Nonequilibrium fluctuation-response relations in diffusion and chemical reaction networks

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Thu. Aug 10, 2023 4:00 PM – 4:15 PM

[T2a-10C-01] Trade-offs between Response and Fluctuations in Nonequilibrium Chemical Reaction Networks

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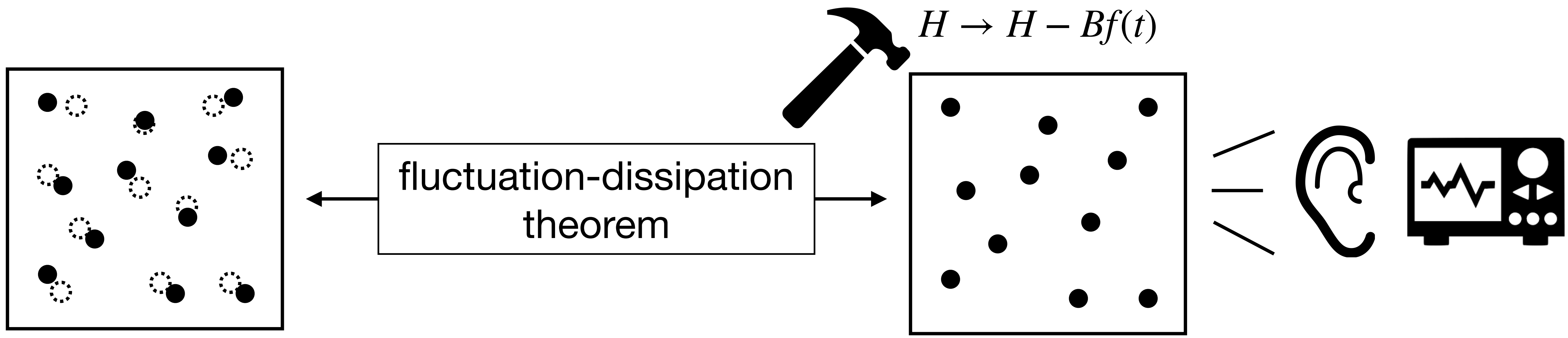
Fluctuation-dissipation theorem

In equilibrium,



$$H \to H - Bf(t)$$

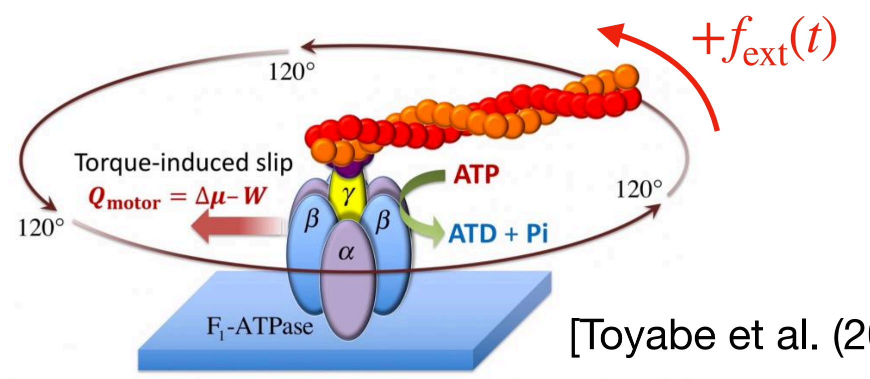
$$\langle A(t)B(s)\rangle_{\text{eq}}$$

$$R_{AB}(t-s) = \left.\frac{\delta\langle A(t)\rangle_f}{\delta f(s)}\right|_{f=0}$$

$$\frac{\partial}{\partial s}\langle A(t)B(s)\rangle_{\text{eq}} = k_B T R_{AB}(t-s) \quad \text{for } t > s$$

Fluctuation-response relations in NEQ

[1] violation of FDT [Harada and Sasa, PRL (2005)]



[Toyabe et al. (2010)]

$$\begin{aligned}(\text{violation of FDT}) &\sim (\text{fluctuation}) - (\text{response}) \\ &\sim (\text{heat dissipation})\end{aligned}$$

