Energetic Variational Approaches (EnVarA) for Active Materials and Reactive Fluids

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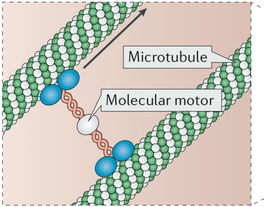
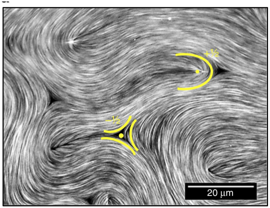
(Joint with Bob Eisenberg, Tom Irving, Pei Liu, Yiwei Wang, Teng-fei Zhang, et al.)

Outline

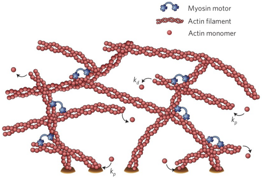
Active Materials and Reactive Fluids

- Active Materials: bacterial suspensions, microtubules, actin network ...
- Reactive Fluids: Internal combustion engine and rockets, astrophysics...
- Transduction of chemical energy into mechanical work



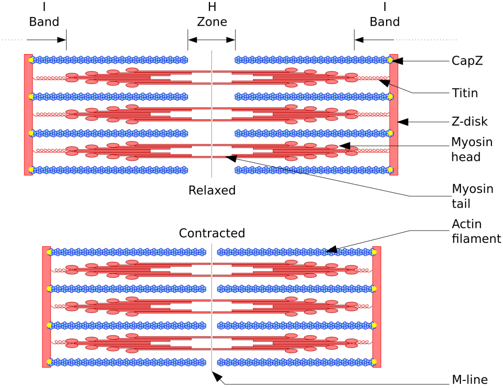


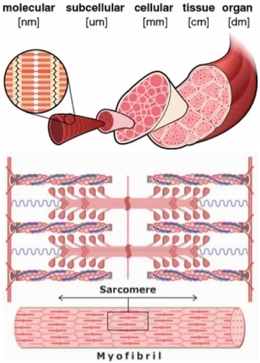
Experiments



1. Prost, J., Julicher, F. and Joanny, JF. Active gel physics. Nature Phys 11, 111-117 (2015).
2. Yang, Xiaogang, Jun Li, M. Gregory Forest, and Qi Wang. "Hydrodynamic theories for flows of active liquid crystals and the generalized onsager principle." Entropy 18, no. 6 (2016): 202.
3. Gao, Tong, Meredith D. Betterton, An-Sheng Jhang, and Michael J. Shelley. Analytical structure, dynamics, and coarse graining of a kinetic model of an active fluid. Physical Review Fluids 2, no. 9 (2017): 093302.
4. Needleman, D., Dogic, Z. Active matter at the interface between materials science and cell biology. Nat Rev Mater 2, 17048 (2017).
5. Doostmohammadi, A., Ignes-Mullol, J., Yeomans, J.M. et al. Active nematics. Nat Commun 9, 3246 (2018).
6. Stewman, Shannon F., Kenneth K. Tsui, and Ao Ma. "Dynamic Instability from Non-equilibrium Structural Transitions on the Energy Landscape of Microtubule." Cell Systems 11.6 (2020): 608-624.

Muscle contraction: sliding filament theory





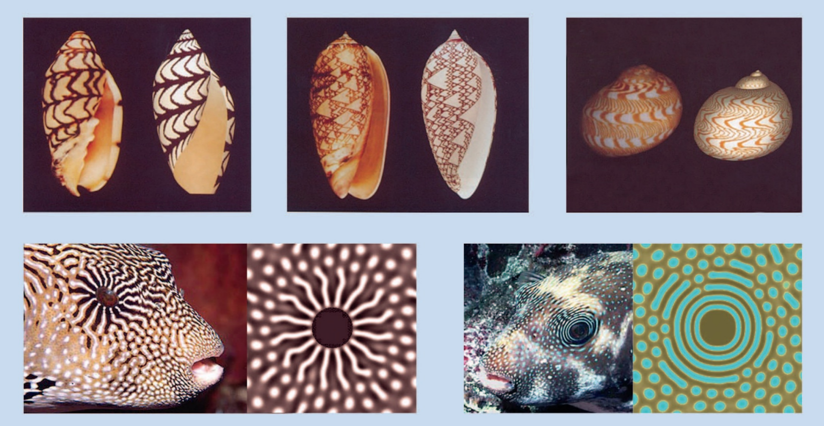
- Myosin: Molecular Motor

1. Huxley, H.E. & Hanson, J. (1954) Changes in the cross-striationsof muscle during contraction and stretch and their structural interpretation. Nature 173, 973-976

2. Huxley, A.F. & Niedergerke, R. (1954) Structural changes inmuscle during contraction. Interference microscopy of living muscle fibres. Nature 173, 971-973.

Reaction-Diffusion: Pattern formation

- Belousov-Zhabotinskii Reaction, Gray-Scott model ....
- Kondo, S. and Miura, T., 2010. Reaction-diffusion model as a framework for understanding biological pattern formation. science, 329(5999), pp.1616-1620.



Energetic Variational Approaches (EnVarA) in Mechanics

- Energy-dissipation law (from first and second law of thermodynamics):

$$\frac{\mathrm{d}}{\mathrm{d}\,t}E^{total} = \frac{\mathrm{d}}{\mathrm{d}\,t}(\mathcal{K} + \underbrace{\mathcal{U} - T\mathcal{S}}_{\mathcal{F}\text{ for isothermal cases}}) = \dot{W} - \triangle$$

- Least Action Principle $\mathcal{A}(\mathbf{x}) = \int_0^T \mathcal{K} - \mathcal{F}\,\mathrm{d}\,t$:

$$\delta\mathcal{A}(\mathbf{x}) = \int_0^T \int_\Omega (\text{force}_{\text{inertial}} - \text{force}_{\text{cons}}) \cdot \delta\,\mathbf{x}\,\mathrm{d}\,\mathbf{x}\,\mathrm{d}\,t$$

- Maximum Dissipation Principle (for linear response region):

$$\delta\mathcal{D}(\mathbf{x}_t) = \int_\Omega \text{force}_{\text{diss}} \cdot \delta\,\mathbf{x}_t\,\mathrm{d}\,\mathbf{x}$$

- Force balance $\text{force}_{inertial} = \text{force}_{\text{cons}} + \text{force}_{\text{diss}}$:

$$\frac{\delta\mathcal{A}}{\delta\,\mathbf{x}} = \frac{\delta\mathcal{D}}{\delta\,\mathbf{x}_t}$$

1. Lars Onsager. Reciprocal relations in irreversible processes. i/ii, Physical review, 1931.
2. J W Strutt (L Rayleigh). Some general theorems relating to vibrations. Proceedings of the London Mathematical Society, 1(1):357-368, 1871.

How about reactive/active fluids?

- Couples chemical reaction with various mechanical process (diffusion, electric field, elasticity ....).
- Quantify energy convection and temperature (thermal) effects.
- Goal:

> Incorporate chemical reaction kinetics, the law of mass action (LMA) into the framework of EnVarA.

Chemical reactions: reactants and products

- Chemical Reactions in physics, chemistry, biology and even social science: Transform one set of species (reactants) to another (products).
- Types of chemical reaction:
  - Synthesis reaction (combination reaction): $A + B \to AB$

$$8F_8 + S_8 \to 8F_eS$$

  - Decomposition reaction: $AB \to A + B$.
  - Single replacement reaction: $A + BC \to AC + B$.

$$Z_n + 2HCl \to Z_nCl_2 + H_2$$

  - Double replacement reaction: $AB + CD \to AD + CB$.

$$\text{Acid-based reaction : } HB_r + N_aOH \to N_aB_r + H_2O$$

$$\text{Hydrolysis reaction: with water } H_2O$$

- Examples: SIR model; BASS model; Battery; Electron transport chain in Mitochondrion; Force generation in Muscle Contraction; Tumor growth, Polymer breakage and reformation in wormlike micellar;...

Kinetics of chemical reaction

A single chemical reaction: $\alpha \mathrm{A} + \beta \mathrm{B} \underset{\mathrm{k}_2}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \gamma \mathrm{C}$

- The conservation of matter (Intrinsic kinematic constraints):

$$\gamma[A] + \alpha[C] = Constant$$
$$\gamma[B] + \beta[C] = Constant$$

- Rate models:

$$\frac{\mathrm{d}[A]}{\mathrm{d}\,t} = -\alpha r([A],[B],[C]),$$
$$\frac{\mathrm{d}[B]}{\mathrm{d}\,t} = -\beta r([A],[B],[C]),$$
$$\frac{\mathrm{d}[C]}{\mathrm{d}\,t} = \quad \gamma r([A],[B],[C]).$$

- Q: How to find $r([A],[B],[C])$?

Keener J P, Sneyd J. Mathematical physiology. New York: Springer, 1998.

Rate model: the Law of Mass Action (LMA)

- the Law of mass action (LMA)

$$r([A],[B],[C]) = k_1[A]^\alpha[B]^\beta - k_2[C]^\gamma$$

- At an equilibrium:

$$K_{eq} \triangleq \frac{k_2}{k_1} = \frac{a^\alpha b^\beta}{c^\gamma},$$

  where (a, b, c) is an equilibrium.

- LMA is an equilibrium treatment of chemical reactions. K_{eq}, k_1 and k_2 are influenced by interactions between chemical reaction and other effects of the system, such as the presence of enzyme, as well as diffusion and drift in an electric field.

Questions and Objectives

- Various derivations/reasoning of the LMA.
- Underlying principles and relations to Thermodynamics and consistency to other principles.
- Coupling and competition with other effects: Chemomechanical and mechanochemical systems.
- Temperature effects.

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- Various derivations/reasoning of the LMA.
- Underlying principles and relations to Thermodynamics and consistency to other principles.
- Coupling and competition with other effects: Chemomechanical and mechanochemical systems.
- Temperature effects.
- Energetic Variational Approaches.
  - Multiple scales, multiple physics/principles coupling and competitions.

