NonEquilibrium Thermodynamics Modeling of the Flow and Deformation of Complex Systems with Internal Microstructure

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Outline

1. **Introduction. Single generator Hamiltonian formalism.**
2. **Simple polymer models: One mode viscoelasticity.**
3. **Stress-induced migration in a polymer solution: Two-fluid model.**
4. **Non-homogeneous and reactive systems: Shear Banding in a concentrated rodlike micellar solution.**

Motivation

- To use a framework that it allows the imposition “ab initio” of the most restrictive physically possible guidelines governing the dynamics of complex systems
- To have a formalism that is rich enough to accommodate a complex, inhomogeneous, internal microstructure, including the possibility of:
  - Internal structural parameters
  - Nonlocal interactions
  - Multiple scales of length
  - Internal phase space of higher dimensions
- Certain limitations are still inevitable: most importantly, that the system we study is “close enough” to equilibrium so that a generalized thermodynamic description in terms of deneralized thermodynamic potentials is still applicable; yet we want the formalism to not be introducing arbitrary constraints.

General Features

- The general formalism has to reduce to well-established ones at characteristic limiting cases:
  - In the limit of infinite time: Equilibrium (Gibbs) thermodynamics
  - In the limit of reversible dynamics: Hamiltonian dynamics
  - In the limit of infinitesimally small deviations from equilibrium: Linear Irreversible Thermodynamics (Onsager/Casimir relations)
- It is inspired by discrete particle dynamics

Hamiltonian Particle Dynamics

- Consider a single particle of mass *m*, moving in a potential field *V*(**x**).
- We can describe its motion in at least 4 different, equivalent ways:
  - – Newton's second law
  - – Lagrangian least action principle
  - – Hamilton's least action principle
  - – Poisson bracket equations
- All 4 have been used in physics; the last one is the most general one, and the one preferred* in Quantum Mechanics:

$$\boxed{\frac{d}{dt}\psi = \left[H,\psi\right] \equiv H\psi - \psi H \equiv i\hbar\left\{H,\psi\right\}}$$

*P.A.M Dirac

Newton’s Second Law of Motion

$$\boxed{m\frac{d^2}{dt^2}\mathbf{x}=\mathbf{F}=-\frac{d}{d\mathbf{x}}V(\mathbf{x})} \tag{1}$$

It can also be written in terms of the momentum $\boxed{\mathbf{p}\equiv m\mathbf{v}=m\,{}^{d\mathbf{x}}\!/_{dt}}$ (2)

as

$$\boxed{\frac{d}{dt}\mathbf{p}=-\frac{d}{d\mathbf{x}}V(\mathbf{x})} \tag{3}$$

It also leads to the law of conservation of energy $\boxed{H\equiv {}^{1}\!/_{(2m)}\,\mathbf{p}^2+V(\mathbf{x})}$ (4)

$$\boxed{\frac{d}{dt}H(\mathbf{x},\mathbf{p})=\frac{\partial}{\partial\mathbf{x}}H\cdot\frac{d}{dt}\mathbf{x}+\frac{\partial}{\partial\mathbf{p}}H\cdot\frac{d}{dt}\mathbf{p}=\frac{d}{d\mathbf{x}}V(\mathbf{x})\cdot\frac{d}{dt}\mathbf{x}+\frac{1}{m}\mathbf{p}\cdot\frac{d}{dt}\mathbf{p}=0} \tag{5}$$

Least Action Principle (1)

Newton's equations of motion can be equivalently derived from the minimization of action *I* integral, where *L* is the Lagrangian

$$\boxed{I \equiv \int_{t_1}^{t_2} L dt} \qquad (6)$$

$$\boxed{L = L(\mathbf{x}, \dot{\mathbf{x}} \equiv \frac{d}{dt}\mathbf{x}) \equiv {}^1\!/_2\, m\dot{\mathbf{x}}^2 - V(\mathbf{x})} \qquad (7)$$

$$\boxed{\delta I = 0 \Rightarrow \begin{cases} \int_{t_1}^{t_2} \left(\frac{\partial}{\partial \mathbf{x}} L \cdot \delta\mathbf{x} + \frac{\partial}{\partial \dot{\mathbf{x}}} L \cdot \delta\dot{\mathbf{x}} \right) dt = \\ \int_{t_1}^{t_2} \left(\frac{\partial}{\partial \mathbf{x}} L \cdot \delta\mathbf{x} - \frac{d}{dt}\left[\frac{\partial}{\partial \dot{\mathbf{x}}} L \right] \cdot \delta\mathbf{x} \right) dt = 0 \end{cases} \Rightarrow \frac{\partial}{\partial \mathbf{x}} L - \frac{d}{dt}\left[\frac{\partial}{\partial \dot{\mathbf{x}}} L \right] = \mathbf{0}} \qquad (8)$$

Least Action Principle (2)

Equivalently, the least action principle can also be expressed in terms of the momentum, **p**, and the Hamiltonian, *H*, which are now formally defined in terms of the Lagrangian

$$\mathbf{p} \equiv \frac{\partial}{\partial \dot{\mathbf{x}}} L = m\dot{\mathbf{x}}$$

$$H \equiv \mathbf{p}\cdot\dot{\mathbf{x}} - L = {}^{1}\!/_{(2m)}\,\mathbf{p}^{2} + V(\mathbf{x}) \qquad (9)$$

$$L \equiv \mathbf{p}\cdot\dot{\mathbf{x}} - H \Rightarrow \quad I = \int_{t_1}^{t_2} \left(\mathbf{p}\cdot\dot{\mathbf{x}} - H\right) dt = \int_{(\mathbf{x}_1,t_1)}^{(\mathbf{x}_2,t_2)} \left(\mathbf{p}\cdot d\mathbf{x} - H dt\right) \qquad (10)$$

$$\delta I = 0 \Rightarrow \begin{cases} \displaystyle\int_{(\mathbf{x}_1,t_1)}^{(\mathbf{x}_2,t_2)} \left(\delta\mathbf{p}\cdot d\mathbf{x} - \frac{d}{d\mathbf{p}} H \cdot \delta\mathbf{p} dt\right) + \int_{(\mathbf{x}_1,t_1)}^{(\mathbf{x}_2,t_2)} \left(\mathbf{p}\cdot\delta d\mathbf{x} - \frac{d}{d\mathbf{x}} H \cdot \delta\mathbf{x} dt\right) = 0 \\ \displaystyle\Rightarrow \int_{t_1}^{t_2} \delta\mathbf{p}\cdot\left(\frac{d\mathbf{x}}{dt} - \frac{d}{d\mathbf{p}} H\right) dt + \int_{t_1}^{t_2} \delta\mathbf{x}\cdot\left(-\frac{d}{dt}\mathbf{p} - \frac{d}{d\mathbf{x}} H\right) dt = 0 \end{cases} \qquad (11)$$

Hamiltonian Dynamics

Yet, the Hamiltonian dynamics can be also equivalently reproduced through the Poisson bracket equations

$$\boxed{\begin{aligned}\frac{d}{dt}\mathbf{x} &= \frac{d}{d\mathbf{p}}H\\ \frac{d}{dt}\mathbf{p} &= -\frac{d}{d\mathbf{x}}H\end{aligned}} \Leftrightarrow \boxed{\frac{d}{dt}F = \{F,H\}}$$

where *F* is any function of **x**, **p** and { . , . } is the Poisson bracket, defined for any two arbitrary functions *F*, *G* as

$$\boxed{\{F,G\} \equiv \frac{\partial F}{\partial \mathbf{x}}\cdot\frac{\partial G}{\partial \mathbf{p}} - \frac{\partial G}{\partial \mathbf{x}}\cdot\frac{\partial F}{\partial \mathbf{p}}} \qquad (12)$$

This is easily shown through a direct comparison to the result from differentiation by parts taking into account that *F* is arbitrary

$$\boxed{\frac{dF}{dt} = \frac{\partial F}{\partial \mathbf{x}}\cdot\frac{\partial \mathbf{x}}{\partial t} + \frac{\partial F}{\partial \mathbf{p}}\cdot\frac{\partial \mathbf{p}}{\partial t} = \{F,H\}} \quad \Rightarrow \quad \boxed{\begin{aligned}\frac{d\mathbf{x}}{dt} &= \frac{d}{d\mathbf{p}}H\\ \frac{d\mathbf{p}}{dt} &= -\frac{d}{d\mathbf{x}}H\end{aligned}} \qquad (13)$$

Hamiltonian Structure

The Hamiltonian structure is therefore presented by the Poisson bracket, {*F*,*G*}. This is

- Bilinear function: linear with respect to *F* and linear with respect to *G*
- Antisymmetric: {*F*,*G*} = - {*G*,*F*}
- Satisfies the Jacobi identity: {*F*,{*G*,*H*}}+{*G*,{*H*,*F*}}+{*H*,{*F*,*G*}} for any *F*,*G*,*H*

By construction therefore it also satisfies that the Hamiltonian is conserved:

- $dH/dt = \{H,H\} = 0$

In general, and in terms of the total vector variable **q**, $\mathbf{q}^T = (\mathbf{x},\mathbf{p})^T$, the Poisson bracket can be represented by a matrix **L**:

$$\boxed{\{F,G\} \equiv \frac{\partial F}{\partial \mathbf{q}} \cdot \mathbf{L} \cdot \frac{\partial G}{\partial \mathbf{q}}}$$

In which case, application of the Poisson bracket equations directly gives the evolution equations:

$$\boxed{\frac{d\mathbf{q}}{dt} = \mathbf{L} \cdot \frac{\partial H}{\partial \mathbf{q}}}$$

Limitations of the Hamiltonian Structure

The main limitation of the Hamiltonian structure is that it can only recreate reversible dynamics (i.e. in the absence of dissipation).