[2] generalized FDT [Agarwal (1972), Seifert & Speck (2010), …]

$$\frac{\partial}{\partial t}P(x,t) = \hat{\mathscr{L}}P(x,t)$$

Fokker-Planck equation
master equation
…

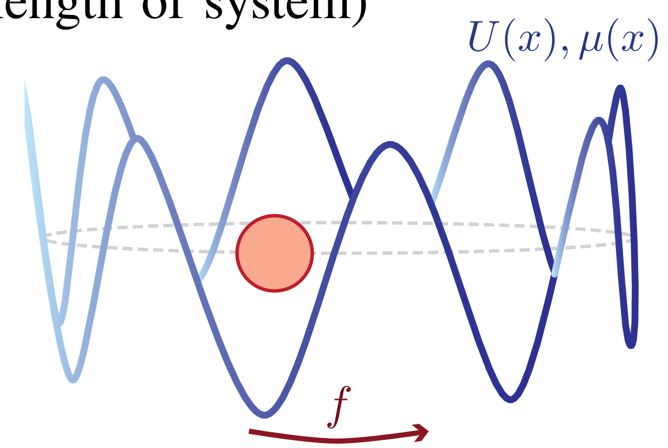
arbitrary perturbation →

$$\partial_t P(x,t) = \hat{\mathscr{L}}P(x,t) + \epsilon(t)\hat{\mathscr{L}}_{ptb}P(x,t)$$

$$(\text{response of } \langle A \rangle) = \underbrace{\langle A(t)\Omega(s)\rangle_{ss}}_{(\text{fluctuation})} \quad \text{with} \quad \Omega(x) = P_{ss}^{-1}(x)\hat{\mathscr{L}}_{ptb}P_{ss}(x)$$

1D nonequilibrium diffusive system

ℓ = (length of system)



$$\frac{\partial}{\partial t}P(x,t) = -\frac{\partial}{\partial x}\mu(x)\left(-U'(x) + f - \frac{\partial}{\partial x}\right)P(x,t)$$

$P_{\rm ss}(x)$ is known !

perturbation on	
force	$\left\| \frac{1}{\ell}\frac{\partial \langle Q \rangle_{\rm ss}}{\partial f} \right\| \le \langle Q \rangle_{\rm ss}$
	for positive valued observables $Q(x) > 0$
mobility	$\left\| \int_a^b \frac{\delta \langle Q \rangle_{\rm ss}}{\delta \ln \mu(y)}\, dy \right\| \le \langle Q \rangle_{\rm ss} \tanh\left(\frac{\|f\ell\|}{4}\right)$
potential + mobility	$\frac{\delta \langle Q \rangle_{\rm ss}}{\delta U(y)} + \frac{\delta \langle Q \rangle_{\rm ss}}{\delta \ln \mu(y)} = P_{\rm ss}(y)\left\{\langle Q \rangle_{\rm ss} - Q(y)\right\} = -\,{\rm Cov}\{\delta(x-y), Q(x)\}$
	for any observables $Q(x)$

Bound on the violation of the FDT

mobility $$\left| \int_a^b \frac{\delta \langle Q \rangle_{ss}}{\delta \ln \mu(y)} \, dy \right| \le \langle Q \rangle_{ss} \tanh \left(\frac{|f\ell|}{4} \right)$$

potential + mobility $$\frac{\delta \langle Q \rangle_{ss}}{\delta U(y)} + \frac{\delta \langle Q \rangle_{ss}}{\delta \ln \mu(y)} = P_{ss}(y) \{ \langle Q \rangle_{ss} - Q(y) \}$$

$U(x) \to U(x) - \lambda V(x)$: energy perturbation

$A = A - B + B$

$$\frac{\partial \langle Q(\lambda) \rangle_{ss}}{\partial \lambda} = - \int_0^L V(y) \frac{\delta \langle Q \rangle_{ss}}{\delta U(y)} dy = - \int_0^L V(y) \left[\frac{\delta \langle Q \rangle_{ss}}{\delta U(y)} + \frac{\delta \langle Q \rangle_{ss}}{\delta \ln \mu(y)} \right] dy + \int_0^L V(y) \frac{\delta \langle Q \rangle_{ss}}{\delta \ln \mu(y)} dy$$