(with Yiwei Wang, Pei Liu, and Bob Eisenberg) Field Theory of Reaction-Diffusion: Mass Action with an Energetic Variational Approach Physical Review E, 102, 062147 (2020).

Lyapunov functional (free energy)

Consider $\alpha\mathrm{A} + \beta\mathrm{B} \underset{\mathrm{k}_2}{\overset{\mathrm{k}_1}{\rightleftharpoons}} \gamma\mathrm{C}$ (take RT $= 1$ for simplicity)

- The Lyapunov function (free energy) [Wei, 1962, Shear, 1967, Mielke, 2011, van der Schaft et al., 2013]:

$$\mathcal{F} = \sum_{i=1}^{3} c_i \left(\ln(c_i/c_i^{\infty}) - 1\right)$$

  - c_i^{∞}: activity constant, internal energy.

- Energy dissipation with LMA ($r = k_1 c_1^{\alpha} c_2^{\beta} - k_2 c_3^{\gamma}$) :

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\mathcal{F} = \sum_{i=1}^{3}(\ln c_i - \ln c_i^{\infty})\frac{\mathrm{d}\,c_i}{\mathrm{d}\,t}$$

$$= -r\ln\left(\frac{c_1^{\alpha}c_2^{\beta}}{c_3^{\gamma}}\frac{(c_3^{\infty})^{\gamma}}{(c_1^{\infty})^{\alpha}(c_2^{\infty})^{\beta}}\right) = -k_2 c_3^{\gamma}(Q-1)\ln Q \leq 0,$$

where

$$Q = \frac{c_1^{\alpha}c_2^{\beta}}{c_3^{\gamma}}\frac{(c_3^{\infty})^{\gamma}}{(c_1^{\infty})^{\alpha}(c_2^{\infty})^{\beta}} = \frac{r}{k_2 c_3^{\gamma}} + 1.$$

Lyapunov functional (free energy)

- Thermodynamics argument [Mielke et al., 2017]

$$\mathcal{F} = \underbrace{\sum_{i=1}^{3} c_i(\ln c_i - 1)}_{\text{Entropy}} + \underbrace{\sum_{i=1}^{3} c_i U_i}_{\text{internal energy}}$$

- K_{eq} is determined by the choice of energy

$$K_{eq} = \frac{(c_1^\infty)^\alpha (c_2^\infty)^\beta}{(c_3^\infty)^\gamma} = \exp(-\underbrace{(\alpha U_1 + \beta U_2 - \gamma U_3)}_{\triangle U}),$$

where $\mu_i = \frac{\delta \mathcal{F}}{\delta c_i} = \ln c_i - \ln c_i^\infty = \ln c_i + U_i$.

  - Arrhenius Law (1889), van't Hoff Law (1884) ....
  - Transition State Theory (TST).

Energy-dissipation law

- Reaction Presentation: $R(t)$ (reaction trajectory [Oster and Perelson, 1974])
- Kinematics (stoichiometric mapping) $\alpha \mathrm{A} + \beta \mathrm{B} \rightleftharpoons \gamma \mathrm{C}$

$$c_i(t) = c_i(0) + \sigma_i R(t), \quad \partial_t R = r$$

where $\boldsymbol{\sigma} = (-\alpha, -\beta, \gamma)$ is the stoichiometric vector.

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$$\frac{\mathrm{d}}{\mathrm{d}\, t} \mathcal{F}(R) = -2\mathcal{D}(\partial_t R, R).$$

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- Generalized energetic variational approach ($\mathcal{D}(\partial_t R, R)$ may be not quadratic in $\partial_t R$):

$$\left(\frac{\delta \mathcal{F}}{\delta R}, R_t\right) = -(\Gamma(R, \partial_t R), \partial_t R) \Rightarrow \Gamma(R, \partial_t R) = -\frac{\delta \mathcal{F}}{\delta R}.$$

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- The reaction rate r is uniquely determined by the independent choice of the dissipation.

Chemical affinity

For the chemical reaction $\alpha \mathrm{A} + \beta \mathrm{B} \rightleftharpoons \gamma \mathrm{C}$

- The Thermodynamic **force** for chemical reactions: *Affinity*

$$\mathcal{A} = -\alpha\mu_A - \beta\mu_B + \gamma\mu_C$$

  as introduced by De Donder [De Donder, 1927]

- The variational of free energy with respect to R results in the chemical affinity $\dfrac{\delta \mathcal{F}}{\delta R} = \mathcal{A}$ (R is the internal variable in [Coleman and Gurtin, 1967])
- Reaction **velocity** (rate of conversion): R_t
- Chemical equilibrium [Kondepudi and Prigogine, 2014]: A $= 0$ and $R_t = 0$ $\Rightarrow$ A $= 0$ when $R_t = 0$
- The choice of dissipation gives relation between R_t and A, which can be written in terms of affinity (as in [Mielke, 2011]) or reaction velocity

Dissipation: LMA

- $\mathcal{D} = \eta_1(R) R_t \ln(\eta_2(R) R_t + 1)$:

$$\eta_1(R) \ln(\eta_2(R)\partial_t R + 1) = -\frac{\partial \mathcal{F}}{\partial R}.$$

- For $\eta_1(R) = 1$ and $\eta_2(R) = \frac{1}{k_2 c_3^\gamma}$:

$$\ln\left(\frac{R_t}{k_2 c_3^\gamma} + 1\right) = \ln\left(\frac{c_1^\alpha c_2^\beta}{c_3^\gamma}\right) - \triangle U$$

- Since $K_{eq} = k_2/k_1$,

$$r = k_1 c_1^\alpha c_2^\beta - k_2 c_3^\gamma$$

we recover the law of mass action (LMA).

Dissipation: linear respons (Onsager)

- Linear Response Approximation : $\mathcal{D} = \eta(R)|\partial_t R|^2$:

$$\eta(R)\partial_t R = -\frac{\partial \mathcal{F}}{\partial R},$$

By $\eta(R) = 1$, we have

$$r = \left(\sum_{i=1}^{3} \sigma_i \ln(c_i) - \ln K_{eq} \right), \quad \boldsymbol{\sigma} = (-\alpha, -\beta, \gamma)$$

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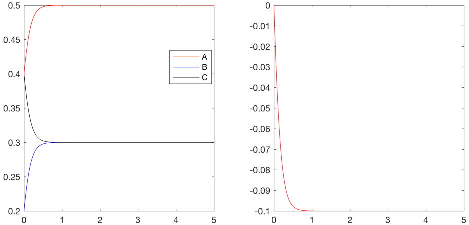
"Linear response approximation" is only valid close to equilibrium, i.e., the late stage of chemical reaction [de Groot and Mazur, 1984].

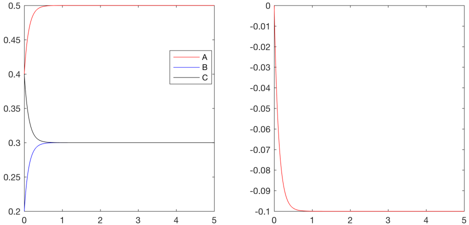
$$\boxed{R_t \ln(R_t + 1) \approx R_t^2 \text{ for } R_t \approx 0}$$

- Reversibility, Detailed Balance.
- Allen-Cahn type of systems, Cahn-Hillard-Allen-Cahn system.
- Tumor models, Keller-Segel chemotaxis ......

How to distinguish different choices of dissipation ?



Law of Mass Action



Linear Response Approximation

- Equilibrium setting cannot distinguish LMA and linear response approximation.
- A non-equilibrium setting: reaction-diffusion with sources.

General cases: multiple reactions

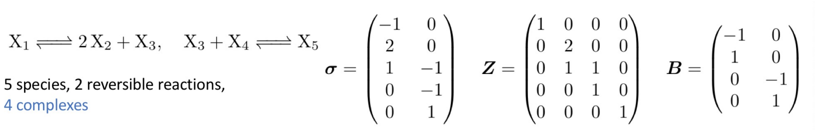
- N species and M **reversible** reactions

$$\alpha_{l1}X_1 + \alpha_{l2}X_2 + \dots \alpha_{lN}X_N \underset{k_-^l}{\overset{k_+^l}{\rightleftharpoons}} \beta_{l1}X_1 + \beta_{l2}X_2 + \dots \beta_{lN}X_N,$$

  for $l = 1, \dots, M$.
- Kinematics:

$$\boldsymbol{c}(t) = \boldsymbol{c}_0 + \boldsymbol{\sigma}\boldsymbol{R}(t),$$

  - $\boldsymbol{\sigma} \in \mathbb{R}^{N\times M}$ stoichiometry matrix ($\sigma_{li} = \beta_{li} - \alpha_{li}$)
  - $N - rank(\boldsymbol{\sigma})$ conserved quantities.
  - $\boldsymbol{R}(t) = (R_1(t), R_2(t), \dots, R_M(t))$, M reaction trajectories.
  - $\boldsymbol{\sigma} = \mathbf{ZB}$, where $\mathbf{Z}$ is the complex stoichiometric matrix, and $\mathbf{B}$ is the incidence matrix [van der Schaft et al., 2013].



$$\mathrm{X}_1 \rightleftharpoons 2\,\mathrm{X}_2 + \mathrm{X}_3, \quad \mathrm{X}_3 + \mathrm{X}_4 \rightleftharpoons \mathrm{X}_5$$

5 species, 2 reversible reactions,
4 complexes

$$\boldsymbol{\sigma} = \begin{pmatrix} -1 & 0 \\ 2 & 0 \\ 1 & -1 \\ 0 & -1 \\ 0 & 1 \end{pmatrix} \quad \boldsymbol{Z} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \boldsymbol{B} = \begin{pmatrix} -1 & 0 \\ 1 & 0 \\ 0 & -1 \\ 0 & 1 \end{pmatrix}$$

General cases: multiple reactions

- Energy-dissipation Law:

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\mathcal{F} = -\mathcal{D}(\partial_t \boldsymbol{R}(t), \boldsymbol{R}(t)),$$

  where

$$\mathcal{F} = \int \sum_{i=1}^{N} c_i(\ln c_i - 1) + c_i U_i \,\mathrm{d}\,\mathbf{x}$$

$$\mathcal{D} = \int \sum_{l=1}^{M} \partial_t R_l \ln\left(\frac{\partial_t R_l}{\eta_l(\boldsymbol{c}(\boldsymbol{R}))} + 1\right) \mathrm{d}\,\mathbf{x}$$

- Governing Equations:

$$\ln\left(\frac{\partial_t R_l}{\eta_l(\boldsymbol{c}(\boldsymbol{R}))} + 1\right) = -\frac{\delta \mathcal{F}}{\delta R_l}$$

- Applications: Michaelis-Menten Kinetics [Oster and Perelson, 1974], Gray-Scott Reaction Diffusion [Pearson, 1993] .....

