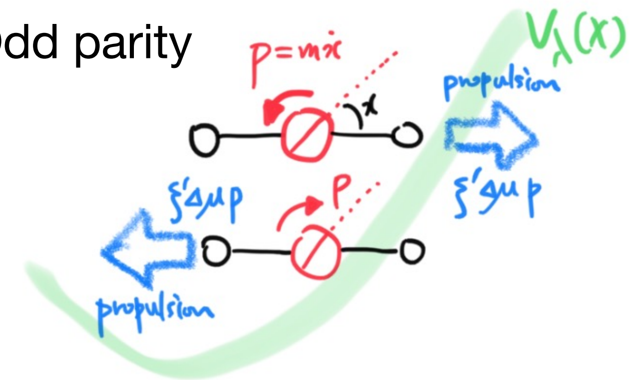
Questions

- How does the self-propulsion parity affect the efficiency at maximum power (EMP)?
- Can the active engine achieve a higher EMP than the passive engine?

Even parity

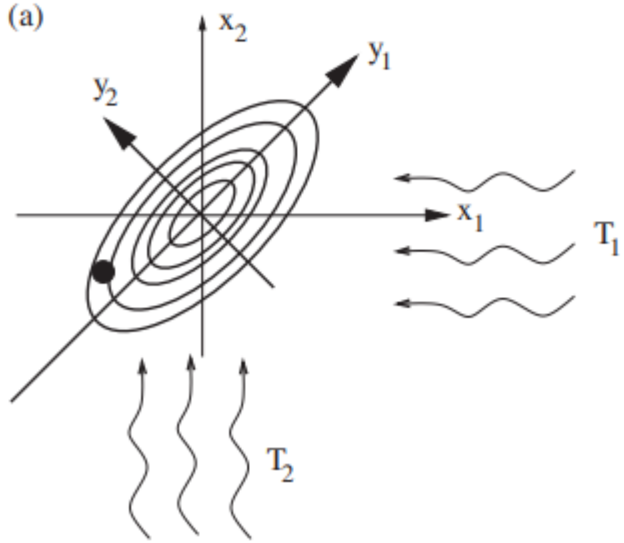


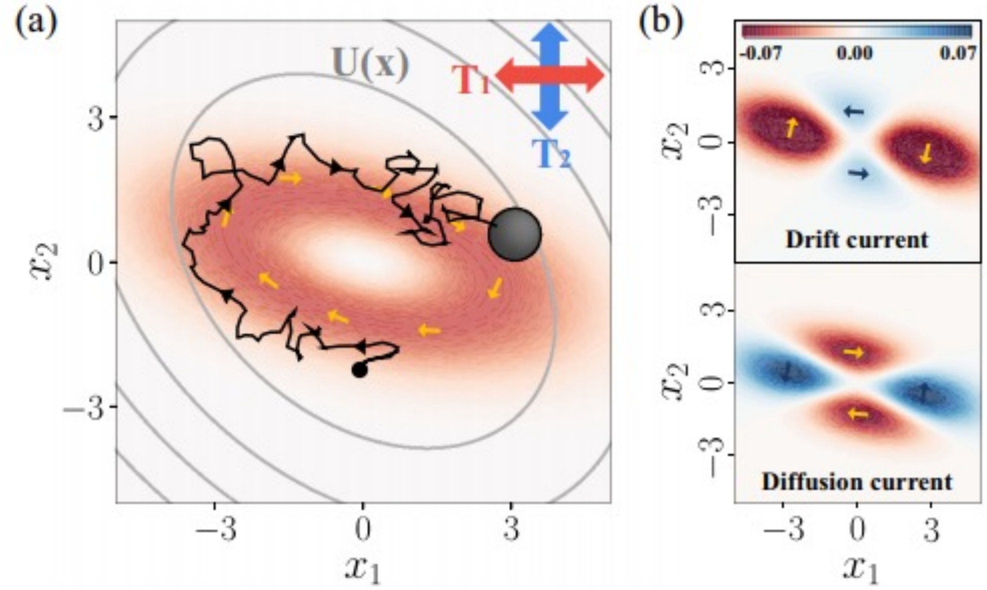
Odd parity



Filliger and Reimann, PRL (2007)

Brownian gyrator





- A particle simultaneously exchanges heat with two reservoirs near a potential minimum (harmonic confining potentials).
- Work is extracted via a fixed nonconservative force field.
- The steady state of the model is exactly solvable.