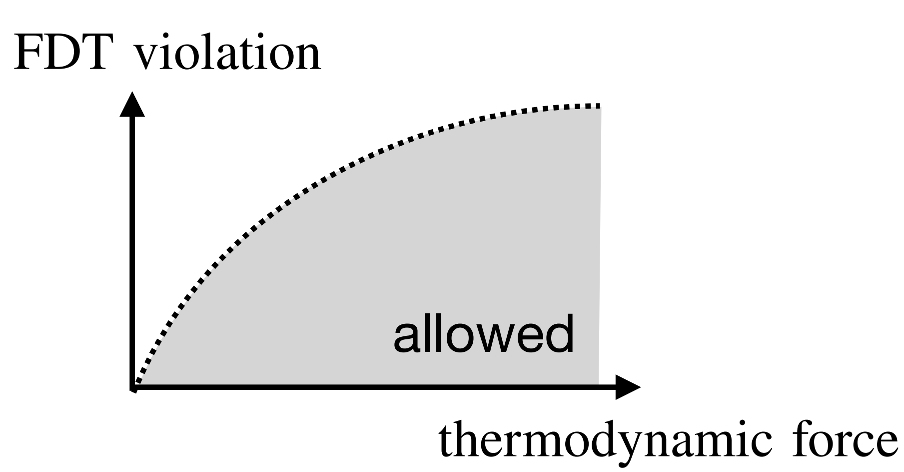
response

$$= \mathrm{Cov}\{Q, V\} - \int_0^L V(y) \frac{\delta \langle Q \rangle_{ss}}{\delta \ln \mu(y)} dy$$

fluctuation

$$\left| \frac{\partial \langle Q(\lambda) \rangle_{ss}}{\partial \lambda} - \mathrm{Cov}\{Q, V\} \right| \le \langle Q \rangle_{ss} |V_{\max}| \tanh \left(\frac{|f\ell|}{4} \right)$$

response **fluctuation**



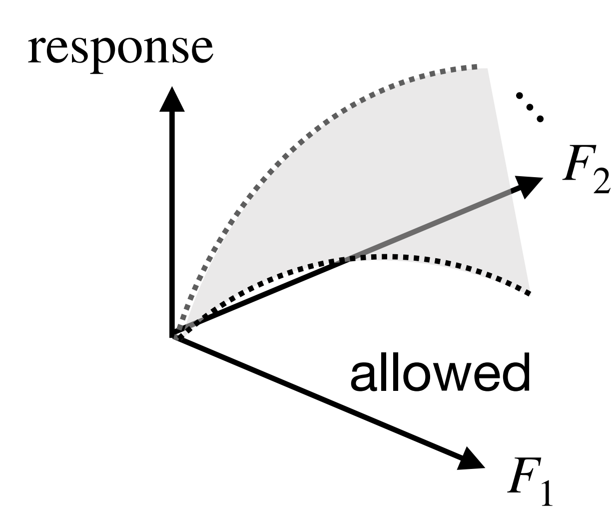
Higher dimensions

$$\frac{\partial}{\partial t}P(\boldsymbol{x},t) = -\nabla_{\boldsymbol{x}}\cdot\mu(\boldsymbol{x})\left\{-\nabla_{\boldsymbol{x}}U(\boldsymbol{x}) + \boldsymbol{f}(\mathbf{x}) - \nabla_{\boldsymbol{x}}\right\}P(\boldsymbol{x},t)$$

$$= -\nabla_{\boldsymbol{x}}\cdot\boldsymbol{j}(\boldsymbol{x},t)$$

$\longrightarrow$ $P_{\rm ss}(\boldsymbol{x}),\ \boldsymbol{j}_{\rm ss}(\boldsymbol{x})$ are unknown