Reactive Fluids: a Reaction-Diffusion System

- Coupling between diffusion (mechanics) and chemical reactions.
- Kinematic:

$$\underbrace{\partial_t c_i(\mathbf{x},t) + \nabla \cdot (c_i\, \mathbf{u}_i)}_{\text{Diffusion}} = \underbrace{\sigma_i R_t(\mathbf{x},t)}_{\text{Reaction}},$$

- Free Energy:

$$\mathcal{F}[\boldsymbol{c}] = \sum_{i=1}^{3} \int_\Omega c_i(\ln c_i - 1) + c_i U_i \,\mathrm{d}\,\mathbf{x}$$

- Dissipation:

$$2\mathcal{D} = \int \underbrace{\textstyle\sum_{i=1}^{3} c_i |\, \mathbf{u}_i\,|^2}_{\text{Diffusion}} + \underbrace{\Gamma(R, R_t)}_{\text{Reaction}} \,\mathrm{d}\,\mathbf{x}$$

- Energy-dissipation law: $\frac{\mathrm{d}}{\mathrm{d}\,t}\mathcal{F} = -2\mathcal{D}$

Reactive Fluids: Reaction-Diffusion

- Notice (corresponding to $\mathrm{d}\,F = -p\,\mathrm{d}\,V + \mu\,\mathrm{d}\,N$)

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\mathcal{F} = \sum_{i=1}^{3}(\frac{\delta \mathcal{F}}{\delta c_i}, \partial_t c_i) = \sum_{i=1}^{3}(c_i \nabla \mu_i, \mathbf{u}_i) + (\sum_{i=1}^{3} \sigma_i \mu_i, R_t)$$

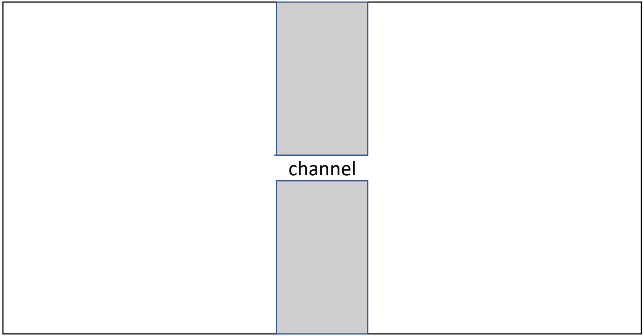
- Governing equation:

$$\begin{cases} c_i\,\mathbf{u}_i = -c_i \nabla \mu_i, & \text{(Diffusion)} \\ \frac{1}{R_t}\Gamma(R, R_t) = -\sum_{i=1}^{3} \sigma_i \mu_i, & \text{(Reaction)} \end{cases}$$

- Reaction-Diffusion system: $\partial_t c_i = \Delta c_i + \sigma_i R_t$
- Operator splitting sheme based on energy-dissipation law.

1. Matthias Liero, and Alexander Mielke. "Gradient structures and geodesic convexity for reaction-diffusion systems." Philos. Trans. Royal Soc. A 371.2005 (2013): 20120346.
2. Chun Liu, Cheng Wang and Yiwei Wang, A Structure-preserving, Operator Splitting Scheme for Reaction-Diffusion Equations Involving the Law of Mass Action, arXiv:2010.16320

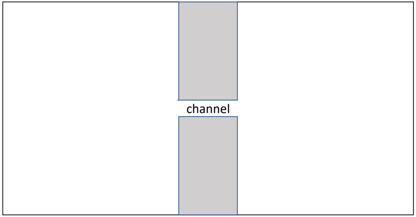
A non-equilibrium setting: a model system



- Consider reaction-diffusion inside the channel $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}$
- Source from the left bath (Dirichlet BC of c_A and c_B)
- Measure the flux of C into the right bath.
- Abstract representation of one component of a complex biological networks.

Yiwei Wang, Chun Liu, Pei Liu, and Bob Eisenberg. "Field theory of reaction-diffusion: Mass action with an energetic variational approach." Phys. Rev. E, arXiv:2001.10149 (2020).

Apply to the model system

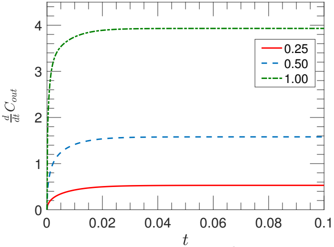


- Channel $(-\epsilon, \epsilon)$
- Boundary condition:

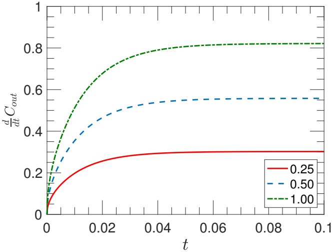
$$\begin{cases} c_A(-\epsilon,t)=c_0, \quad \partial_x c_A(\epsilon,t)=0, \\ c_B(-\epsilon,t)=c_0, \quad \partial_x c_B(\epsilon,t)=0, \\ \partial_x c_C(-\epsilon,t)=0, \quad c_C(\epsilon,t)=0.1, \end{cases}$$

- c_0 is the input
- Output: Accumulated flux of C

$\mathcal{D} = R_t \ln(R_t+1)$

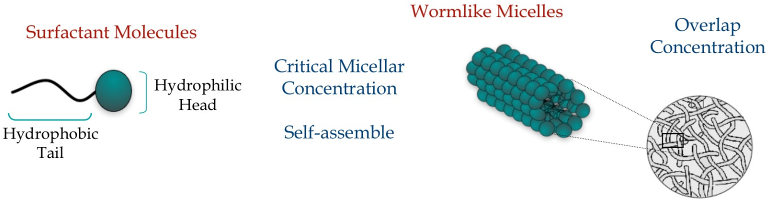


$\mathcal{D} = |R_t|^2$



Wormlike micellar solutions

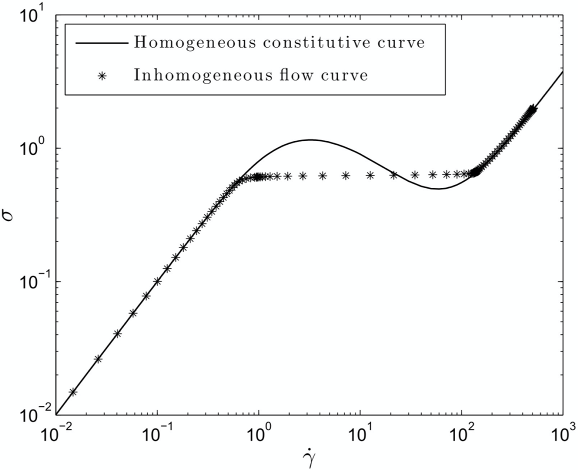
- Wormlike micelles, also known as living polymers, are long, cylindrical aggregates of self-assembled surfactants that dynamically break and recombine [Cates, 1987].



- Applications: Household and cosmetic products / Oil industry (fracturing fluids, EOR) / ...
- "Chemomechanical" system: couples chemical reactions with Viscoelastic effects.

Shear banding in steady shear flow

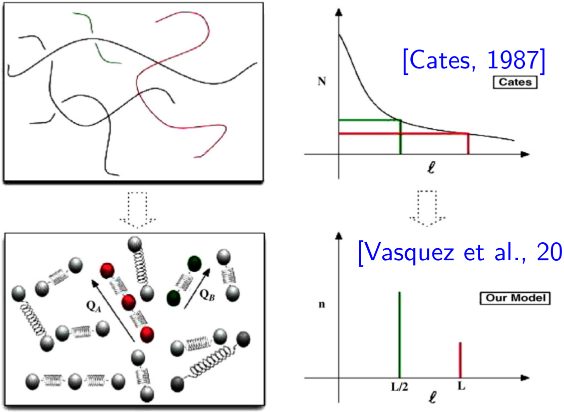
- The breaking and recombing procures lead to unusual rheological properties.
- Non-monotonic strain-stress curve in homogeneous shear flow.



Cromer, Michael, L. Pamela Cook, and Gareth H. McKinley. "Interfacial instability of pressure-driven channel flow for a two-species model of entangled wormlike micellar solutions." Journal of non-newtonian fluid mechanics 166.11 (2011): 566-577.

A Reactive Fluid

- Dynamically break and recombine [Cates, 1987, Vasquez et al., 2007, Germann et al., 2013].



[Cates, 1987]

[Vasquez et al., 2007]

Cates' model: continuous distribution of lengths $N(L)$

Vasquez-Cook-McKinley (VCM) model: two species model, breakable and deformable elastic segments

Thermodynamically consistent revision: Germann-Cook-Beris (GCB model) [Germann et al., 2013]

Cates' Model

- $c(L)$: number density of chains of arc-length L.
- A long chain can break at each position with an equal rate k_1, and arbitrary two chain can combine together with an equal rate k_2, and

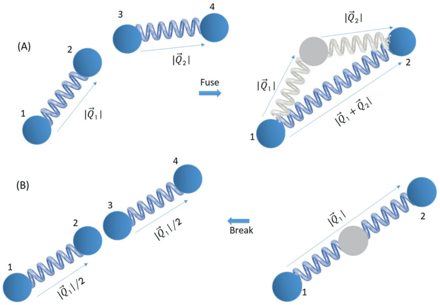
$$\begin{aligned}\dot{c}(L) = &-k_1 L c(L) - 2k_2 c(L)\int_0^\infty c(L')\,\mathrm{d}\,L' \\ &+ 2k_1\int_L^\infty c(L')\,\mathrm{d}\,L' + k_2\int_0^\infty c(L')c(L'')\delta(L'+L''-L)\,\mathrm{d}\,L'\,\mathrm{d}\,L'',\end{aligned}$$

- Chemical rection: $L + L' <=> L''$

Cates, M. E. "Reptation of living polymers: dynamics of entangled polymers in the presence of reversible chain-scission reactions."