For example, let us assume that we have a 1d oscillator subject to a spring force with a spring coefficient *K*:

$$\boxed{m\frac{d^2x}{dt^2} = -K\left(x - x_0\right)}$$

This can be trivially presented with a Hamiltonian canonical structure:

$$\boxed{\mathbf{L} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}}$$

and a quadratic expression for the spring potential:

$$\boxed{V(x) = \tfrac{1}{2}K\left(x - x_0\right)^2}$$

In which case, the Hamiltonian, represented by the sum of kinetic and potential energies is automatically conserved. The question now arises what happens in the presence of dissipation, such as for example represented in this example by a dashpot of dashpot damping coefficient μ:

Dissipative Structure

For example, let us assume that we have a 1d oscillator subject to a spring force with a spring coefficient *K* and a dashpot with damping coefficient μ:

$$\boxed{m\frac{d^2x}{dt^2} = -K\left(x - x_0\right) - \mu\frac{dx}{dt}}$$

In this case the Hamiltonian, represented again by the sum of kinetic and potential energies is not conserved but rather monotonically decays:

$$\boxed{\frac{dH}{dt} = -\mu\left(\frac{dx}{dt}\right)^2}$$

To allow the representation of such dissipative structures, the Hamiltonian structure of the equations needs to be changed. It is postulated here that such a generalization can be done at the bracket level introducing a generalized bracket form:

$$\boxed{\frac{dF}{dt} = \{[F,H]\} = \underbrace{\{F,H\}}_{\substack{Poisson\\Bracket}} + \underbrace{[F,H]}_{\substack{Dissipation\\Bracket}}}$$

where

$$\boxed{[F,G] \equiv -\frac{\partial F}{\partial p}\mu\frac{\partial G}{\partial p}}$$

Properties of the Dissipative Structure

By comparison to the Poisson bracket the dissipative bracket has the following properties:

- It reduces to bilinear close to equilibrium; just linear in F otherwise
- its bilinear approximation is symmetric/antisymmetric satisfying the Onsager-Casimir relations
- it does not satisfy a Jacobi identity; however, there are restrictions on the material coefficients: $\mu \geq 0$ so that the useful energy represented by the Hamiltonian only dissipates

This simple example is only indicative of the concepts involved. In the actual applications, several extensions are involved, as outlined next. Most importantly, the Hamiltonian is extended to include all energy, including internal and the variables include the entropy; as a result, there is now an extra energy correction term in the dissipation bracket

Eulerian Description of Dynamics

We need to make the transition from a finite-dimensional Lagrangian dynamics to an infinite-dimensional Eulerian description:

- Instead of discrete components we have an infinite dimensional phase space represented macroscopically by a position vector **x** (and possibly microscopically by another vector **Q**)
- instead of the finite-dimensional **q** state vector with a fixed number of components (6 per particle) we have a system-dependent vector **v** of state variable fields that are functions of the phase space (like velocity, mass density, internal variables etc)
- Instead of functions *F*, *G*, *H* of the **q** vector we have *F*, *G*, *H* defined as general functionals in the **x**, **Q** phase space
- Instead of dependencies of the brackets on the partial derivatives of the functions *F*,*G*,*H* with respect to the components of the **q** vector we have dependencies on the Volterra derivatives of the functionals with respect to the components v_i of the **v** state vector field
- Most importantly, the **Hamiltonian** now involves the total energy of the system. This includes, in addition to the kinetic and the potential energy, the internal energy of the system, including the bulk and any surface interactions.

GENERIC*

See also: H.C. Oettinger, Beyond Equilibrium Thermodynamics, Wiley, 2005

- The most general formalism for the dynamics of a structured system, macroscopic as well as microscopic, described by **x,** is the one developed (after many years multiple-investigator efforts) by Oettinger and Grmela* and called as “GENERIC”

(for General Equation for Non-Equilibrium Reversible-Irreversible Coupling) :

$$\frac{d\mathbf{x}}{dt} = L\frac{\delta E}{\delta \mathbf{x}} + M\frac{\delta S}{\delta \mathbf{x}}$$

where L and M are linear differential operators of specific structure (Poissonian and Dissipation) subject to the additional degeneracy requirements:

$$L\frac{\delta S}{\delta \mathbf{x}} = 0; \quad M\frac{\delta E}{\delta \mathbf{x}} = 0$$

and E, S are the total energy (Hamiltonian) and total entropy, functionals of **x**.

* H. C. Oettinger and M. Grmela, Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism, Phys. Rev. E 56, 6633-6655 (1997).

Features of GENERIC

- It can be shown to be consistent with all well accepted dynamic transport equations ranging from the very microscopic (Maxwell-Boltzmann) to the microscopic (kinetic theory in polymers) and macroscopic (transport phenomena) levels
- It can provide corrections/suggestions to many complex modeling problems, such as:
  - Reptation theory models
  - Closure approximations

see Öttinger's homepage: http://www.polyphys.mat.ethz.ch/ and Öttinger H-C, Beyond Equilibrium Thermodynamics, Wiley 2005

Single Generaror Approximation

- For macroscopic systems, it is possible to deduce a simpler structure, the **Single Generator Hamiltonian Formalism**:
  - the entropy and energy potentials are directly related:

$$S = S(E, \mathbf{x}) \;\Rightarrow$$

$$0 = \left.\frac{\partial S}{\partial \mathbf{x}}\right|_{S=ct} = \left.\frac{\partial S}{\partial E}\right|_{\mathbf{x}=ct} \left.\frac{\partial E}{\partial \mathbf{x}}\right|_{S=ct} + \left.\frac{\partial S}{\partial \mathbf{x}}\right|_{E=ct} \;\Rightarrow$$

$$\left.\frac{\partial S}{\partial \mathbf{x}}\right|_{E=ct} = -\left.\frac{\partial S}{\partial E}\right|_{\mathbf{x}=ct} \left.\frac{\partial E}{\partial \mathbf{x}}\right|_{S=ct} = -\frac{1}{T} \left.\frac{\partial E}{\partial \mathbf{x}}\right|_{S=ct}$$

  - we can express the dynamics solely in terms of energy (Hamiltonian) potentials!
- This is shown to be equivalent to GENERIC:
  - Edwards BJ, J. Non-Equil. Thermodyn., 23:300-332 (1998)

Hamiltonian Functional Formalism*

*Beris and Edwards, Thermodynamics of Flowing Systems, Oxford UP, 1994

- For any arbitrary functional *F*, its time evolution can be described as the sum of two contributions:
  - a reversible one, represented by a Poisson bracket:
    - {F,H}
  - an irreversible one, represented by a dissipative bracket:
    - [F,H]
- The final dynamic equations are recovered through a direct comparison with the expression derived by differentiation by parts:

$$dF/dt = \{F,H\} + [F,H] = \int \delta F/\delta \mathbf{x} \cdot d\mathbf{x}/dt \, dV$$

Poisson Structure

- Defined for two arbitrary functionals *F*, *G* as the bilinear functional {*F*,*G*}:

$$\{F,G\} \equiv \int \frac{\delta F}{\delta \mathbf{x}} L \frac{\delta G}{\delta \mathbf{x}} d\Omega$$

- such that:
  - It is antisymmetric: {*F,G*} = - {*G,F*}
  - It satisfies the Jacobi identity:

    {*F*,{*G,H*}} + {*G*,{*H,F*}} + {*H*,{*F,G*}} = 0

Dissipation Structure

- Defined for two arbitrary functionals *F*, *G* as the bilinear functional [*F*,*G*]:

$$[F,G] \equiv \int \frac{\delta F}{\delta \mathbf{x}} \cdot \mathbf{M} \cdot \frac{\delta G}{\delta \mathbf{x}} d\Omega - \int \frac{1}{T} \frac{\delta F}{\delta s} \frac{\delta G}{\delta \mathbf{x}} \cdot \mathbf{M} \cdot \frac{\delta G}{\delta \mathbf{x}} d\Omega$$

- such that the matrix operator M_{ij}, in the limit of small departures from equilibrium:
  - is symmetric or antisymmetric with respect to an interchange of *i*, *j* depending on whether the corresponding x_i, x_j components have the same or different parities upon time reversal (Generalized Onsager-Casimir relations of Linear Irreversible Thermodynamics)

Advantages of Hamiltonian Formalism (1)

- It only requires knowledge of the following:
  - A set of macroscopic variables, taken uniformly as volume densities. The include, in addition to the equilibrium thermodynamic ones (the component mass density, ρ_i, for every component *i*, the entropy density s_i), the momentum density, $\rho\mathbf{v}$, and any additional structural parameter, again expressed as a density
  - The total energy of the system or any suitable Legendre transform of it, typically the total Helmholtz free energy, expressed as a functional of all other densities with the temperature substituting for the entropy density
  - The Poisson bracket, {F,H}
  - The dissipation bracket, [F,H] (with properties: [H,H]=0; [S,H]≥0)

Advantages of Hamiltonian Formalism (2)

A set of macroscopic variables can easily be assumed depending on the physics that we want to incorporate to the problem

The total Helmholtz free energy can also easily be constructed as the sum of kinetic energy plus an extended thermodynamic free energy that typically includes an easily derived expression (in terms of the structural parameters) in addition to a standard equilibrium expression

The Poisson bracket, $\{F,H\}$ is rarely needed by itself: only when an equation is put together for the first time characteristic of the variables involved in this system; otherwise, its effect is probably already known from previous work: it corresponds to a standard reversible dynamics. For viscoelastic flows, this corresponds to the terms defining an upper convected derivative

The dissipation bracket, $[F,H]$ is the only one to contain major new information and is typically where our maximum ignorance lies. Barren any other information (say, by comparison against a microscopic theory) the main information that we can use is a linear irreversible thermodynamics expression: according to that, the dissipation bracket becomes a bilinear functional in terms of all the nonequilibrium Hamiltonian gradients with an additional nonlinear (in H) correction with respect to $\delta F/\delta s$ (entropy correction) that can be easily calculated so that the conservation of the total energy is satisfied: $[H,H] = 0$.