perturbation on	
mobility	$\dfrac{\delta P_{\rm ss}(\boldsymbol{x})}{\delta \ln\mu(\boldsymbol{y})} = \int_0^\infty dt\ \boldsymbol{j}_{\rm ss}(\boldsymbol{y})\cdot\nabla_{\boldsymbol{y}}P(\boldsymbol{x},t\,\vert\,\boldsymbol{y},0)$ if $\boldsymbol{j}_{\rm ss}(\boldsymbol{y})\to 0,\quad \dfrac{\delta P_{\rm ss}(\boldsymbol{x})}{\delta \ln\mu(\boldsymbol{y})}\to 0$
potential + mobility	$\dfrac{\delta P_{\rm ss}(\boldsymbol{x})}{\delta U(\boldsymbol{y})} + \dfrac{\delta P_{\rm ss}(\boldsymbol{x})}{\delta \ln\mu(\boldsymbol{y})} = P_{\rm ss}(\boldsymbol{y})\left\{P_{\rm ss}(\boldsymbol{x}) - \delta(\boldsymbol{x}-\boldsymbol{y})\right\} = -\mathrm{Cov}\{\delta(\boldsymbol{z}-\boldsymbol{x}),\delta(\boldsymbol{z}-\boldsymbol{y})\}$



EQ-like fluctuation-response relation

$$\frac{\partial}{\partial t}P(x,t) = \hat{\mathscr{L}}P(x,t) \xrightarrow{\text{arbitrary perturbation}} \partial_t P(x,t) = \hat{\mathscr{L}}P(x,t) + \epsilon(t)\hat{\mathscr{L}}_{\rm ptb}P(x,t)$$

$$(\text{response of } \langle A \rangle) = \langle A(t)\Omega(s)\rangle_{\rm ss} \quad \text{with} \quad \Omega(x) = P_{\rm ss}^{-1}(x)\hat{\mathscr{L}}_{\rm ptb}P_{\rm ss}(x)$$

a special choice of perturbation

$$\hat{\mathscr{L}}_{\rm ptb} = -\hat{\mathscr{L}}B(x) \longrightarrow \langle A(t)\Omega(s)\rangle_{\rm ss} = \frac{\partial}{\partial s}\langle A(t)B(s)\rangle_{\rm ss}$$

$$(\text{response of } \langle A \rangle) = \langle A(t)\dot{B}(s)\rangle_{\rm ss}$$

: EQ-like fluctuation-response relation

for $A = B = \rho_{\boldsymbol{k}}$,

EQ-like fluctuation-response relation $\longrightarrow$ (response / fluctuation)

$$\frac{\langle \delta\rho_{\boldsymbol{k}}(t)\rangle}{\langle \delta\rho_{\boldsymbol{k}}(0)\rangle} = \frac{\langle \rho_{\boldsymbol{k}}(t)\rho_{-\boldsymbol{k}}(0)\rangle_{\rm ss}}{\langle \rho_{\boldsymbol{k}}(0)\rho_{-\boldsymbol{k}}(0)\rangle_{\rm ss}}$$

$$\partial_t\langle \delta\rho_{\boldsymbol{k}}(t)\rangle = -M_{\boldsymbol{k}}\langle \delta\rho_{\boldsymbol{k}}(t)\rangle \longleftrightarrow \partial_t\langle \rho_{\boldsymbol{k}}(t)\rho_{-\boldsymbol{k}}(0)\rangle_{\rm ss} = -M_{\boldsymbol{k}}\langle \rho_{\boldsymbol{k}}(t)\rho_{-\boldsymbol{k}}(0)\rangle_{\rm ss} \quad \text{for long times } t$$