Macromolecules 20.9 (1987): 2289-2296.

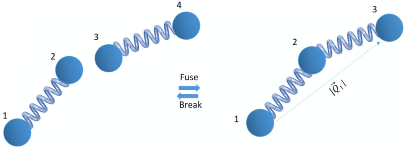
Reactions in VCM model



Adams, Abdulrazaq A., Michael J. Solomon, and Ronald G. Larson, Journal of Rheology 62, no. 6 (2018): 1419-1427.

- Break in the middle to give two short dumbbells
- Recombine short chains by adding end-to-end vector.
- Breaking/Reforming:
  $$-k_1\psi_A + k_2\psi_B * \psi_B$$
- Macroscopic $\left(n_\alpha = \int \psi_\alpha \, \mathrm{d}\,\mathbf{q},\ \mathbf{M}_\alpha = \int \mathbf{q}\otimes\mathbf{q}\,\psi_\alpha\,\mathrm{d}\,\mathbf{q}\right)$:
  $$-k_1 n_A + k_2 n_B^2$$
  $$-k_1\mathbf{M}_A + k_2 n_B \mathbf{M}_B$$
- Irreversible on microscopic.

Microscopic reversible reactions



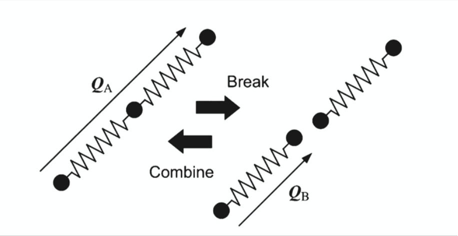
Adams, Abdulrazaq A., Michael J. Solomon, and Ronald G. Larson, Journal of Rheology 62, no. 6 (2018): 1419-1427.

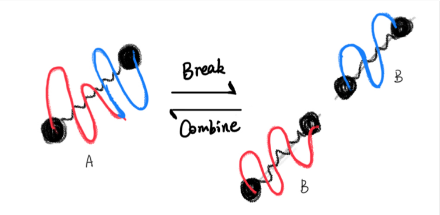
- Larger micellar (tribells) chains have two springs (three beads)
- Smaller micellar (dumbbells) chains have one spring (two beads)

$$\begin{cases} \frac{\mathrm{d}}{\mathrm{d}\,t}\psi(\mathbf{q}) = -\int R_t(\mathbf{q},\mathbf{q}';\mathbf{q}'')\,\mathrm{d}\,\mathbf{q}'\,\mathrm{d}\,\mathbf{q}'' - \int R_t(\mathbf{q}',\mathbf{q};\mathbf{q}'')\,\mathrm{d}\,\mathbf{q}'\,\mathrm{d}\,\mathbf{q}'' + \int R_t(\mathbf{q}',\mathbf{q}'';\mathbf{q})\,\mathrm{d}\,\mathbf{q}'\,\mathrm{d}\,\mathbf{q}'' \\ R_t(\mathbf{q},\mathbf{q}',\mathbf{q}'') = W^+(\mathbf{q},\mathbf{q}';\mathbf{q}'')\psi(\mathbf{q})\psi(\mathbf{q}') - W^-(\mathbf{q},\mathbf{q}';\mathbf{q}'')\psi(\mathbf{q}'') \quad \text{(LMA)} \end{cases}$$

- Existence of energy-dissipation law.
- Affinity at the equilibrium: $(\mu(\mathbf{q}'') - \mu(\mathbf{q}) - \mu(\mathbf{q}'))W(\mathbf{q},\mathbf{q}';\mathbf{q}'') = 0. \forall\, \mathbf{q},\mathbf{q}',\mathbf{q}'' \in \mathbb{R}^d$.
- Diffusion limit.

Microscopic reversible reactions (more simplification)





- $|Q_A| = |Q_B| = \mathbf{q}$
- LMA for fixed $\mathbf{q}$ and x:
  $-k_1\psi_A + k_2\psi_B^2$
- Reversible on microscopic
- Need a moment closure to get macroscopic equations.

A micro-macro model for micellar solution

- Two species A and B, which are breakable and deformable elastic segments
- ψ_α : number density at $\mathbf{x}$ with end-to-end verctor $\mathbf{q}$
- (LMA for given $\mathbf{x}$ and $\mathbf{q}$): A molecule at position $\mathbf{x}$ with end-to-end vector $\mathbf{q}$ can only break into two B molecules with same end-to-end vector, and the reforming can only happen between two B molecules at the same position $\mathbf{x}$ with the same end-to-end vector.
- Kinematic:

$$\begin{cases} \partial_t \psi_A + \nabla \cdot (\mathbf{u}_A \, \psi_A) + \nabla_{\mathbf{q}} \cdot (V_A \psi_A) = -R_t \\ \partial_t \psi_B + \nabla \cdot (\mathbf{u}_B \, \psi_B) + \nabla_{\mathbf{q}} \cdot (V_B \psi_B) = 2R_t, \end{cases}$$

  $\mathbf{u}_\alpha$: Microscopic velocity of specie α; $\mathbf{V}_\alpha$: microscopic velocity of species α; $R(\mathbf{q}, \mathbf{x}, t)$: reaction trajectory for given $\mathbf{x}$ and $\mathbf{q}$.

- $\mathbf{u}_A = \mathbf{u}_B = \mathbf{u}$, the velocity of the fluids.

(with Yiwei Wang and Teng-Fei Zhang) On a two species micro-macro model of worm- like micellar solutions: dynamic stability analysis (2021).

(with Yiwei Wang and Teng-Fei Zhang) A two species micro-macro model of wormlike micellar solutions and its maximum entropy closure approximations: An energetic vari- ational approach (2021).

New micro-macro model for micellar solution

- Free energy

$$E^{total} = \int_{\Omega} \frac{1}{2} |\,\mathbf{u}\,|^2 (\text{Kinetic energy}) \\ + \int_{\mathbb{R}^3} \psi_A \left(\ln \psi_A - 1 + U_A\right) + \psi_B \left(\ln \psi_B - 1 + U_B\right) \mathrm{d}\,\mathbf{q}\,\mathrm{d}\,\mathbf{x}$$

- Dissipation

$$2\mathcal{D} = -\int_{\Omega} \nu |\nabla\,\mathbf{u}\,|^2 + \int_{\mathbb{R}^d} \frac{1}{\xi_A} \psi_A |\boldsymbol{V}_A - \nabla\,\mathbf{u}\,\mathbf{q}\,|^2 + \frac{1}{\xi_B} \psi_B |\boldsymbol{V}_B - \nabla u\,\mathbf{q}\,|^2 \,\mathrm{d}\,\mathbf{q} \\ - \underbrace{\int_{\mathbb{R}^d} \partial_t \mathcal{R} \ln\left(\eta(R)\partial_t \mathcal{R} + 1\right) \mathrm{d}\,\mathbf{q}}_{\text{Reaction: break and reform}} \,\mathrm{d}\,\mathbf{x}$$

New micro-macro model for micellar solution

- Free energy

$$E^{total} = \int_{\Omega} \frac{1}{2}|\,\mathbf{u}\,|^2(\text{Kinetic energy})$$
$$+ \int_{\mathbb{R}^3} \psi_A\left(\ln\psi_A - 1 + U_A\right) + \psi_B\left(\ln\psi_B - 1 + U_B\right)\mathrm{d}\,\mathbf{q}\,\mathrm{d}\,\mathbf{x}$$

- Dissipation

$$2\mathcal{D} = -\int_{\Omega}\nu|\nabla\,\mathbf{u}\,|^2 + \int_{\mathbb{R}^d}\frac{1}{\xi_A}\psi_A|\boldsymbol{V}_A - \nabla\,\mathbf{u}\,\mathbf{q}\,|^2 + \frac{1}{\xi_B}\psi_B|\boldsymbol{V}_B - \nabla u\,\mathbf{q}\,|^2\,\mathrm{d}\,\mathbf{q}$$
$$\underbrace{-\int_{\mathbb{R}^d}\partial_t\mathcal{R}\ln\left(\eta(R)\partial_t\mathcal{R} + 1\right)\mathrm{d}\,\mathbf{q}}_{\text{Reaction: break and reform}}\,\mathrm{d}\,\mathbf{x}$$

- Equilibrium (Microscopic detailed balance for given $\mathbf{x}$ and $\mathbf{q}$):

$$K_{eq} = \frac{\psi_A^{\infty}}{(\psi_B^{\infty})^2}$$

New micro-macro model for micellar solution

- Governing equations be determined through EnVarA:

$$\begin{cases} \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p = \nu \Delta \mathbf{u} + \nabla \cdot \boldsymbol{\tau} \\ \nabla \cdot \mathbf{u} = 0 \\ \partial_t \psi_A + \mathbf{u} \cdot \nabla \psi_A + \nabla_q \cdot (\nabla \mathbf{u} \, \mathbf{q} \, \psi_A) - \xi_A \nabla_q \cdot (\nabla \psi_A + \nabla_q U_A \psi_A) = -\partial_t \mathcal{R} \\ \partial_t \psi_B + \mathbf{u} \cdot \nabla \psi_B + \nabla_q \cdot (\nabla \mathbf{u} \, \mathbf{q} \, \psi_B) - \xi_B \nabla_q \cdot (\nabla \psi_B + \nabla_q U_B \psi_B) = 2\partial_t \mathcal{R} \end{cases}$$

where $\boldsymbol{\tau}$ is the induced stress from the microscopic configurations

$$\boldsymbol{\tau} = \int (\nabla_q U_A \otimes \mathbf{q} \, \psi_A + \nabla_q U_B \otimes \mathbf{q} \, \psi_B) \, \mathrm{d} \mathbf{q} - (n_A + n_B) \mathrm{I}$$

and

$$\partial_t \mathcal{R} = k_1 \psi_A - k_2 \psi_B^2, \quad n_\alpha = \int \psi_\alpha \, \mathrm{d} \mathbf{q} (\alpha = A, B)$$