Example Case: Single Mode Viscoelasticity

- Reference:
  - **A.N. Beris, Simple Nonequilibrium Thermodynamics Applications to Polymer Rheology** (As it appeared on: RHEOLOGY REVIEWS 2003, The British Society of Rheology (publisher), 37-75)

Variables

- For an incompressible, homogeneous (uniform polymer concentration, n=chain number density is constant) system we have
  - **v**, the velocity
  - s, the entropy density (alternatively, T, temperature)
  - **c**, the conformation tensor where
    - **C** = <**RR**> (second moment of the end-to-end distribution function) = $n\mathbf{c}$
- At equilibrium, $\mathbf{c}=k_B T/K\,\mathbf{I}$ where K is the equilibrium equivalent entropic elastic energy constant of the polymer chain and **I** the unit tensor

Hamiltonian

- The Hamiltonian (extended Helmholtz free energy of the system) is assumed to have the form:

$$A = \int_{\mathrm{V}} \left({}^{1}\!/_{2}\, \rho v^{2} + a \right) \mathrm{dV}$$

where various expressions can be assumed to represent the elastic free energy density, a, depending on the nature of the polymer phase (i.e, dilute solution, polymer melt etc). A list of the most widely used ones is supplied in Table 1 together, for convenience, with the corresponding expressions for the corresponding thermodynamic potential.

Table 1 List of commonly used expressions for the Helmholtz free energy energy density a and the corresponding thermodynamic potential, $\partial a / \partial \mathbf{c}$, with respect to the conformation tensor, **c**. The expressions are provided in dimensionless form. The free energy is made dimensionless with respect to nk_BT, where n is a chain number density, k_B is the Boltzmann factor and T the temperature, and **c** is made dimensionless with respect to the square of the equilibrium end-to-end chain distance, k_BT/K where K is the (apparent) elastic constant for the chain's elastic energy. In the random flight model, $k_BT/K=1/3Nl^2$, where N, l is the number, length of repeating (Kuhn) segments [Kuhn and Grün, 1942].

Model	$a(\mathbf{c})$	$\partial a / \partial \mathbf{c}$	Remarks /References
Maxwell Oldroyd-B	$\frac{1}{2}\left\{\operatorname{tr}(\mathbf{c})-\ln\left(\det(\mathbf{c})\right)\right\}$	$\frac{1}{2}\mathbf{I}-\frac{1}{2}\mathbf{c}^{-1}$	Also called Hookean or Linear Dumbbell model [Bird et al., 1987]
FENE-P	$-\frac{1}{2}L^2\ln\left(1-\frac{\operatorname{tr}(\mathbf{c})}{L^2}\right)$ $-\frac{1}{2}\ln\left(\det(\mathbf{c})\right)$	$\frac{1}{2}\left(\frac{1}{1-\frac{\operatorname{tr}(\mathbf{c})}{L^2}}\right)\mathbf{I}-\frac{1}{2}\mathbf{c}^{-1}$	L represents the dimensionless maximum chain extensibility; L^2 also appears as b [Bird et al., 1987]
Bird and DeAguiar (modified)	$\frac{1}{2}\left\{\operatorname{tr}(\mathbf{c})-\ln\left(\det(\mathbf{c})\right)\right\}$ $+\frac{(1-\alpha)}{2}\ln\left(\frac{\left(\frac{1}{3}\operatorname{tr}(\mathbf{c})\right)^3}{\det(\mathbf{c})}\right)$	$\frac{1}{2}\left(1-\frac{3(\alpha-1)}{\operatorname{tr}(\mathbf{c})}\right)\mathbf{I}$ $-\frac{1}{2}(2-\alpha)\mathbf{c}^{-1}$	α is an aniso-tropic mobility parameter; [Bird and DeAguiar, 1983]

Leonov	$W(a_1, a_{-1})$; $a_1 \equiv \frac{I_1}{I_3^{1/3}}; a_{-1} \equiv I_{-1} I_3^{1/3}; I_{-1} = \frac{I_2}{I_3}$	$\frac{\partial W}{\partial a_1}\frac{1}{I_3^{1/3}}\left(\mathbf{I} - \frac{1}{3} I_1 \mathbf{c}^{-1}\right)+$ $\frac{\partial W}{\partial a_{-1}}\frac{1}{I_3^{2/3}}\left(I_1 \mathbf{I} - \mathbf{c} - \frac{2}{3} I_2 \mathbf{c}^{-1}\right)$	I_n is the n-th invariant of **c**; in the original model $I_3=1$ [Leonov, 1976]
Marrucci and Acierno (modified)	$\frac{1}{2}(\chi+1)\left(\mathrm{tr}(\mathbf{c}) - \ln\left(\det(\mathbf{c})\right)\right)$ $-\frac{3}{2}\chi_0 \ln(\chi)$	$\frac{1}{2}(\chi+1)\left(\mathbf{I} - \mathbf{c}^{-1}\right)$	χ is the number of entanglements per chain [Marrucci et al., 1973, Acierno et al., 1976a,b]
MGI (modified)	$-\ln\left(\det\left(\frac{\mathbf{c}}{\left(\mathrm{tr}\left(\mathbf{c}^{1/2}\right)\right)^2}\right)\right)$ $= 6\ln\left(\mathrm{tr}\left(\mathbf{c}^{1/2}\right)\right) - \ln\left(\det(\mathbf{c})\right)$	$\frac{3\mathbf{c}^{-1/2}}{\mathrm{tr}\left(\mathbf{c}^{1/2}\right)} - \mathbf{c}^{-1}$	[Marrucci et al., 2001; Leygue et al., 2001]
Pompon	$\frac{1}{2}\left\{3\ln\left(\mathrm{tr}(\mathbf{c})\right) - \ln\left(\det(\mathbf{c})\right)\right\}$ $+\frac{3}{2}\left\{\begin{matrix}\lambda^{*2} - (\lambda^* - q)^2\, \mathrm{H}(\lambda^* - q) \\ -1 - 2\ln(\lambda^*)\end{matrix}\right\}$	$\frac{3}{2}\frac{\mathbf{I}}{\mathrm{tr}(\mathbf{c})} - \frac{1}{2}\mathbf{c}^{-1}$	λ^* is an extended stretch factor [Öttinger, 2001; McLeish and Larson, 1998]

Poisson Bracket: Reversible Equations

- For an isothermal system, we get the standard reversible dynamics for an elastic medium (together with the divergence-free velocity constraint):

$$\rho \frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{v} = -\nabla p + \nabla \cdot \mathbf{T}^T$$

$$\frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = 0$$

$$\mathbf{T}^T = 2\mathbf{c} \cdot \frac{\partial a}{\partial \mathbf{c}}$$

General Dissipation Bracket

- The general dissipation bracket (within an entropy correction) can be easily formulated as a bilinear expression in terms of the nonequilibrium components of the Hamiltonian potential, δH/δ**c** and ∇(δH/δ**v**) as

$$[F,G] = -\int \Lambda_{\alpha\beta\gamma\varepsilon} \frac{\delta F}{\delta c_{\alpha\beta}} \frac{\delta G}{\delta c_{\gamma\varepsilon}} dV - \int Q_{\alpha\beta\gamma\varepsilon} \nabla_\alpha \left(\frac{\delta F}{\delta v_\beta} \right) \nabla_\gamma \left(\frac{\delta G}{\delta v_\varepsilon} \right) dV$$

$$-\int L_{\alpha\beta\gamma\varepsilon} \left(\nabla_\alpha \left(\frac{\delta F}{\delta v_\beta} \right) \frac{\delta G}{\delta c_{\gamma\varepsilon}} - \nabla_\alpha \left(\frac{\delta G}{\delta v_\beta} \right) \frac{\delta F}{\delta c_{\gamma\varepsilon}} \right) dV$$

where, to preserve Onsager's relations, the matrices **Λ** and **Q** are symmetric with respect to an exchange of γ,ε by α,β and, moreover, given the symmetry of **c**, the matrix **Λ** does not change upon an exchange of γ by ε and/or α by β; additional constraints on **Q** can also be derived based on the principle of material indifference