Brownian gyrator with an active dimer

Even-parity case

$$\dot{X}_1 = -\frac{1}{\Gamma} K X_1 + \frac{\zeta x}{\Gamma} \Delta\mu + \eta_1 + \frac{\epsilon}{\Gamma} X_2$$

$$\dot{X}_2 = -\frac{1}{\Gamma} K X_2 + \eta_2 + \frac{\delta}{\Gamma} X_1$$

$$\dot{x} = -\frac{1}{\gamma} k x + \eta_x$$

$$\dot{c} = -\zeta x \dot{X}_1$$

Odd-parity case

$$\dot{X}_1 = -\frac{1}{\Gamma} K X_1 + \frac{\zeta' p}{\Gamma} \Delta\mu + \eta_1 + \frac{\epsilon}{\Gamma} X_2$$

$$\dot{X}_2 = -\frac{1}{\Gamma} K X_2 + \eta_2 + \frac{\delta}{\Gamma} X_1$$

$$\dot{p} = -\frac{\gamma'}{m} p + \eta_p$$

$$\dot{c} = -\frac{\zeta' p}{\Gamma}\left(-\Gamma \dot{X}_1 + \zeta' p \Delta\mu + \Gamma \eta_1\right)$$

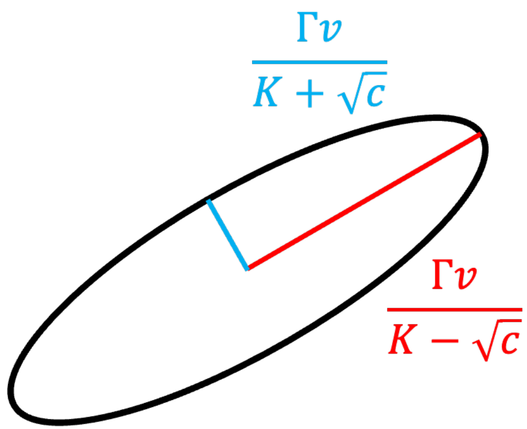
Nonconservative forces (as long as $\epsilon \neq \delta$)   Noises from hot reservoir   Noises from cold reservoir

- For simplicity, the active component is placed in contact with reservoir 1 (the hot reservoir).
- The efficiency of the engine, bounded from above by 1, can be defined in the same way as in the case of a single active dimer.

Maximization of power

- Reparameterization of force coefficients: $\{\epsilon, \delta\}$ to $\{r = \epsilon/\delta,\ c = \delta\epsilon\}$
- An active particle of typical velocity v moves in an area $\frac{\Gamma^2 v^2}{K^2 - c}$.
- For a given engine size (fixed c), we may choose r that maximizes the power.
- The EMP is then obtained as:

$$\eta^{(\mathrm{e/o}),\mathrm{MP}} = \frac{1}{\dfrac{\eta_{\mathrm{C}}}{1 - \dfrac{1}{A(c)}\sqrt{1-\eta_{\mathrm{C}}}} + 2b^{(\mathrm{e/o})}\dfrac{[A(c)^2 - 1]\sqrt{1-\eta_{\mathrm{C}}}}{\left[\dfrac{A(c)}{\sqrt{1-\eta_{\mathrm{C}}}} - 1\right]^2}}$$



$$b^{(\mathrm{e})} = 2\frac{K(\Gamma + K\tau)}{\tau c},\ b^{(\mathrm{o})} = 2\frac{[\Gamma K + (K^2 - c)\tau]K}{\Gamma c}$$

Apparent efficiency

- The **apparent efficiency** considered in Lee, Park, and Park (2020) is equivalent to

$$\eta_{\mathrm{appr}} \equiv \frac{\langle \dot{W}_{\mathrm{out}} \rangle}{\langle \dot{Q}_1 \rangle + \langle \dot{W}_{\mathrm{chem}} \rangle} = 1 - \frac{\delta}{\epsilon}$$