- Hookean spring:

$$U_A = \frac{1}{2} H_A |\mathbf{q}|^2, \quad U_B = \frac{1}{2} H_B |\mathbf{q}|^2$$

Wellposedness: global existence near the equilibrium (dynamic stability)

- The global equilibrium satisfies ($H_A = 2H_B$ [Germann et al., 2013]):

$$\begin{cases} M_A(q) = \frac{n_A^\infty}{Z_A} e^{-U_A}, \quad Z_A = \int e^{-U_A} \,\mathrm{d}\,\mathbf{q} \\ M_B(q) = \frac{n_B^\infty}{Z_B} e^{-U_B}, \quad Z_B = \int e^{-U_B} \,\mathrm{d}\,\mathbf{q} \\ \\ k_1 M_A - k_2 M_B^2 = 0, \text{detailed balance at the microscopic} \end{cases}$$

- Equilibrium constant: $K_{\text{eq}} = \frac{M_A}{M_B^2} = \frac{n_A^\infty Z_A}{(n_B^\infty)^2 Z_B} = \frac{k_2}{k_1}$ (Assume $K_{eq} = 1$ in proving the global existence near the equilibrium)
- Define the fluctuations of Ψ_A and Ψ_B around the global Maxwellian

$$\psi_A = M_A + \sqrt{M_A} f_A, \quad \psi_B = M_B + \sqrt{M_B} f_B$$

- Main difficulty:

$$\int \sqrt{M_\alpha} f_\alpha \,\mathrm{d}\,\mathbf{q} \neq 0, \quad \int 2\sqrt{M_A} f_A + \sqrt{M_B} f_B \,\mathrm{d}\,\mathbf{q} = 0.$$

Perturbative system

- Inserting the perturbation relations into the original system enables us to get the perturbative system.

$$\begin{cases} \partial_t f_A + \mathbf{u}\cdot\nabla f_A + \nabla\mathbf{u}\, q\nabla_q f_A = \boxed{\mathcal{L}_A f_A} + r_A + \nabla\mathbf{u}\,\mathbf{q}\,\nabla_{\mathbf{q}} U_A(\sqrt{M_A} + \frac{1}{2} f_A), \\ \partial_t f_B + \mathbf{u}\cdot\nabla f_B + \nabla\mathbf{u}\, q\nabla_q f_B = \boxed{\mathcal{L}_B f_B} + r_B + \nabla\mathbf{u}\,\mathbf{q}\,\nabla_{\mathbf{q}} U_B(\sqrt{M_B} + \frac{1}{2} f_B), \\ \partial_t\,\mathbf{u} + \mathbf{u}\cdot\nabla\,\mathbf{u} + \nabla p = \nu\Delta u + \nabla\cdot\int \mathbf{q}\otimes(\nabla_q U_A f_A\sqrt{M_A} + \nabla_q U_B f_B\sqrt{M_B})\underset{\cdot}{\mathsf{q}}, \\ \nabla\cdot\mathbf{u} = 0. \end{cases}$$

- Technical difficulties: How to deal with Fokker-Planck, Micro-Macro (kinetic-fluids) coupling, Reversible reactions, and close an *a-priori* estimates

Global existence near the equilibrium

Theorem (Global existence near the equilibrium)

Let $(\mathbf{u},\, f_A,\, f_B)$ be the fluctuation near the global equilibrium $(0,\, M_A,\, M_B)$ with their initial data $(u_0,\, f_{A,0},\, f_{B,0})$ satisfying

$$\psi_{\alpha,0} = M_\alpha + \sqrt{M_\alpha} f_{\alpha,0} > 0, \text{ and } \int (2\psi_A + \psi_B)|_{t=0} \,\mathrm{d}\, q = 1.$$

There exists some constant ϵ sufficiently small, such that,
if the initial fluctuation satisfies

$$\mathcal{E}_s(0) = |\,\mathbf{u}_0\,|^2_{H^s_x} + \|(f_{A,0},\, f_{B,0})\|^2_{H^s_{x,q}} + \|(\mathbf{q}\, f_{A,0},\, \mathbf{q}\, f_{B,0})\|^2_{H^{s-1}_x L^2_q} \le \epsilon,$$

$$\int_\Omega \tfrac{1}{2}|\,\mathbf{u}_0\,|^2 \,\mathrm{d}\, x + \iint_{\Omega\times\mathbb{R}^3} \textstyle\sum_{\alpha=A,\,B} (\psi_{\alpha,0} \ln \frac{\psi_{\alpha,0}}{M_\alpha} - \psi_{\alpha,0} + M_\alpha) \,\mathrm{d}\,\mathbf{q}\,\mathrm{d}\,\mathbf{x} \le \epsilon,$$

then the perturbative system admits **a unique global classical solution** $(\mathbf{u},\, \psi_A,\, \psi_B)$ with $\psi_\alpha = M_\alpha + \sqrt{M_\alpha} f_\alpha > 0$, and moreover,

$$\sup_{t\in[0,+\infty)} \mathcal{E}(t) + \int_0^{+\infty} \mathcal{D}(t) \,\mathrm{d}\, t \le C\epsilon.$$

Momentum closure system

- Momentum closure is needed due to the microscopic reaction
- Maxium Entropy Approximation [Hyon et al., 2008, Wang et al., 2008]: Approximate ψ_α based on n_α and $\mathbf{M}_\alpha$ (second momentum) by solving the constrained optimization problem

$$\psi_\alpha^* = \arg\min_{\mathcal{A}} \int_{\mathbb{R}^d} \psi \ln \psi + U_\alpha \psi \,\mathrm{d}\,\mathbf{q},$$

where $\mathcal{A} = \{\psi : \mathbb{R}^d \to \mathbb{R}, \psi \geq 0 \mid \int \psi \,\mathrm{d}\,\mathbf{q} = n_\alpha, \quad \int \psi(\mathbf{q} \otimes \mathbf{q}) \,\mathrm{d}\,\mathbf{q} = \mathbf{M}_\alpha\}$.

- Explicit form with $U_\alpha = \frac{1}{2} H_\alpha |\,\mathbf{q}\,|^2$
- Maximum enetropy manifolds:

$$\mathcal{M}^* = \left\{ \psi^* = \frac{n}{(2\pi)^{d/2} (\det \widetilde{\mathbf{M}})^{1/2}} \exp\left(-\frac{1}{2}\, \mathbf{q}^{\mathrm{T}}\, \widetilde{\mathbf{M}}^{-1}\, \mathbf{q} \right) \right\}$$

- Second moment: $\mathbf{M} = n\widetilde{\mathbf{M}}$ on $\mathcal{M}^*$

Maximum entropy closure: free energy

- Free energy (in term of ψ_A^* and ψ_B^*):

$$\mathcal{F}^{\mathrm{CL}} = \int\int \psi_A^* \left(\ln\left(\frac{\psi_A^*}{\psi_A^\infty}\right) - 1\right) + \psi_B^* \left(\ln\left(\frac{\psi_B^*}{\psi_B^\infty}\right) - 1\right) \mathrm{d}\,\mathbf{q}\,\mathrm{d}\,\mathbf{x}$$

- Free energy (in terms $n_A, n_B, \mathbf{A}, \mathbf{B}$):

$$\begin{aligned}\mathcal{F}^{\mathrm{CL}}(n_A, n_B, \mathbf{A}, \mathbf{B}) = \int & n_A \left(\ln\left(\frac{n_A}{n_A^\infty}\right) - 1\right) + n_B \left(\ln\left(\frac{n_B}{n_B^\infty}\right) - 1\right) \\ & - \frac{n_A}{2} \ln\det\left(\frac{H_A \mathbf{A}}{n_A}\right) + \frac{1}{2}\operatorname{tr}(H_A \mathbf{A} - n_A \mathbf{I}) \\ & - \frac{n_B}{2} \ln\det\left(\frac{H_B \mathbf{B}}{n_B}\right) + \frac{1}{2}\operatorname{tr}(H_B \mathbf{B} - n_B \mathbf{I}))\ \mathrm{d}\,\mathbf{x},\end{aligned}$$

Hu, Dan, and Tony Lelievre. "New entropy estimates for the Oldroyd-B model and related models." Communications in Mathematical Sciences 5.4 (2007): 909-916.