Typical Choices for **L**, **Q**

- If **L** is symmetric upon change of γ by ε and/or α by β it turns out that it does not contribute to the entropy production; thus there is no need for further constraints. A typical choice is therefore (following the simplest choice for **Λ**, see Table 2)

$$L_{\alpha\beta\gamma\varepsilon} = -\xi/2(c_{\alpha\gamma}\delta_{\beta\varepsilon} + permutations\, of\ \alpha \leftrightarrow \beta\ and\ \gamma \leftrightarrow \varepsilon)$$

where ξ is a scalar parameter between 0 and 1

Similarly, for **Q**, we use the expression which is valid for a homogeneous and isotropic (Newtonian) system of viscosity η_s:

$$Q_{\alpha\beta\gamma\varepsilon} = \eta_s(\delta_{\alpha\gamma}\delta_{\beta\varepsilon} + \delta_{\alpha\varepsilon}\delta_{\beta\gamma})$$

Final Equations

- For an isothermal system, we get the standard dynamics for a viscoelastic medium (together with the divergence-free velocity constraint):

$$\rho \frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{v} = -\nabla p + \eta_s \Delta \mathbf{v} + \nabla \cdot \mathbf{T}^T$$

$$\frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = -\frac{\xi}{2}\left(\dot{\boldsymbol{\gamma}} \cdot \mathbf{c} + \mathbf{c} \cdot \dot{\boldsymbol{\gamma}}\right) - \boldsymbol{\Lambda} : \frac{\partial a}{\partial \mathbf{c}}$$

$$\mathbf{T}^T = 2(1-\xi)\mathbf{c} \cdot \frac{\partial a}{\partial \mathbf{c}}$$

Typical Choices for **Λ**

- Various models can be generated using different expressions for the relaxation tensor **Λ.**
- A compilation of some of the most often employed forms can be found in Table 2

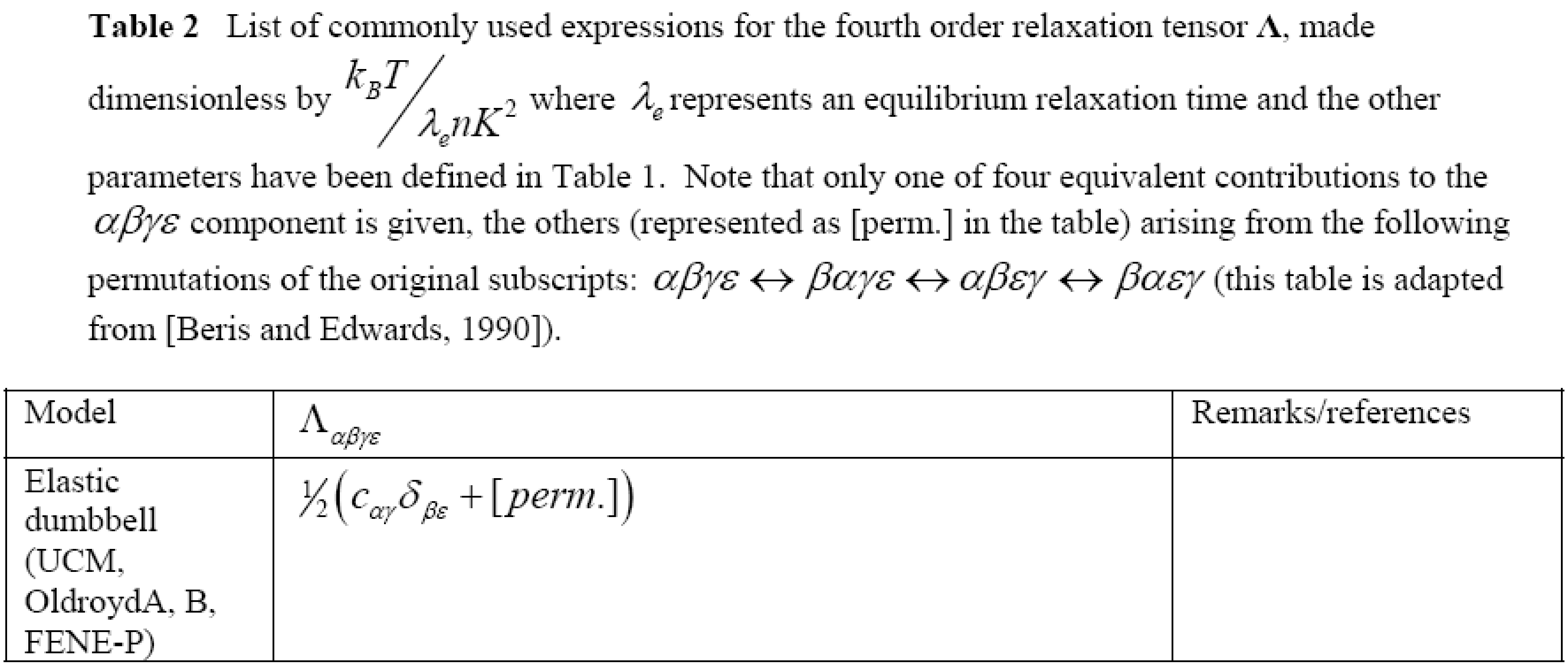

Table 2 List of commonly used expressions for the fourth order relaxation tensor **Λ**, made dimensionless by $k_BT \big/ \lambda_e n K^2$ where λ_e represents an equilibrium relaxation time and the other parameters have been defined in Table 1. Note that only one of four equivalent contributions to the $\alpha\beta\gamma\varepsilon$ component is given, the others (represented as [perm.] in the table) arising from the following permutations of the original subscripts: $\alpha\beta\gamma\varepsilon \leftrightarrow \beta\alpha\gamma\varepsilon \leftrightarrow \alpha\beta\varepsilon\gamma \leftrightarrow \beta\alpha\varepsilon\gamma$ (this table is adapted from [Beris and Edwards, 1990]).

Model	$\Lambda_{\alpha\beta\gamma\varepsilon}$	Remarks/references
Elastic dumbbell (UCM, OldroydA, B, FENE-P)	$½\left(c_{\alpha\gamma}\delta_{\beta\varepsilon} + [perm.]\right)$	

Elastic dumbbell with hydrodynamic interactions	$\frac{1}{2}\left(c_{\alpha\gamma}\left(\delta_{\beta\varepsilon}-\frac{3}{4}h\sqrt{\frac{\pi}{\mathrm{tr}(\mathbf{c})}}\left(\delta_{\beta\varepsilon}+\frac{c_{\beta\varepsilon}}{\mathrm{tr}(\mathbf{c})}\right)\right)+[perm.]\right)$	$0\le h\le \frac{2}{3}\sqrt{\frac{I_1}{\pi}}$; [Bird et al, 1987]
Modified encapsulated dumbbell	$\frac{1}{2}\left(\sigma c_{\alpha\gamma}\delta_{\beta\varepsilon}+(1-\sigma)\frac{1}{\mathrm{tr}(\mathbf{c})}c_{\alpha\beta}c_{\gamma\varepsilon}+[perm.]\right)$	$\sigma\ge 0$; [Bird and DeAguiar, 1983]
Giesekus	$\frac{1}{2}\left(c_{\alpha\gamma}\left((1-\alpha)\delta_{\beta\varepsilon}+\alpha c_{\beta\varepsilon}\right)+[perm.]\right)$	$0\le\alpha\le 1$; [Giesekus, 1982a]
Leonov	$\left(c_{\alpha\varepsilon}c_{\gamma\beta}-\frac{1}{3}c_{\alpha\beta}c_{\gamma\varepsilon}+[perm.]\right)$	[Leonov, 1976]
Phan-Thien/Tanner (linear)	$\frac{1}{2}\left(1+\varepsilon\left(\mathrm{tr}(\mathbf{c})-3\right)\right)\left(c_{\alpha\gamma}\delta_{\beta\varepsilon}+[perm.]\right)$	[Phan-Thien and Tanner, 1977]
Extended White/ Metzner	$\frac{1}{2}\frac{1}{\lambda^*(I_1,I_2,I_3)}\left(c_{\alpha\gamma}\delta_{\beta\varepsilon}+[perm.]\right)$	λ^* is a dimensionless, positive function of the invariants of **c**; for example, $\lambda^*=K(I_1)^k$ [Souvaliotis and Beris, 1992]
Leygue, Beris and Keunings	$\frac{1}{2}\left(c_{\alpha\gamma}\left(\alpha c_{\beta\varepsilon}+(1-\alpha)\frac{\mathrm{tr}\left(\mathbf{c}^{1/2}\right)}{3}c_{\beta\varepsilon}^{1/2}\right)+[perm.]\right)$	$0\le\alpha\le 1$; [Leygue et al., 2001]

In the remarks column a number of sufficient conditions known to assure the non-negative character of the relaxation dissipation are listed (see [Beris and Edwards, 1994] for more details regarding their derivation).