: Onsager's regression hypothesis around NESS

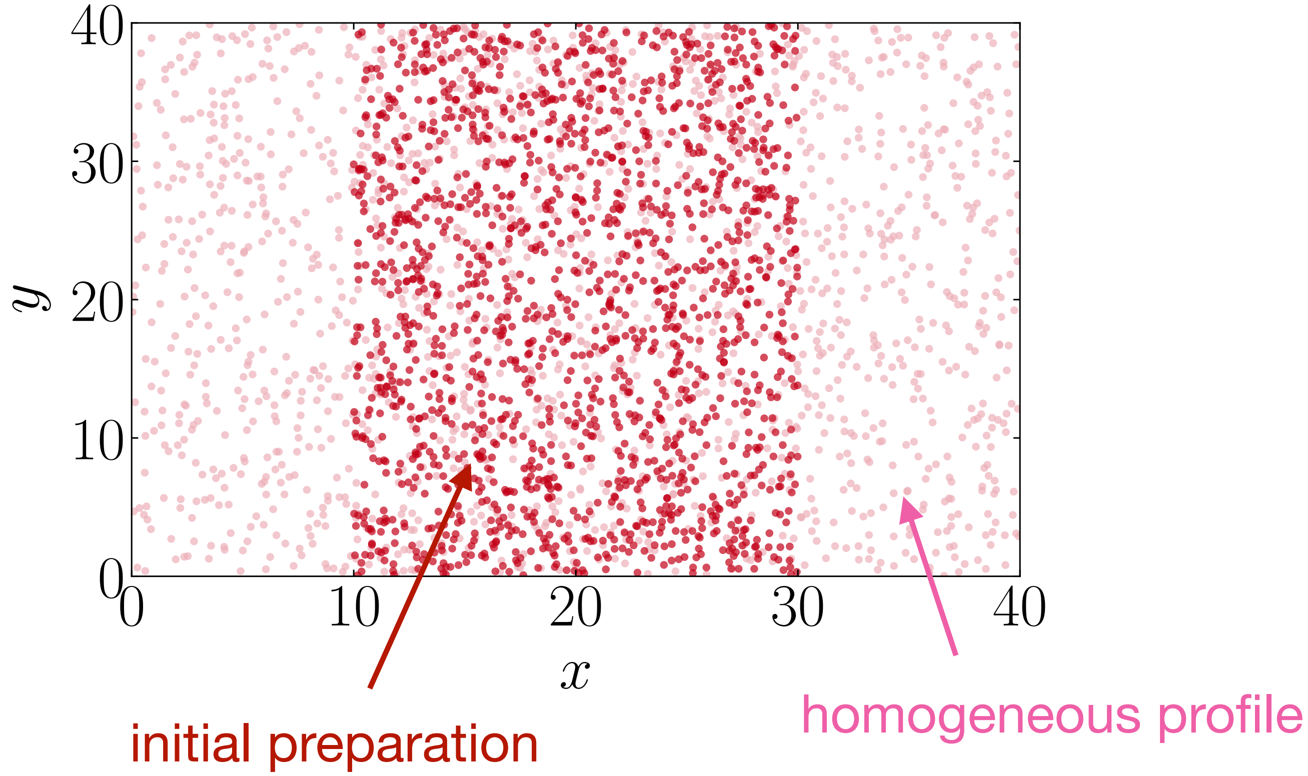
Implication: Green-Kubo relation

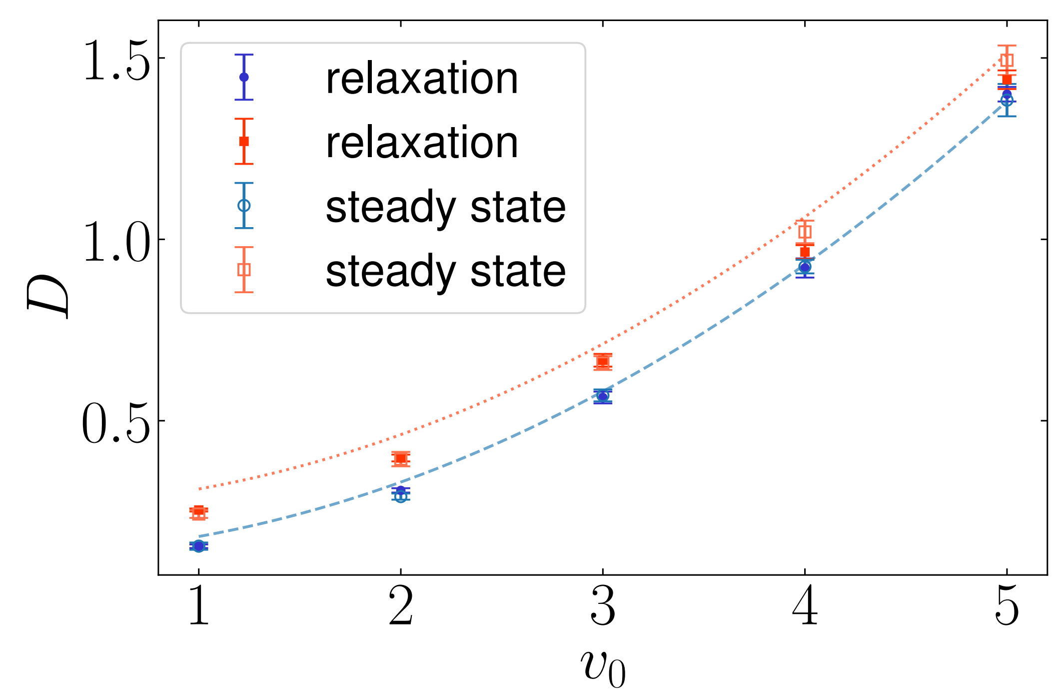
relaxation

$$\partial_t \langle \delta\rho_{\boldsymbol{k}}(t)\rangle = -k^2 D \langle \delta\rho_{\boldsymbol{k}}(t)\rangle$$

steady-state fluctuation

$$D \propto \int_0^\infty dt \int_V d\boldsymbol{r} \int_V d\boldsymbol{r}' \, \langle \dot{\rho}_{\boldsymbol{r}}(t)\dot{\rho}_{\boldsymbol{r}'}(0)\rangle_{\mathrm{ss}}$$





blue: weak interaction

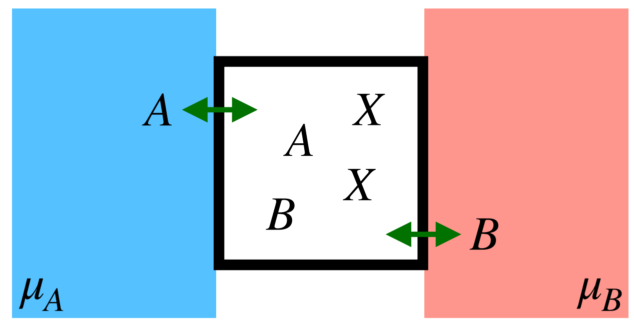
red: strong interaction

dashed: linear theory

Chemical reaction networks

$$A + 2X \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} 3X$$

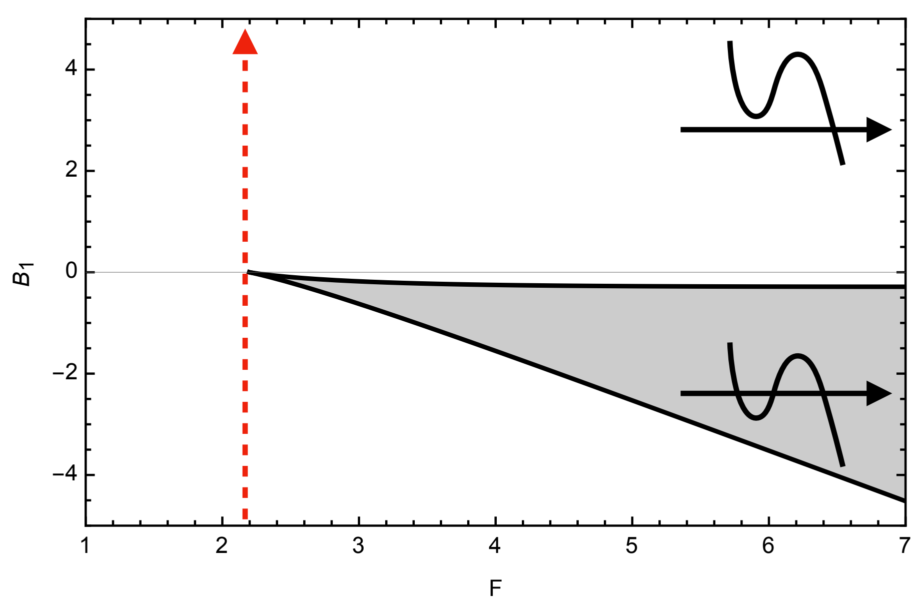
$$X \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} B$$