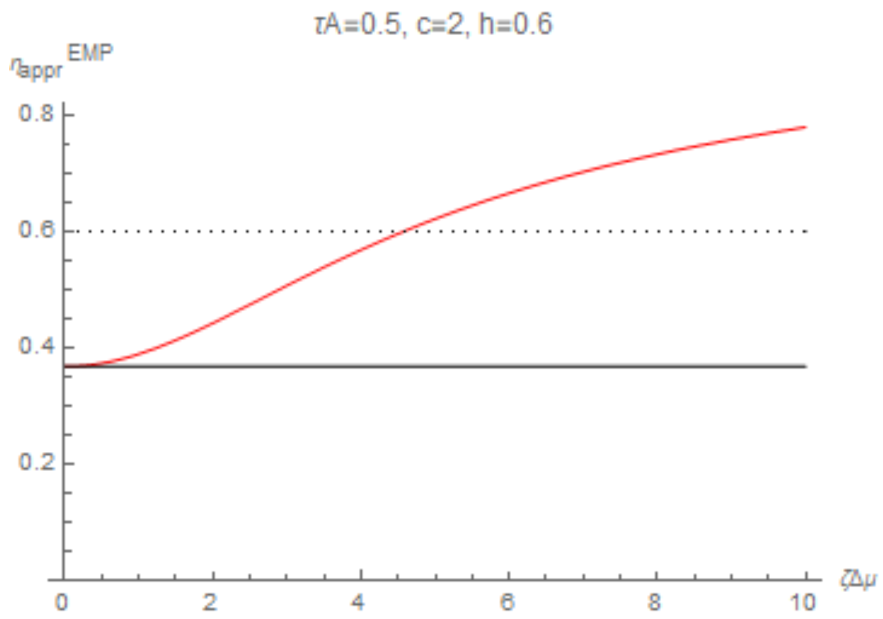
- The **apparent EMP** is obtained as

$$\eta_{\mathrm{appr}}^{\mathrm{MP}} = 1 - \frac{1}{r^*} = 1 - \frac{1}{A(c)}\sqrt{1 - \eta_{\mathrm{C}}}$$

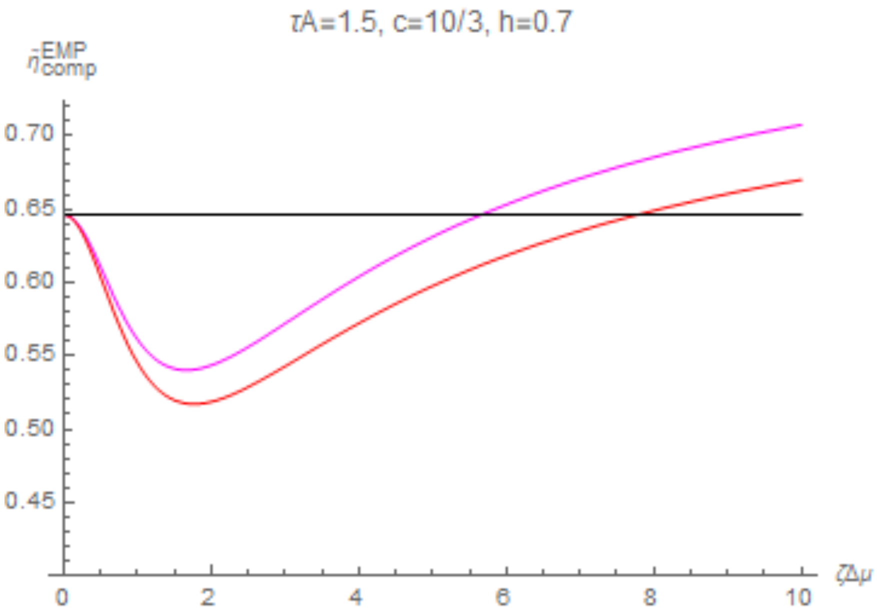
$$A(c) = \sqrt{1 + \frac{\Gamma\tau^2}{\gamma[(\Gamma + K\tau)^2 - \tau^2 c]}(\zeta\Delta\mu)^2} > 1$$

- The **apparent EMP** is **always larger** than the passive EMP $\eta_{\mathrm{CA}} = 1 - \sqrt{1 - \eta_{\mathrm{C}}}$.