Single Mode Viscoelasticity: Conclusions

- The Hamiltonian formalism can provide a uniform representation for viscoelastic models
- New possibilities thus arise for new model development through "mix and match" of terms
- In addition, the evaluation of thermodynamic consistency is facilitated: new constraints can be easily derived on acceptable parameter values and suitable approximations for the dissipative terms of the equations
- The extension of the above-mentioned work to multimode models is straightforward! See the mentioned references (book and review) for several characteristic examples

Stress-Induced Migration in a Viscoelastic Fluid*

- Two approaches: Single and two-fluid system
- Formalism can tell you what it CAN be, but not what it ACTUALLY is! (Comparison with underlying microscopic theory is necessary)
- The cruder the structure, the easier to work out the predictions but also the more cloudy those predictions are
- Single fluid model: coarser; 2-fluid model: finer
- Next: Develop general equations

*Following the development in “Beris and Edwards, 1994, Section 9.2”

Single Fluid Model: Variables

- For an incompressible, inhomogeneous (variable polymer concentration, n=chain number density is variable) system we have
  - ρ_1, the polymer density ($n=N_A\rho_1/MW_1$)
  - $\mathbf{v}$, the velocity
  - s, the entropy density (alternatively, T, temperature)
  - $\mathbf{c}$, the conformation tensor where
    - $\mathbf{C} = \langle\mathbf{RR}\rangle$ (second moment of the end-to-end distribution function) = $n\mathbf{c}$
- At equilibrium, $\mathbf{c}=k_BT/K\,\mathbf{I}$ where K is the equilibrium equivalent entropic elastic energy constant of the polymer chain

Single Fluid Hamiltonian

- The Hamiltonian (extended Helmholtz free energy of the system) is assumed to have the form:

$$A = \int_{\mathrm{V}} \left({}^{1}\!/_{2}\, \rho v^{2} + a_{e} + a_{m} \right) \mathrm{dV}$$

where a_e is the elastic free energy density corresponding to a dilute solution:

$$a_{e} = {}^{1}\!/_{2} (K \,\mathrm{tr}\, \mathbf{C} - n k_{B} T \log\left(\det\left({(K\mathbf{C})} \big/ {(n k_{B} T)} \right) \right))$$

and a_m represents the mixing energy density (approximated by a Flory-Huggins) term:

$$a_{m} = k_{B} T (n \log \varphi + n_{s} \log(1 - \varphi))$$

where n_s is the solvent number density and φ is the polymer volume fraction:

$$\varphi = {(nN)} \big/ {(nN + n_{s})}$$

Single Fluid Poisson Bracket: Reversible Equations

- For an isothermal system, we get the standard reversible dynamics for an elastic medium together with a convection equation for the polymer density:

$$\frac{\mathrm{D}}{\mathrm{Dt}}\rho_1 = 0$$

$$\rho\frac{\mathrm{D}}{\mathrm{Dt}}\mathbf{v} = -\nabla p + \nabla\cdot\mathbf{T}^T$$

$$\frac{\mathrm{D}}{\mathrm{Dt}}\mathbf{C} - \nabla\mathbf{v}^T\cdot\mathbf{C} - \mathbf{C}\cdot\nabla\mathbf{v} = \mathbf{0}$$

$$\mathbf{T}^T = 2\mathbf{C}\cdot\frac{\partial a_e}{\partial\mathbf{C}}$$

Single Fluid: Dissipation Structure

- Defined for two arbitrary functionals *F*, *G* by the bilinear functional [*F*,*G*] (to within an entropy correction term):

$$
\begin{aligned}
[F,G] \equiv & -\int \frac{\eta_s}{2}\left(\nabla_\alpha \frac{\delta F}{\delta v_\beta} + \nabla_\beta \frac{\delta F}{\delta v_\alpha}\right)\left(\nabla_\alpha \frac{\delta G}{\delta v_\beta} + \nabla_\beta \frac{\delta G}{\delta v_\alpha}\right) d\Omega \\
& - \int \Lambda_{\alpha\beta\gamma\varepsilon} \frac{\delta F}{\delta C_{\alpha\beta}} \frac{\delta G}{\delta C_{\gamma\varepsilon}} d\Omega \\
& - \int D_{\alpha\beta}\left(\nabla_\alpha \frac{\delta F}{\delta \rho_1}\right)\left(\nabla_\beta \frac{\delta G}{\delta \rho_1}\right) d\Omega \\
& - \int E_{\alpha\beta}\left(\nabla_\gamma\left(C_{\gamma\lambda} \frac{\delta F}{\delta C_{\lambda\alpha}}\right)\nabla_\beta \frac{\delta G}{\delta \rho_1} + \nabla_\gamma\left(C_{\gamma\lambda} \frac{\delta G}{\delta C_{\lambda\alpha}}\right)\nabla_\beta \frac{\delta F}{\delta \rho_1}\right) d\Omega \\
& - \int B_{\alpha\beta}\left(\nabla_\gamma\left(C_{\gamma\lambda} \frac{\delta F}{\delta C_{\lambda\alpha}}\right)\right)\left(\nabla_\varepsilon\left(C_{\varepsilon\kappa} \frac{\delta G}{\delta C_{\kappa\beta}}\right)\right) d\Omega
\end{aligned}
$$

Single Fluid: Final Equations

$$\frac{\mathrm{D}}{\mathrm{Dt}}\rho_1 = \nabla_\alpha\left(D_{\alpha\beta}\nabla_\beta\frac{\delta H}{\delta\rho_1}\right) + \nabla_\alpha\left(\tfrac{1}{2}E_{\beta\alpha}\nabla_\varepsilon T_{\beta\varepsilon}\right)$$

$$\rho\frac{\mathrm{D}}{\mathrm{Dt}}v_a = -\nabla_\alpha p + \nabla_\beta T_{\alpha\beta} + \nabla_\beta\left(\eta_s\left(\nabla_\beta v_\alpha + \nabla_\alpha v_\beta\right)\right)$$

$$\frac{\mathrm{D}}{\mathrm{Dt}}C_{\alpha\beta} - \nabla_\gamma v_\alpha C_{\gamma\beta} - C_{\alpha\gamma}\nabla_\gamma v_\beta = -\Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta H}{\delta C_{\gamma\varepsilon}}$$

$$+C_{\gamma\alpha}\nabla_\gamma\left(E_{\beta\varepsilon}\nabla_\varepsilon\frac{\delta H}{\delta\rho_1}\right) + C_{\gamma\alpha}\nabla_\gamma\left(\tfrac{1}{2}B_{\beta\varepsilon}\nabla_\kappa T_{\varepsilon\kappa}\right)$$

$$\mathbf{T}^T = 2\mathbf{C}\cdot\frac{\partial a_e}{\partial\mathbf{C}}$$

Single Fluid Formalism

- The general formalism leads to new terms to the polymer mass balance and conformation evolution equations:
  - In the polymer mass balance: A new driving force appears proportional to the gradient to the polymer stress
  - In the polymer conformation evolution equation: Two new terms appear, involving second derivatives of the chemical potential and the stress
  - In addition, there are other dependencies (*n* hidden within **C**)
- Moreover, many uncertainties still remain (too many adjustable parameters) and the nonnegative entropy production is hard to ascertain in the general case

Particular Case: **D**=-1/2**E**=1/4**B**=D**δ**

$$\frac{\mathrm{D}}{\mathrm{Dt}}\rho_1 = D\nabla_\alpha\left(\nabla_\alpha \frac{\delta H}{\delta\rho_1} - \nabla_\varepsilon T_{\alpha\varepsilon}\right)$$

$$\rho\frac{\mathrm{D}}{\mathrm{Dt}}v_a = -\nabla_\alpha p + \nabla_\beta T_{\alpha\beta} + \nabla_\beta\left(\eta_s\left(\nabla_\beta v_\alpha + \nabla_\alpha v_\beta\right)\right)$$

$$\frac{\mathrm{D}}{\mathrm{Dt}}C_{\alpha\beta} - \nabla_\gamma v_\alpha C_{\gamma\beta} - C_{\alpha\gamma}\nabla_\gamma v_\beta = -\Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta H}{\delta C_{\gamma\varepsilon}}$$

$$-2C_{\gamma\alpha}D\nabla_\gamma\left(\nabla_\beta\frac{\delta H}{\delta\rho_1} - \nabla_\kappa T_{\beta\kappa}\right)$$

$$\mathbf{T}^T = 2\mathbf{C}\cdot\frac{\partial a_e}{\partial \mathbf{C}}$$

Two- Fluid Model: Variables

- For an incompressible, inhomogeneous (variable polymer concentration, n=chain number density is variable) system we have (keeping $\rho=\rho_1+\rho_2$=constant)
  - ρ_1, the polymer density ($n=N_A\rho_1/MW_1$); ρ_2, the solvent density
  - $\mathbf{g}_1=\rho_1\mathbf{v}_1$, the polymer momentum density; $\mathbf{g}_2=\rho_2\mathbf{v}_2$
  - s, the entropy density (alternatively, T, temperature)
  - $\mathbf{c}$, the conformation tensor where
    - $\mathbf{C} = \langle\mathbf{RR}\rangle$ (second moment of the end-to-end distribution function) = $n\mathbf{c}$
- At equilibrium, $\mathbf{c}=k_B T/K\,\mathbf{I}$ where K is the equilibrium equivalent entropic elastic energy constant of the polymer chain