Maximum entropy closure: variation-then-closure

- Variation-then-closure:

$$\begin{cases} \rho(\partial_t \mathbf{u} + (\mathbf{u}\cdot\nabla)\mathbf{u}) + \nabla p = \eta\Delta\mathbf{u} + \lambda\nabla\cdot(H_A\mathbf{A} + H_B\mathbf{B} - (n_A + n_B)\mathbf{I}) \\ \nabla\cdot\mathbf{u} = 0 \\ \partial_t n_A + \nabla\cdot(n_A\mathbf{u}) = -k_1 n_A + \widetilde{k}_2(\mathbf{B})n_B^2, \\ \partial_t n_B + \nabla\cdot(n_B\mathbf{u}) = 2k_1 n_A - 2\widetilde{k}_2(\mathbf{B})n_B^2, \\ \partial_t\mathbf{A} + (\mathbf{u}\cdot\nabla)\mathbf{A} - (\nabla\mathbf{u})\mathbf{A} - \mathbf{A}(\nabla\mathbf{u})^{\mathrm{T}} = 2\xi_A(n_A\mathbf{I} - H_A\mathbf{A}) - k_1\mathbf{A} + \frac{1}{2}\widetilde{k}_2(\mathbf{B})n_B\mathbf{B} \\ \partial_t\mathbf{B} + (\mathbf{u}\cdot\nabla)\mathbf{B} - (\nabla\mathbf{u})\mathbf{B} - \mathbf{B}(\nabla\mathbf{u})^{\mathrm{T}} = 2\xi_B(n_B\mathbf{I} - H_B\mathbf{B}) + 2k_1\mathbf{A} - \widetilde{k}_2(\mathbf{B})n_B\mathbf{B}. \end{cases}$$

- Macroscopic reaction rate after closure: $\widetilde{k}_2(\mathbf{B}) = \frac{n_B^{d/2}}{2^d(\pi)^{d/2}(\det(\mathbf{B}))^{1/2}}k_2$
- Dissipation:

$$\begin{aligned} \triangle^{\mathrm{CL}} = \int & \xi_A \operatorname{tr}\left((H_A\mathbf{I} - n_A\mathbf{A}^{-1})^2\mathbf{A}\right) + \xi_B \operatorname{tr}\left((H_B\mathbf{I} - n_B\mathbf{B}^{-1})^2\mathbf{B}\right) \\ & + (k_1 n_A - \widetilde{k}_2(\mathbf{B})n_B^2)\left(\ln\left(\frac{n_A}{n_A^\infty}\right) - 2\ln\left(\frac{n_B}{n_B^\infty}\right) + \ln\frac{\det(H_B\mathbf{B}/n_B)}{\sqrt{\det(H_A\mathbf{A}/n_A)}}\right) \\ & + \operatorname{tr}\left((k_1\mathbf{A} - \frac{1}{2}\widetilde{k}_2(\mathbf{B})n_B\mathbf{B})(n_B\mathbf{B}^{-1} - \frac{1}{2}n_A\mathbf{A}^{-1})\right)\mathrm{d}\,\mathbf{x}\,. \end{aligned}$$

- The dynamics not necessary lie on $\mathcal{M}^*$: no explicit equations of $\widetilde{A}$ and $\widetilde{B}$.

Maxium entropy closure: closure-then-variation

- Closure-then-variation: a dissipation on $\mathcal{M}^*$

$$\widetilde{\triangle}^* = \int \eta|\nabla \mathbf{u}|^2 + \mathrm{tr}\left(\mathsf{M}_A\left(\frac{\mathrm{d}\widetilde{\mathbf{A}}}{\mathrm{d}t}\right)^2\right) + \mathrm{tr}\left(\mathsf{M}_B\left(\frac{\mathrm{d}\widetilde{\mathbf{B}}}{\mathrm{d}t}\right)^2\right)\,\mathrm{d}\mathbf{x} + \widetilde{D}_{\mathrm{chem}}$$

- Kinematics for n_α: $\partial_t n_\alpha + \nabla \cdot (n_\alpha \mathbf{u}) = \sigma_\alpha R^n$ $(\sigma_A = -1, \sigma_B = 2)$.
- Chemical potential of A and B:

$$\mu_A^n = \ln n_A - \ln n_A^\infty - \frac{1}{2}\ln\left(\det\left(H_A\widetilde{\mathbf{A}}\right)\right) + \frac{1}{2}\,\mathrm{tr}\left(H_A\widetilde{\mathbf{A}} - \mathbf{I}\right),$$
$$\mu_B^n = \ln n_B - \ln n_B^\infty - \frac{1}{2}\ln\left(\det\left(H_B\widetilde{\mathbf{B}}\right)\right) + \frac{1}{2}\,\mathrm{tr}\left(H_B\widetilde{\mathbf{B}} - \mathbf{I}\right),$$

- Taking $\widetilde{D}_{\mathrm{chem}}(R^n, \partial_t R^n) = \partial_t R^n \ln\left(\frac{\partial_t R^n}{\eta_n(R^n)} + 1\right)$ with $\eta_n(\mathcal{R}^n) = \widetilde{k}_2 \exp(\mathrm{tr}(\boldsymbol{\tau}_B)/n_B)/\det(H_B\widetilde{\mathbf{B}})n_B^2$ leads nonequilibrium reaction rate

$$k_1^{\mathrm{neq}} = k_1^{eq}\frac{\exp(\frac{1}{2}\,\mathrm{tr}(\boldsymbol{\tau}_A/n_A))}{\sqrt{\det(H_A\widetilde{\mathbf{A}})}}, \quad k_2^{\mathrm{neq}} = \widetilde{k}_2^{eq}\frac{\exp(\mathrm{tr}(\boldsymbol{\tau}_B/n_B))}{\det(H_B\widetilde{\mathbf{B}})}.$$

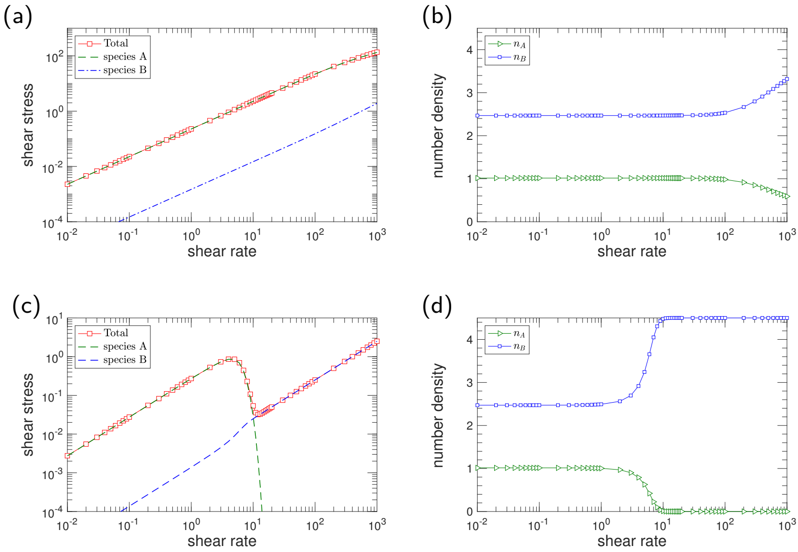
Maxium entropy closure: closure-then-variation

- Dynamics on $\mathcal{M}^*$:

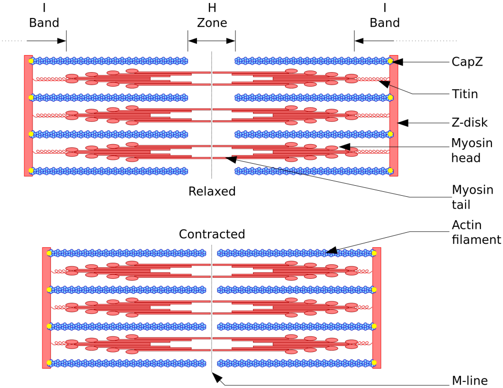
$$\begin{cases} \rho(\partial_t \mathbf{u} + (\mathbf{u}\cdot\nabla)\mathbf{u}) + \nabla p = \eta\Delta\mathbf{u} + \lambda\nabla\cdot\Big(H_A(n_A\widetilde{\mathbf{A}}) + H_B(n_B\widetilde{\mathbf{B}}) - (n_A+n_B)\mathbf{I}\Big) \\ \nabla\cdot\mathbf{u} = 0 \\ \partial_t n_A + \nabla\cdot(n_A\,\mathbf{u}) = -k_1^{\mathrm{neq}} n_A + k_2^{\mathrm{neq}} n_B^2, \\ \partial_t n_B + \nabla\cdot(n_B\,\mathbf{u}) = 2k_1^{\mathrm{neq}} n_A - 2k_2^{\mathrm{neq}} n_B^2, \\ \partial_t\widetilde{\mathbf{A}} + (\mathbf{u}\cdot\nabla)\widetilde{\mathbf{A}} - (\nabla\mathbf{u})\widetilde{\mathbf{A}} - \widetilde{\mathbf{A}}(\nabla\mathbf{u})^{\mathrm{T}} = 2\xi_A(\mathbf{I} - H_A\widetilde{\mathbf{A}}) \\ \partial_t\widetilde{\mathbf{B}} + (\mathbf{u}\cdot\nabla)\widetilde{\mathbf{B}} - (\nabla\mathbf{u})\widetilde{\mathbf{B}} - \widetilde{\mathbf{B}}(\nabla\mathbf{u})^{\mathrm{T}} = 2\xi_B(\mathbf{I} - H_B\widetilde{\mathbf{B}}), \end{cases}$$

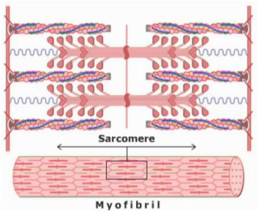
- Reactions are only on number densities.
- Second moment: $\mathbf{A} = n_A\widetilde{A}$ and $\mathbf{B} = n_B\widetilde{B}$
- Active stress due to the reaction on the number density $(n_\alpha = n_\alpha^0 + n_\alpha^{\mathrm{active}})$

Numerics: Homogeneous shear flows



Muscle Again





- Transduction of chemical energy, derived from ATP hydrolysis, into mechanical work. [Duke, 1999]
- Myosin: Molecular Motor

1. Huxley, H.E. & Hanson, J. (1954) Changes in the cross-striationsof muscle during contraction and stretch and their structural interpretation. Nature 173, 973-976

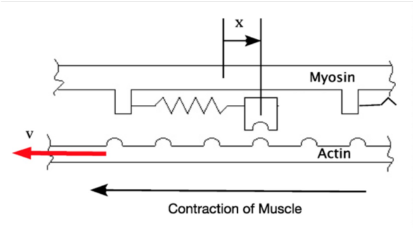
2. Huxley, A.F. & Niedergerke, R. (1954) Structural changes inmuscle during contraction. Interference microscopy of living muscle fibres. Nature 173, 971-973.