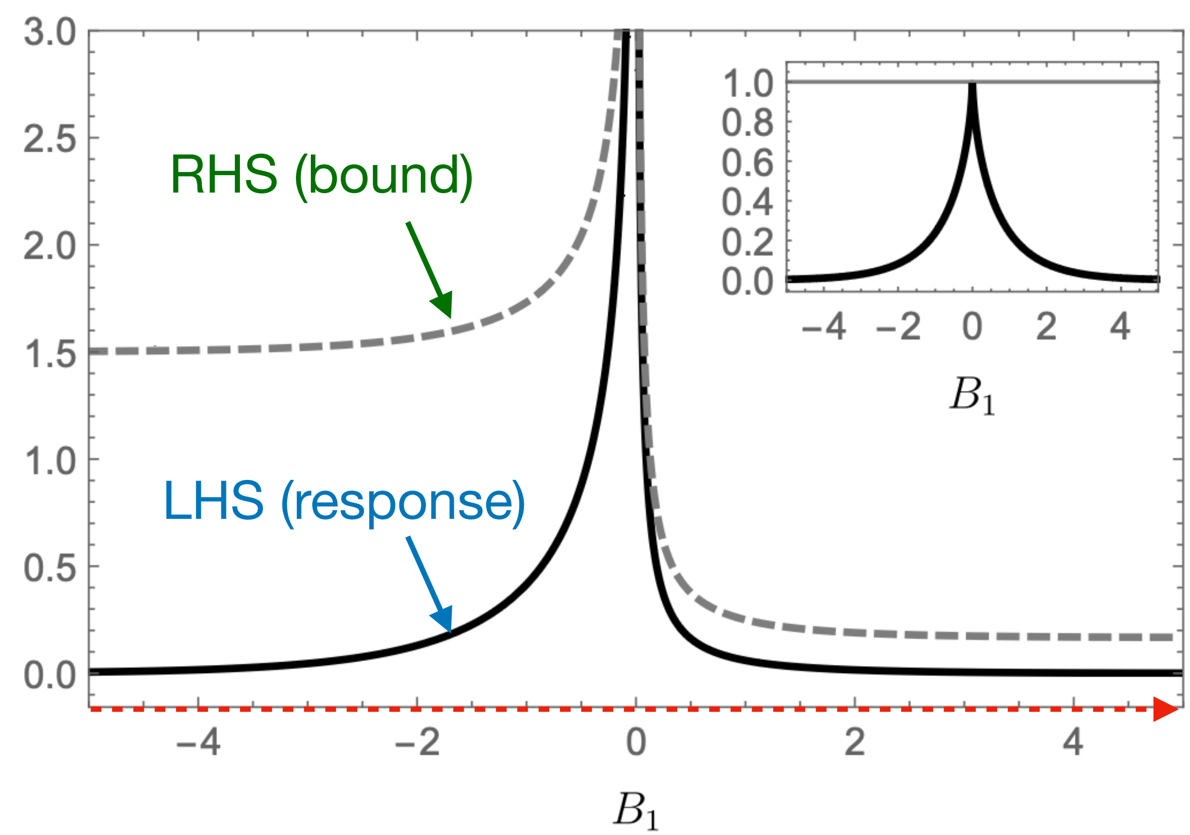


$$\left| k_{+\rho}\frac{\partial[X]_{ss}}{\partial k_{+\rho}} + k_{-\rho}\frac{\partial[X]_{ss}}{\partial k_{-\rho}} \right| \le D_X \tanh\left(\frac{\mathscr{F}}{4}\right)$$