Two-Fluid Hamiltonian

- The Hamiltonian (extended Helmholtz free energy of the system) is assumed to have the form:

$$A = \int_{\mathrm{V}} \left({}^{1}\!/_{2}\,\rho_1 v_1^2 + {}^{1}\!/_{2}\,\rho_2 v_2^2 + a_e + a_m \right) \mathrm{dV}$$

where a_e is the elastic free energy density corresponding to a dilute solution:

$$a_e = {}^{1}\!/_{2}\left(K\,\mathrm{tr}\,\mathbf{C} - nk_BT\log\left(\det\left({}^{(K\mathbf{C})}\!/_{(nk_BT)} \right)\right)\right)$$

and a_m represents the mixing energy density (approximated by a Flory-Huggins) term:

$$a_m = k_BT(n\log\varphi + n_s\log(1-\varphi))$$

where n_s is the solvent number density and φ is the polymer volume fraction:

$$\varphi = {}^{(nN)}\!/_{(nN + n_s)}$$

Two- Fluid Poisson Bracket: Reversible Equations

- For an isothermal system, we get the standard reversible dynamics for 2 interpenetrating continua of which one is an elastic medium

$$\frac{\partial \rho_1}{\partial \mathrm{t}} + \nabla_\alpha \left(v_{1\alpha} \rho_1 \right) = 0 \qquad \frac{\partial \rho_2}{\partial \mathrm{t}} + \nabla_\alpha \left(v_{2\alpha} \rho_2 \right) = 0$$

$$\rho_1 \left(\frac{\partial v_{1\alpha}}{\partial \mathrm{t}} + v_{1\beta} \nabla_\beta v_{1\alpha} \right) = -\nabla_\alpha p_1 + \nabla_\beta T_{\alpha\beta} \qquad \rho_2 \left(\frac{\partial v_{2\alpha}}{\partial \mathrm{t}} + v_{2\beta} \nabla_\beta v_{2\alpha} \right) = -\nabla_\alpha p_2$$

$$\frac{\partial C_{\alpha\beta}}{\partial \mathrm{t}} + \nabla_\gamma \left(v_{1\gamma} C_{\alpha\beta} \right) - \left(\nabla_\gamma v_{1\alpha} \right) C_{\gamma\beta} - C_{\alpha\gamma} \nabla_\gamma v_{1\beta} = 0$$

$$\mathbf{T}^T = 2\mathbf{C} \cdot \frac{\partial a_e}{\partial \mathbf{C}}$$

Transformation of Variables

- To introduce the dissipation terms it is first necessary to make a transformation of variables

$$\rho = \rho_+ = \rho_1 + \rho_2 \,; \quad \rho_- = \rho_1$$

$$\mathbf{g}_+ = \mathbf{g}_1 + \mathbf{g}_2 \equiv \rho_+ \mathbf{v} \,; \quad \mathbf{g}_- = \frac{\rho_2}{\rho}\mathbf{g}_1 - \frac{\rho_1}{\rho}\mathbf{g}_2 = \frac{\rho_1 \rho_2}{\rho}\Delta\mathbf{v}$$

where

$$\mathbf{g}_1 \equiv \rho_1 \mathbf{v}_1 \,; \quad \mathbf{g}_2 \equiv \rho_2 \mathbf{v}_2 \,; \quad \mathbf{v} = \frac{\rho_1}{\rho}\mathbf{v}_1 + \frac{\rho_2}{\rho}\mathbf{v}_2 \,; \quad \Delta\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2$$

therefore

$$\frac{\delta H}{\delta \mathbf{g}_+} = \mathbf{v} \,; \quad \frac{\delta H}{\delta \mathbf{g}_-} = \Delta\mathbf{v}$$

Two- Fluid: Reversible Equations in Transformed Variables

$$\nabla \cdot \mathbf{v} = 0 \qquad \frac{\partial \rho_-}{\partial\,\mathrm{t}} + v_\alpha \nabla_\alpha \rho_- + \nabla_\alpha \Big(\big(1-\varphi\big) \Delta v_a \rho_- \Big) = 0$$

$$\frac{\partial g_{+\alpha}}{\partial\,\mathrm{t}} + \nabla_\beta \left(v_{1\beta} g_{1\alpha} + v_{2\beta} g_{2\alpha} \right) + g_{1\beta} \nabla_\alpha v_{1\beta} + g_{2\beta} \nabla_\alpha v_{2\beta} = -\nabla_\alpha p + \nabla_\beta T_{\alpha\beta}$$

$$\frac{\partial g_{-\alpha}}{\partial\,\mathrm{t}} + (1-\varphi)\nabla_\beta \left(v_{1\beta} g_{1\alpha} \right) - \varphi \nabla_\beta \left(v_{2\beta} g_{2\alpha} \right) + (1-\varphi) g_{1\beta} \nabla_\alpha v_{1\beta} - \varphi g_{2\beta} \nabla_\alpha v_{2\beta} = -(1-\varphi)\left(\nabla_\beta \Pi - \nabla_\beta T_{\alpha\beta} \right)$$

$$\frac{\partial C_{\alpha\beta}}{\partial\,\mathrm{t}} + \nabla_\gamma \left(v_{1\gamma} C_{\alpha\beta} \right) - \nabla_\gamma v_{1\alpha} C_{\gamma\beta} - C_{\alpha\gamma} \nabla_\gamma v_{1\beta} = 0$$

$$\Pi \equiv n_1 \frac{\delta H}{\delta n_1} + \mathbf{C} : \frac{\delta H}{\delta \mathbf{C}} - a_e \qquad \mathbf{T}^T = 2\mathbf{C} \cdot \frac{\partial a_e}{\partial \mathbf{C}}$$

Two-Fluid: Dissipation Structure

- Defined for two arbitrary functionals *F*, *G* by the bilinear functional [*F*,*G*] (to within an entropy correction term):

$$
\begin{aligned}
[F,G] \equiv & -\int \frac{\eta_s}{2}\left(\nabla_\alpha \frac{\delta F}{\delta g_{+\beta}} + \nabla_\beta \frac{\delta F}{\delta g_{+\alpha}}\right)\left(\nabla_\alpha \frac{\delta G}{\delta g_{+\beta}} + \nabla_\beta \frac{\delta G}{\delta g_{+\alpha}}\right) d\Omega \\
& -\int Z_{\alpha\beta} \frac{\delta F}{\delta g_{-\alpha}} \frac{\delta G}{\delta g_{-\beta}} d\Omega \\
& -\int \Lambda_{\alpha\beta\gamma\varepsilon} \frac{\delta F}{\delta C_{\alpha\beta}} \frac{\delta G}{\delta C_{\gamma\varepsilon}} d\Omega
\end{aligned}
$$

Two- Fluid: Final Momentum and Conformation Equations

$$\frac{\partial g_{+\alpha}}{\partial \mathrm{t}} + \nabla_\beta \left(v_{1\beta} g_{1\alpha} + v_{2\beta} g_{2\alpha} \right) + g_{1\beta} \nabla_\alpha v_{1\beta} + g_{2\beta} \nabla_\alpha v_{2\beta} =$$

$$-\nabla_\alpha p + \nabla_\beta T_{\alpha\beta} + \nabla_\beta \left(\eta_s \left(\nabla_\beta v_\alpha + \nabla_\alpha v_\beta \right) \right)$$

$$\frac{\partial g_{-\alpha}}{\partial \mathrm{t}} + (1-\varphi) \nabla_\beta \left(v_{1\beta} g_{1\alpha} \right) - \varphi \nabla_\beta \left(v_{2\beta} g_{2\alpha} \right) + (1-\varphi) g_{1\beta} \nabla_\alpha v_{1\beta} - \varphi g_{2\beta} \nabla_\alpha v_{2\beta} =$$

$$-Z_{\alpha\beta} \Delta v_\beta - (1-\varphi) \left(\nabla_\beta \Pi - \nabla_\beta T_{\alpha\beta} \right)$$

$$\frac{\partial C_{\alpha\beta}}{\partial \mathrm{t}} + \nabla_\gamma \left(v_{1\gamma} C_{\alpha\beta} \right) - \nabla_\gamma v_{1\alpha} C_{\gamma\beta} - C_{\alpha\gamma} \nabla_\gamma v_{1\beta} = -\Lambda_{\alpha\beta\gamma\varepsilon} \frac{\delta H}{\delta C_{\gamma\varepsilon}}$$

Two- Fluid: Small Differential Inertia

$$\Delta v_{\beta} = -Z_{\alpha\beta}^{-1}(1-\varphi)\left(\nabla_{\alpha}\Pi - \nabla_{\gamma}T_{\alpha\gamma}\right)$$

and therefore, substituting this relationship into the polymer density equation, we have:

$$\frac{\partial \rho_{-}}{\partial \mathrm{t}} + v_{\alpha}\nabla_{\alpha}\rho_{-} = \nabla_{\alpha}\left(\left(1-\varphi\right)^{2}\rho_{-}Z_{\alpha\beta}^{-1}\left(\nabla_{\beta}\Pi - \nabla_{\gamma}T_{\beta\gamma}\right)\right)$$

Two- Fluid Formalism: Conclusions

- The general formalism leads to specific new terms to the polymer mass balance and conformation evolution equations:
  - In the polymer mass balance: A new driving force appears proportional to the gradient to the polymer stress
  - In the polymer conformation evolution equation: The reference velocity with respect to which it is calculated is the polymer phase velocity
  - In addition, there are other dependencies (n hidden with C)
- The 2-fluid equation leaves no uncertainties!
- It has been confirmed from microscopic theory (Curtiss and Bird, 1996).