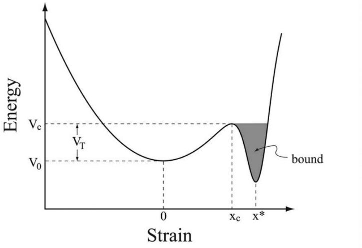
Huxley-type molecular model

- Physiological model / Half-Sarcomere model
- Assume a large number of contraction sites all with the binding site in the same position relative position
- $n(x,t)$: fraction of cross-bridges with length x is attached

$$\frac{\partial n}{\partial t} + v\frac{\partial n}{\partial x} = (1 - n(x))f(x) - g(x)$$

- Strain-dependent chemical reaction rate

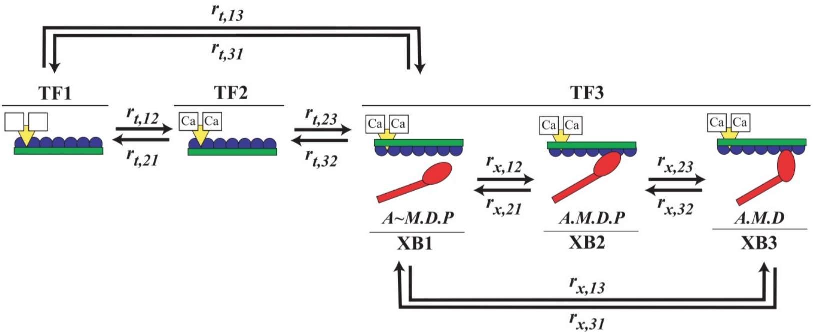




Huxley, A.F., Muscle structure and theories of contraction[J]. Progress in biophysics and biophysical chemistry, 1957, 7: 255.

More details: ATP driven cross-bridge cycle

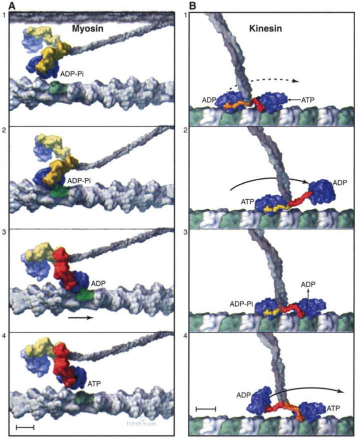
Kinetic Scheme: coupled, three-state cycles for thin-filament activation and cross-bridge formation [Tanner et al., 2007].

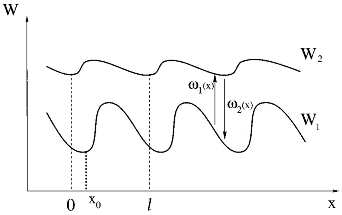


$$\mathrm{A} + \mathrm{M} + \mathrm{ATP} \longrightarrow \mathrm{A} + \mathrm{M} + \mathrm{ADP} + \mathrm{Pi} + \mathrm{Force}$$

(Pi stands for an inorganic phosphate group ${\rm PO_4}^{3-}$)

Variational modeling for molecular motors





Frank Julicher, Armand Ajdari, and Jacques Prost, Rev. Mod. Phys. 69, 1269, 1997

$$\begin{cases} \partial_t p_1 + \nabla(\nabla p_1 + \nabla W_1 p_1) = -w_1 p_1 + w_2 p_2 \\ \partial_t p_2 + \nabla(\nabla p_2 + \nabla W_2 p_2) = w_1 p_1 - w_2 p_2 \end{cases}$$

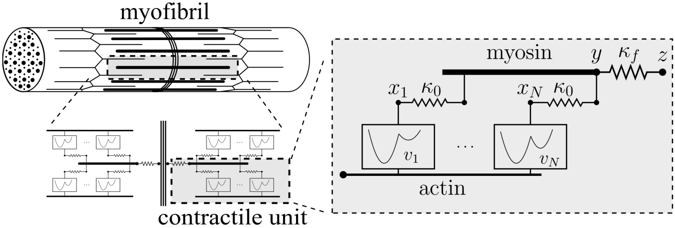
Michel Chipot, David Kinderlehrer and Michal Kowalczyk, A Variational Principle for Molecular Motors, Meccanica 38, 505–518 (2003).

Mechanochemical model for muscle contraction

- Proposed model:

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\int\left[\frac{1}{2}\rho|\,\mathbf{u}\,|^2+\frac{1}{\det\widetilde{\mathsf{F}}}W(\widetilde{\mathsf{F}},f)+\int\sum_i\psi_i\ln\psi_i+\psi_iU_i\,\mathrm{d}\,\xi\right]\mathrm{d}\,\mathbf{x}$$

$$=-\int\eta|\,\mathbf{u}\,|^2+\int\sum_i\psi_i|\,\mathbf{u}-\boldsymbol{V}_i|^2+\Gamma(\boldsymbol{R},\partial_t\boldsymbol{R})\,\mathrm{d}\,\xi\,\mathrm{d}\,\mathbf{x}$$



Hudson Borja da Rocha and Lev Truskinovsky Phys. Rev. Lett. 122, 088103, 2019

Conclusion

- We extend the energetic variational approach to include chemical reactions with Law of Mass Action, which enable us to couple LMA with various other mechanisms, including mechanical effects such as diffusion, drift in an electric field, as well as the thermal effects.

Conclusion

- We extend the energetic variational approach to include chemical reactions with Law of Mass Action, which enable us to couple LMA with various other mechanisms, including mechanical effects such as diffusion, drift in an electric field, as well as the thermal effects.
- Ongoing and future work:
  - Extend to non-isothermal system (with Jan-Eric Sulzbach) Well-Posedness for the Reaction-Diffusion Equation with Temperature in a Critical Besov Space (2021).
  - Micro-Macro model with law of mass action for micellar solutions.
  - Other active materials and applications.
  - Variational modeling of charge transfer in batteries
  - SIR type models, Michaelis-Menten kinetics, Gary-Scott system ...
  - Analytical Issues: existence, stability and regularities.
  - Structure-preserving numerical scheme.

Thank you for your attention!

Thermal effect: non-isothermal case

- Helmoholtz free energy density: $\psi(\boldsymbol{c}, \vartheta)$
- Entropy: $\eta = -\psi_\vartheta$
- Internal Energy density: $\epsilon(\boldsymbol{c}, \vartheta) = \psi(\boldsymbol{c}, \vartheta) + \vartheta\eta := \epsilon_1(\boldsymbol{c}, \eta)$
- Thermodynamical relation:

$$\mu = \frac{\partial \epsilon_1}{\partial c_1}, \quad \vartheta = \frac{\partial \epsilon_1}{\partial \eta}$$

- Clausius-Duhem relation ($\mathbf{q}$: heat absorbed):

$$\partial_t \eta + \nabla \cdot (\eta\, \mathbf{u}) = \nabla \cdot \left(\frac{\mathbf{q}}{\vartheta} \right) + \triangle$$

- First law of the thermodynamics:

$$\frac{\mathrm{d}}{\mathrm{d}\, t} \epsilon_1 = \nabla \cdot \mathbb{T} + \nabla \cdot \mathbf{q}$$

Ericksen, J. L. (1992). Introduction to the Thermodynamics of Solids.

Ideal gas

- Free energy: $\Psi(\rho, \theta) = \kappa_1 \theta \rho \ln \rho - \kappa_2 \rho \theta \ln \theta$,
- Pressure: $p = \kappa_1 \rho \theta$, and internal energy: $\epsilon_1 = \kappa_2 \rho \theta$,
- Final system:

$$\begin{cases} \partial_t \rho = \kappa_1 \Delta(\rho\theta), \\ \kappa_2 (\rho\theta)_t - \kappa_1(\kappa_1 + \kappa_2) \nabla \cdot (\theta \nabla(\rho\theta)) = \nabla \cdot (\kappa_3 \nabla \theta) \, . \end{cases}$$

- Jan-Eric Sulzbach and Chun Liu (2020): The Brinkman-Fourier System with Ideal Gas Equilibrium. Ning-An Lai, Chun Liu and Andrei Tarfulea (2020): Positivity of temperature for some non-isothermal fluid models.
- Francesco De Anna and Chun Liu (2018): Non-isothermal general Ericksen-Leslie system: derivation, analysis and thermodynamics-consistency. Pei Liu, Simo Wu and Chun Liu (2018): Non-Isothermal Electrokinetics: Energetic Variational Approach.

Nonisothermal reaction-diffusion systems

- Helmoholtz free energy density [1]:

$$\psi(\boldsymbol{c},\vartheta) = k_B\vartheta\left(\sum_{i=1}^{3} c_i(\ln c_i - 1) + c_iU_i - \sum_{i=1}^{3} Q_i c_i \ln\vartheta\right), \quad Q_i : \text{Heat capcity}$$

- First law of thermodynamics:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\,t}\int \epsilon_1 \,\mathrm{d}\,\mathbf{x} &= \int \sum_{i=1}^{3} \frac{\partial\epsilon_1}{\partial c_i}\partial_t c_i + \frac{\partial\epsilon_1}{\partial\eta}\partial_t\eta \,\mathrm{d}\,t \\ &= \int \sum_{i=1}^{3}(\mu_i(-\nabla\cdot(c_i\,\mathbf{u}_i) + \sigma_i\partial_t R) + \vartheta\left(-\nabla\cdot(\eta\,\mathbf{u}) + \nabla\cdot\left(\frac{\mathbf{q}}{\vartheta}\right) + \triangle\right)\mathrm{d}\,\mathbf{x} \\ &= \int \nabla\cdot\mathbb{T} + \nabla\cdot\mathbf{q} + \underbrace{\sum_{i=1}^{3} c_i\nabla\mu_i\cdot\mathbf{u}_i + \sum_{i=1}^{3}\mu_i(\sigma_i\partial_t R) - \nabla\vartheta\cdot\left(\frac{\mathbf{q}}{\vartheta}\right) + \vartheta\triangle}_{=0}\,\mathrm{d}\,\mathbf{x}\end{aligned}$$

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[1] Gorban, A. N., Karlin, I. V., & Zinovyev, A. Y. (2004). Constructive methods of invariant manifolds for kinetic problems. Physics Reports, 396(4-6), 197-403.