Active vs. passive EMP



Apparent EMP



EMP

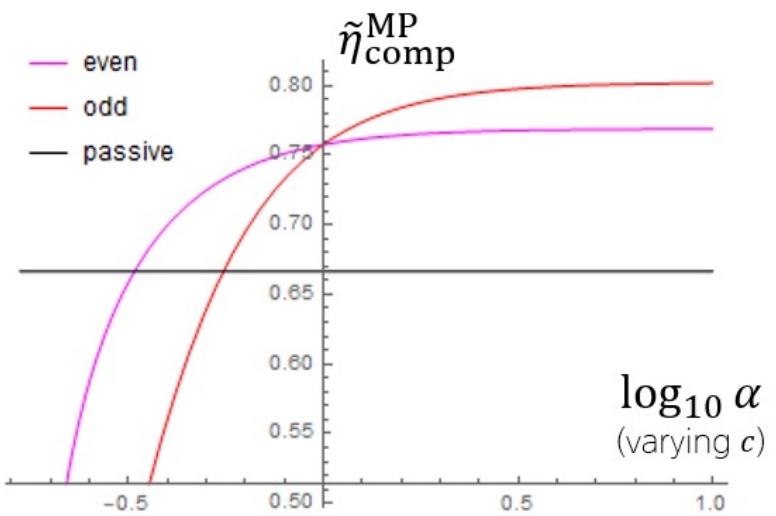
- The **apparent EMP** is **always larger** than the passive EMP $\eta_{CA} = 1 - \sqrt{1 - \eta_C}$.
- The **EMP** is larger in the active engine **when the chemical driving is sufficiently strong.**

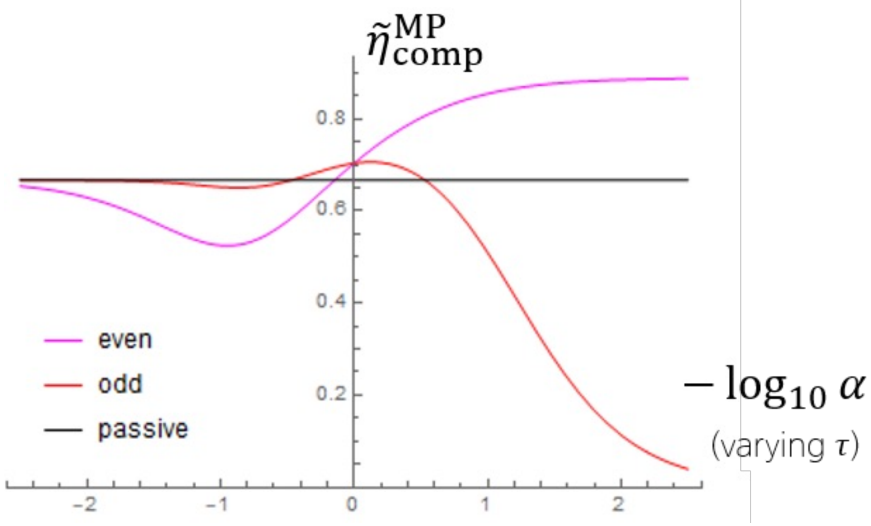
Parity dependence of the EMP

$$\frac{1}{\eta^{(\mathbf{e}),\mathrm{MP}}} - \frac{1}{\eta^{(\mathbf{o}),\mathrm{MP}}} = \frac{2[A(c)^2-1][1-\eta_c]^{3/2}K}{c\left[A(c)-\sqrt{1-\eta_c}\right]^2\Gamma\tau}\left(\Gamma^2-(K^2-c)\tau^2\right)$$

$\propto \alpha^2 - 1$

Defining $\alpha = \frac{\text{engine size}}{\text{run length}} = \frac{\Gamma}{\tau\sqrt{K^2-c}}$, $\begin{cases} \alpha > 1 & \text{: odd-parity is more efficient} \\ \alpha < 1 & \text{: even-parity is more efficient} \end{cases}$





- The even-parity (odd-parity) engine is more efficient when the engine size is smaller (larger) than the run length.

Summary

Phys. Rev. E **108**, 024602 (2023)

- We constructed a thermodynamically consistent model of active engines driven by fuel consumption.
- The dissipation of this engine has a clear energetic interpretation involving the amount of fuel consumed.
- We find the engine efficiency with a concrete upper bound originating from the second law of thermodynamics.
- While the apparent EMP is always higher in an active engine than in a passive engine, the EMP is higher in an active engine only when self-propulsion is sufficiently strong.
- The even-parity (odd-parity) self-propulsion achieves higher EMP when the engine size is smaller (larger) than the run length.

Our group

Noneq. Stat. Phys. Lab @ SNU