Applications

- **Coupled mass/momentum transport in a dilute polymer system: Two-fluid model.**
  - Apostolakis MV, Mavrantzas VG, Beris AN Stress gradient-induced migration effects in the Taylor-Couette flow of a dilute polymer solution J. NON-NEWTONIAN FLUID MECH. 102: 409-445 (2002)
- **Non-homogeneous systems: Surface Effects on the Rheology and Chain Conformation in Dilute Polymer Solutions.**
  - Mavrantzas VG, Beris AN A hierarchical model for surface effects on chain conformation and rheology of polymer solutions. I. General formulation JOURNAL OF CHEMICAL PHYSICS 110: 616-627 (1999)
  - II. Application to a neutral surface JOURNAL OF CHEMICAL PHYSICS 110: 628-638 (1999)

Coupling Reactions and Molecular Conformations in the Modeling of Shear Banding in Wormlike Micellar Systems

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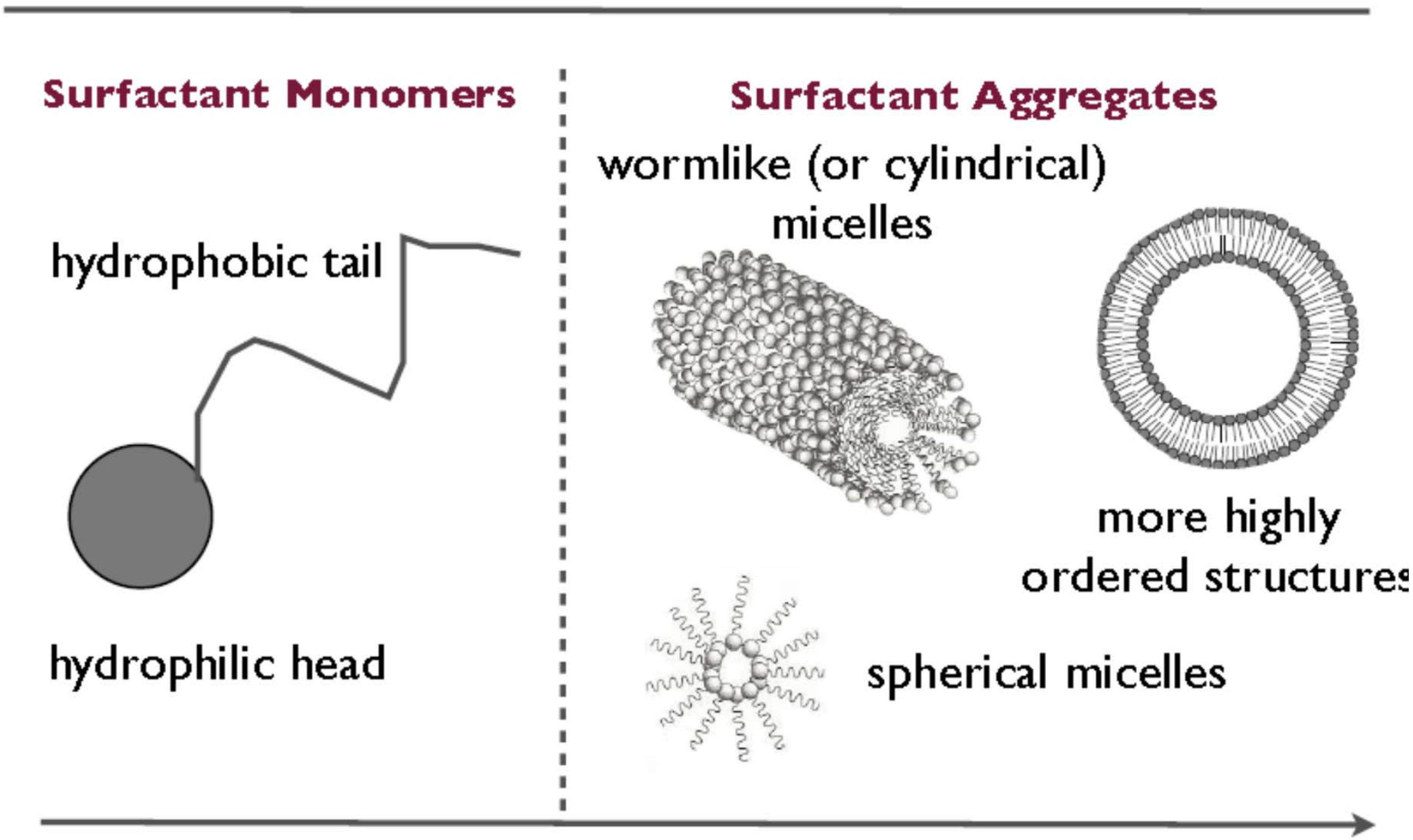
University of Delaware, Newark, DE 19716

References: Germann, Beris and Cook, JNNFM 2013, 2014

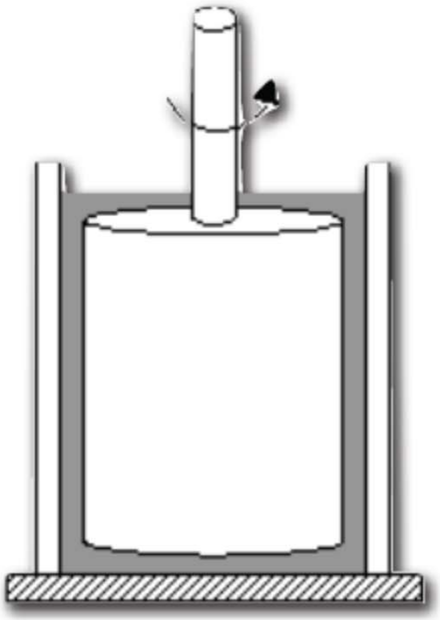
Micellar systems: concentrated suspensions of surfactants