Nonisothermal reaction-diffusion systems

- Entropy production:

$$\triangle = \int \sum_{i=1}^{3} \frac{1}{\vartheta} c_i |\, \mathbf{u}_i \,|^2 + \frac{1}{\vartheta}(R_t, \Gamma(R, R_t)) + k_3 \frac{|\nabla \vartheta|^2}{|\vartheta|^2} \geq 0$$

- Governing equations:

$$\begin{cases} c_i \, \mathbf{u}_i = -c_i \nabla \mu_i \quad \text{Mechanical} \\ \Gamma(R, R_t) = -\sum_{i=1}^{3} \sigma_i \mu_i(c_i, \vartheta) \quad \text{Chemical} \\ \mathbf{q} = k_3 \nabla \vartheta \quad \text{Thermal: Fourier Law} \end{cases}$$

Another Application: Dynamic Boundary Conditions

- In some applications, such as modeling of Batteries, chemical reaction only happens at the boundary
- Mass exchange between surface and bulk.
- The concentrations might be discontinuous at the boundary.
- Kinematic:

$$\begin{aligned}
&\partial_t c_i + \nabla \cdot (c_i\, \mathbf{u}_i) = 0, \mathbf{x} \in \Omega \\
&c_i\, \mathbf{u}_i = \boldsymbol{j}^{ex}, \quad \mathbf{x} \in \Gamma \\
&\bar{c}_i + \nabla_\Gamma \cdot (\bar{c}_i \boldsymbol{v}_i) = \boldsymbol{j}_i^{ex} \cdot \nu + \sigma_i R_t(\mathbf{x}), \quad \mathbf{x} \in \Gamma
\end{aligned}$$

  - c_i: Concentrations in the bulk Ω.
  - $\bar{c}_i$: concentrations on the surface Γ.
  - $\boldsymbol{j}_i^{ex}$: mass exchange between bulk and surface.
  - R: reaction trajectory on the boundary.

Reactions On the Boundary

- Energy-dissipation law:

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\left(\int_\Omega \omega(\boldsymbol{c})\,\mathrm{d}\,\mathbf{x}+\int_\Gamma \omega_s(\boldsymbol{c})\,\mathrm{d}\,S\right)$$
$$= -\int_\Omega \textstyle\sum_{i=1}^3 c_i|\,\mathbf{u}_i\,|^2\,\mathrm{d}\,x - \int_\Gamma \sum_{i=1}^3 \bar{c}_i|\boldsymbol{v}_i|^2 + \eta_0|R_t|^2 + |\boldsymbol{j}_i^{ex}\cdot\boldsymbol{\nu}|^2\,\mathrm{d}\,S$$

- Governing equation:

$$\begin{cases} c_i\,\mathbf{u}_i = c_i\nabla\mu_i, & \mathbf{x}\in\Omega \\ \boldsymbol{j}_i^{ex}\cdot\boldsymbol{\nu} = \mu_i-\mu_i^s, & \mathbf{x}\in\Gamma \quad \text{Difference of chemical potentials} \\ \bar{c}_i\boldsymbol{v}_i = \bar{c}_i\nabla_\Gamma\mu_i^s, & \mathbf{x}\in\Gamma \\ \frac{1}{R_t}\Gamma(R,R_t) = -\sum_{i=1}^3 \sigma_i\mu_i^s, & \mathbf{x}\in\Gamma \end{cases}$$

Knopf, P., Lam, K. F., Liu, C., & Metzger, S. (2020). Phase-field dynamics with transfer of materials: The Cahn–Hillard equation with reaction rate dependent dynamic boundary conditions. arXiv preprint arXiv:2003.12983.

Multiscale modeling of chemical reaction

- Kramers-Smoluchowski equation:
  Diffusion on a potential landacape
- Chemical master equation:
  Discrete state Markov jump process
- Chemical Fokker-Planck equation (chemical Langevin equation):
  Continuous state, continous time Markov chain
- The reaction rate equation:
  Large volume limit, most probability path

1. Gaveau, Bernard, Michel Moreau, and Janos Toth. Variational nonequilibrium thermodynamics of reaction-diffusion systems. I. The information potential. The Journal of chemical physics 111.17:7736-7747, 1999.

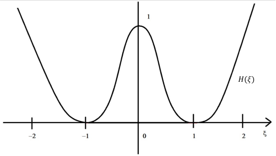
2. D.T. Gillespie, The chemical Langevin equation. J. Chem. Phys., 113(1), 297-306, 2000.

3. Montefusco, A., Peletier, M. A., & Ottinger, H. C. A framework of nonequilibrium statistical mechanics. II. Coarse-graining. Journal of Non-Equilibrium Thermodynamics, 46(1), 15-33, 2021

From Kramers diffusion to reaction

- Fokker-Planck equation:

$$\partial_t \rho^\epsilon = \partial_\xi(\partial_\xi \rho^\epsilon + \epsilon^{-2}\rho^\epsilon H'(\xi)),$$



- Invariant distribution: $\sigma^\epsilon(\xi) = \frac{1}{Z_\epsilon}\exp\left(\frac{-H(\xi)}{\epsilon^2}\right)$
- Scaling factor: $\tau_\epsilon = \frac{1}{\epsilon}\exp\left(-\frac{1}{\epsilon}\right)$
- Scaled energy-dissipation law

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\int_{-\infty}^{\infty} v^\epsilon \ln v^\epsilon \sigma^\epsilon \,\mathrm{d}\,\xi = -\int_{-\infty}^{\infty} \frac{\sigma^\epsilon}{\tau_\epsilon}\frac{1}{v^\epsilon}|\nabla v^\epsilon|^2 \,\mathrm{d}\,\xi,$$

$$\frac{\tau_\epsilon}{\sigma_\epsilon} \to \frac{2}{\kappa}\delta_0,\ \ \epsilon \to 0$$

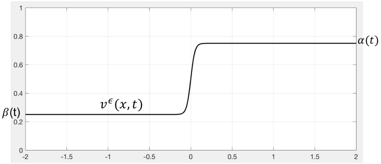
$$\kappa = \frac{\sqrt{|H''(0)|H''(1)}}{2\pi}$$

Evans, Lawrence C., and Peyam R. Tabrizian. "Asymptotics for scaled Kramers–Smoluchowski equations." SIAM Journal on Mathematical Analysis 48.4 (2016): 2944-2961.

From Kramers diffusion to reaction

- Profile of v^ϵ

$$v^\epsilon(x,t) = \frac{\alpha(t)+\beta(t)}{2} + \left(\frac{\alpha(t)-\beta(t)}{2}\right)\eta_\epsilon(\mathbf{x})$$



- Formal limit:

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\frac{1}{2}(\alpha\ln\alpha+\beta\ln\beta) = -\frac{\kappa}{2}\left(\frac{2}{\alpha+\beta}\right)(\alpha-\beta)^2, \quad \kappa = \frac{\sqrt{|H''(0)|H''(1)}}{2\pi}$$

.

- Reaction $\mathrm{A} \rightleftharpoons \mathrm{B}$:

$$R_t = \kappa\frac{2}{\alpha+\beta}\frac{\alpha-\beta}{\ln\alpha-\ln\beta}(\alpha-\beta) \approx \kappa(\alpha-\beta)$$

Herrmann, Michael, and Barbara Niethammer. Kramers' formula for chemical reactions in the context of Wasserstein gradient flows. Communications in Mathematical Sciences 9, no. 2 (2011): 623-635.

From chemical master equation to LMA

- Chemical Master equation (Discrete state, continuous time markov chain)

$$\frac{\mathrm{d}}{\mathrm{d}\,t} p_i = p_{i-1} q_{i-1,i} + p_{i+1} q_{i+1,i} - p_i q_{i,i-1} - p_i q_{i,i+1},$$

  - Ordering along a reaction trajectory, $q_{i,j}$: transition probability;
  - $p_i^{ss} q_{i,i+1} = p_{i+1}^{ss} q_{i+1,i}$ (detailed balance condition)
- Energy-dissipation law:

$$\frac{\mathrm{d}}{\mathrm{d}\,t} \sum_i p_i \ln\left(\frac{p_i}{p_i^{ss}}\right) = -\sum_i \left(\frac{p_i}{p_i^{ss}} - \frac{p_{i+1}}{p_{i+1}^{ss}}\right)\left(\ln\left(\frac{p_i}{p_i^{ss}}\right) - \ln\left(\frac{p_{i+1}}{p_{i+1}^{ss}}\right)\right)$$

Ge, Hao, and Hong Qian. "Physical origins of entropy production, free energy dissipation, and their mathematical representations." Physical Review E 81.5 (2010): 051133.

Terebus, Anna, Chun Liu, and Jie Liang. "Discrete flux and velocity fields of probability and their global maps in reaction systems." The Journal of chemical physics 149, no. 18 (2018): 185101

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From chemical master equation to LMA

- Continuous state limit: the chemical Fokker-Planck equation

$$\frac{\mathrm{d}}{\mathrm{d}\,t}\int p\ln p - p\ln p^{ss}\,\mathrm{d}\,y = -\int \eta(p)\left|\nabla \ln p - \nabla \ln p^{ss}\right|^2\mathrm{d}\,y$$

- Deterministic limit: the Law of Mass Action.

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2. H. Ge, and H, Qian., Mathematical formalism of nonequilibrium thermodynamics for nonlinear chemical reaction systems with general rate law. J. Stat. Phys., 166(1), 190-209, 2017.

3. A. Mielke, R.I.A. Patterson, M.A. Peletier and D.R.M. Renger, Non-equilibrium thermodynamical principles for chemical reactions with mass-action kinetics. SIAM J. Appl. Math., 77(4), 1562-1585, 2017.

4. J. Maas, A. Mielke. Modeling of Chemical Reaction Systems with Detailed Balance Using Gradient Structures. J. Stat. Phys. 181, 2257-2303, 2020.

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