<u>chemical rate equation</u>

$$\frac{d[X]}{dt} = k_{+1} - k_{-1}[X] + k_{+2}[X]^2 - k_{-2}[X]^3$$





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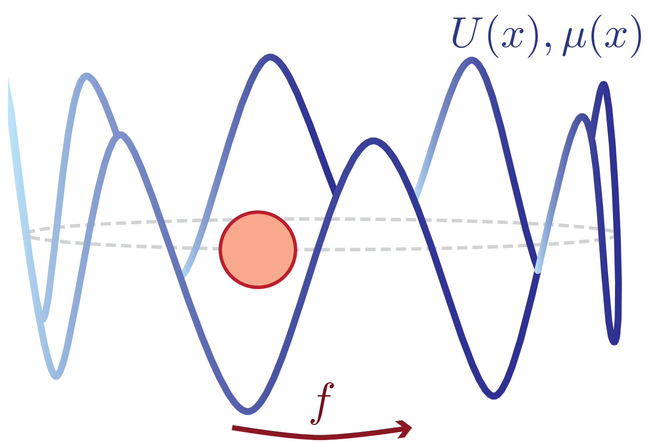
Summary

One-dimensional diffusions



$$\left| \frac{1}{\ell} \frac{\partial \langle Q \rangle_{\rm ss}}{\partial f} \right| \leq \langle Q \rangle_{\rm ss},$$

$$\left| \frac{\partial \langle Q(\lambda) \rangle_{\rm ss}}{\partial \lambda} - {\rm Cov}\{Q, V\} \right| \leq \langle Q \rangle_{\rm ss} \tanh\left(\frac{|f\ell|}{4} \right)$$

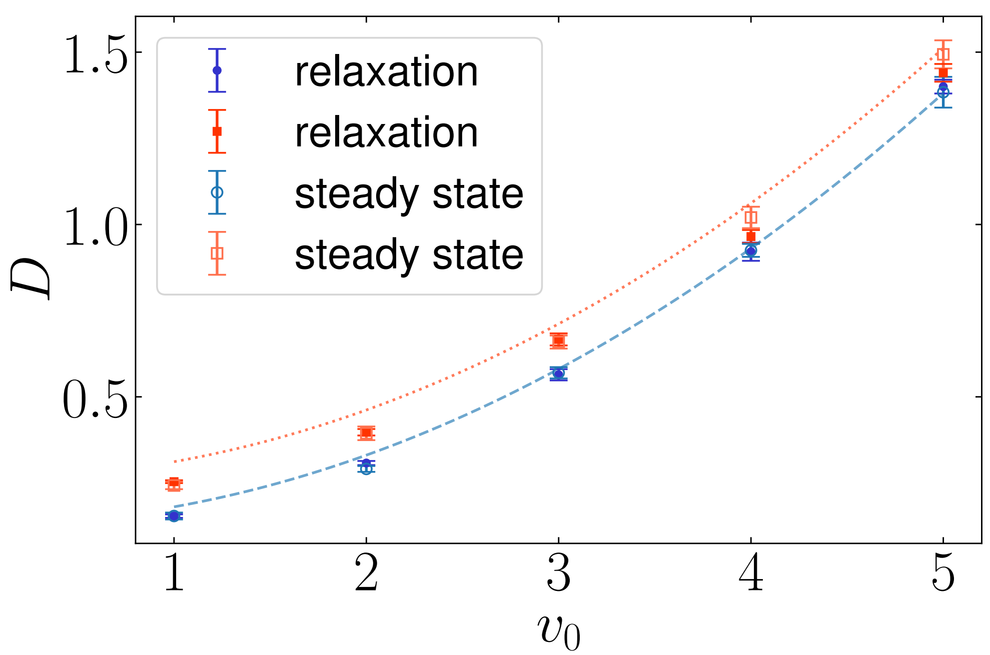
EQ-like fluctuation-response relation

$$\hat{\mathscr{L}}_{\rm ptb} = -\hat{\mathscr{L}} B(x)$$

$$\downarrow$$

$$(\text{response of } \langle A \rangle) = \langle A(t) \dot{B}(s) \rangle_{\rm ss}$$

$$D \propto \int_0^\infty dt \int_V d\boldsymbol{r} \int_V d\boldsymbol{r}' \, \langle \dot{\rho}(\boldsymbol{r}, t) \dot{\rho}(\boldsymbol{r}', 0) \rangle_{\rm ss}$$



Thanks for your attention!

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