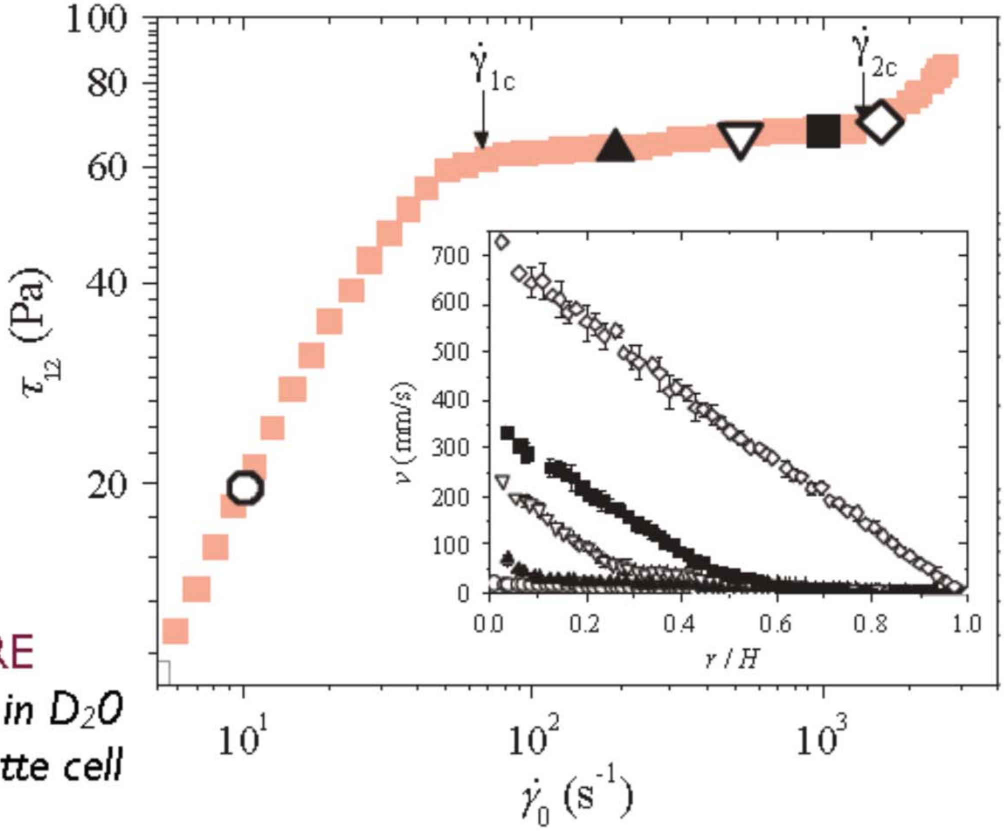


CMC

Concentration

Rodlike Micellar Systems: Shear-Banding



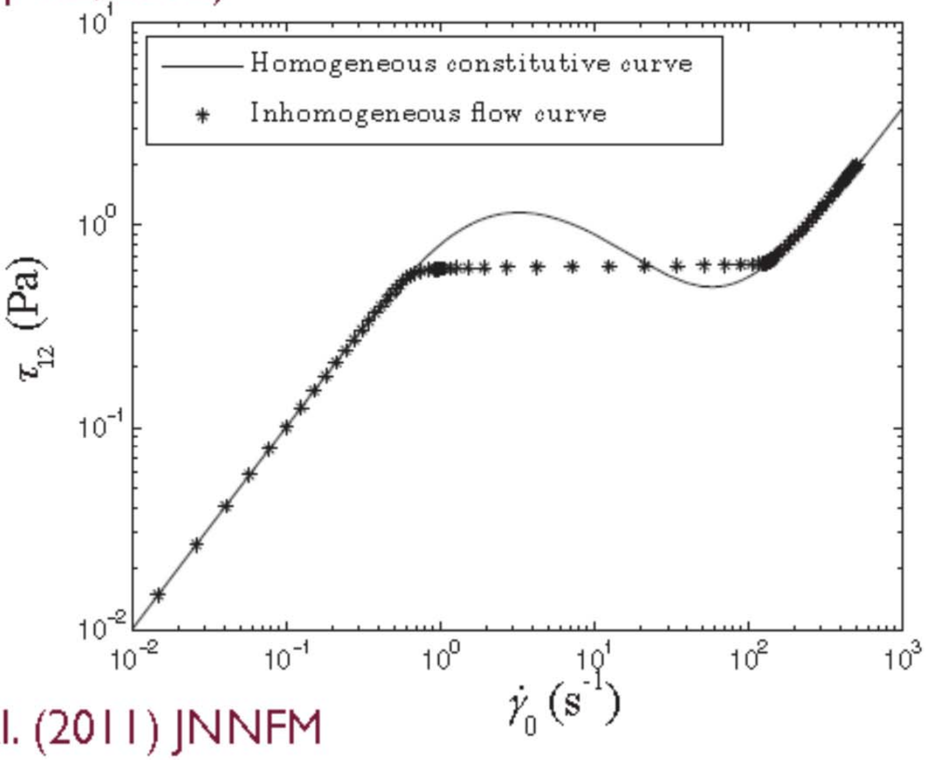


Helgeson *et al.* (2010a) PRE

- *16.7 wt% CTAB dissolved in D_2O*
- *Shear-rate controlled Couette cell*

Previous Models for Rodlike Micellar Solutions

- •Johnson-Segalmann-Olmsted model (Olmsted *et al.*, J. Rheol., 2000)
- •Giesekus model with stress-driven diffusion (Helgeson *et al.*, J. Rheol., 2009)
- •Vasquez-Cook-McKinley (VCM) model (Vasquez *et al.*,JNNFM., 2007; Zhou *et al.*, accepted, 2012)

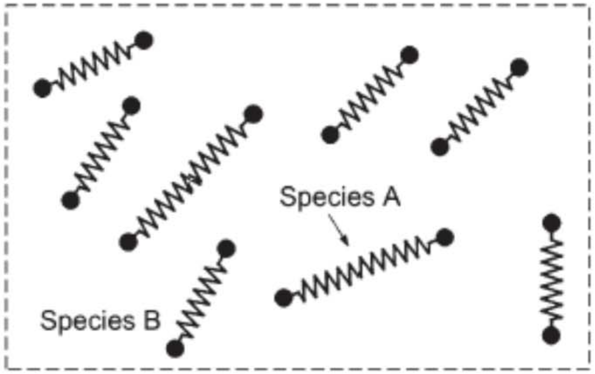


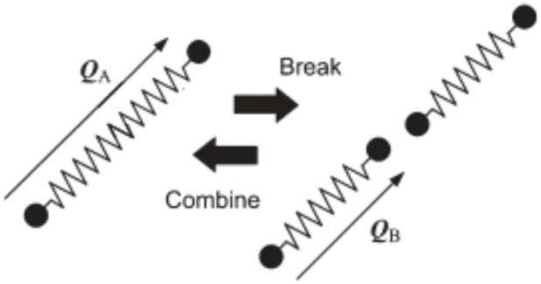
Cromer et al. (2011) JNNFM

VCM Central Concept: A -> B Reaction

Two-species represenation of population:

- Species A ("longer chains")
- Species B ("shorter chains")





Source: Yamamoto & Sawa (2011) JSRJ

System variables

Number Densities: $n_A = {}^{\rho_A}\!/\!_{M_A} N_A$; $n_B = {}^{\rho_B}\!/\!_{M_B} N_A$

Conformation Tensor Densities: $C_A = n_A \mathbf{c}_A$; $C_B = n_B \mathbf{c}_B$; $\mathbf{c}_i = \langle \mathbf{Q}_i \mathbf{Q}_i \rangle$

$\langle \mathbf{Q}_i \mathbf{Q}_i \rangle$ is the second moment of the end-to-end connection vector, $\mathbf{Q}_i$, for component i

Momentum Density: $\mathbf{M}=\rho\mathbf{v}$; $\rho=\rho_A+\rho_B+\rho_S$

General reaction kinetics in multicomponent systems

- Assume that the system:
  - involves *n* components, optionally with internal structure and
  - participates in *l* chemical reactions
- For each component, *i* = 1, 2, … *n*, the following primary variables are defined:
  - the mass density, ρ_i
  - the momentum density, $\mathbf{m}^i$, $\mathbf{m}^i = \rho_i \boldsymbol{v}^i$
  - (optionally) the internal structural tensor parameter density, $\mathbf{C}^i$, $\mathbf{C}^i = n_i\, \mathbf{c}^i$

where:

$\mathbf{v}^i$ is the mass-based velocity of component i

$n_i = {\rho_i}/{M_i}\, N_A$ is the number density of component i

$\mathbf{c}^i$ is the conformation tensor of component i; $\mathbf{c}^i = \left\langle \mathbf{Q}^i \mathbf{Q}^i \right\rangle$

$\left\langle \mathbf{Q}^i \mathbf{Q}^i \right\rangle$ is the second moment of the end-to-end connection vector, $\mathbf{Q}^i$, for component i

NET Extension for Chemical Reaction Rates

- It preserves standard transition theory kinetics that assigns for the corresponding forward (-) and reverse (+) flux of the reaction *I*, an Arhenius dependence on the corresponding affinity:

$$J_I^{\mp} = k_I\left(P,T\right)\exp\left(-\frac{A_I^{\mp}}{RT}\right)$$

- However, a generalized affinity is proposed in order to also accommodate other, nonequilibrium, changes associated with the reaction *I*, such as momentum and conformation (for entropy one needs a more general (GENERIC) formulation):

$$A_I^{\mp} = -\sum_{k=1}^{n}\gamma_{Ik}^{\mp}M_k\left(\frac{\delta H}{\delta\rho_k}+\frac{m_\alpha^k}{\rho_k}\left(\frac{\delta H}{\delta m_\alpha^k}\right)_G+\frac{C_{\alpha\beta}^k}{\rho_k}\frac{\delta H}{\delta C_{\alpha\beta}^k}\right)$$

where $\left(\frac{\delta H}{\delta m_\alpha^k}\right)_G$ represents the Galilean invariant contribution:

$$\left(\frac{\delta H}{\delta m_\alpha^k}\right)_G \equiv v_\alpha^k - v_\alpha = \frac{\delta H}{\delta m_\alpha^k}-\frac{\delta H}{\delta m_\alpha} = \frac{\delta H}{\delta m_\alpha^k}-\sum_{m=1}^{n}\frac{\rho_m}{\rho}\frac{\delta H}{\delta m_\alpha^m}$$

Corresponding Dissipation Bracket*

$$
\begin{aligned}
\left[F,H\right]_I = {} & J_I^- \left(-\sum_{k=1}^{n} \gamma_{Ik}^- M_k \left(\frac{\delta F}{\delta \rho_k} + \frac{m_\alpha^k}{\rho_k} \left(\frac{\delta F}{\delta m_\alpha^k} \right)_G + \frac{C_{\alpha\beta}^k}{\rho_k} \frac{\delta F}{\delta C_{\alpha\beta}^k} \right.\right. \\
& \left.\left. - \frac{1}{\sum_{k'=1}^{n} \gamma_{Ik'}^+ M_{k'}} \sum_{k''=1}^{n} \gamma_{Ik''}^+ M_{k''} \left(\frac{\delta F}{\delta \rho_{k''}} + \frac{m_\alpha^k}{\rho_k} \left(\frac{\delta F}{\delta m_\alpha^{k''}} \right)_G + \frac{C_{\alpha\beta}^k}{\rho_k} \frac{\delta F}{\delta C_{\alpha\beta}^{k''}} \right) \right) \right) \\
& + J_I^+ \left(-\sum_{k=1}^{n} \gamma_{Ik}^+ M_k \left(\frac{\delta F}{\delta \rho_k} + \frac{m_\alpha^k}{\rho_k} \left(\frac{\delta F}{\delta m_\alpha^k} \right)_G + \frac{C_{\alpha\beta}^k}{\rho_k} \frac{\delta F}{\delta C_{\alpha\beta}^k} \right.\right. \\
& \left.\left. - \frac{1}{\sum_{k'=1}^{n} \gamma_{Ik'}^- M_{k'}} \sum_{k''=1}^{n} \gamma_{Ik''}^- M_{k''} \left(\frac{\delta F}{\delta \rho_{k''}} + \frac{m_\alpha^k}{\rho_k} \left(\frac{\delta F}{\delta m_\alpha^{k''}} \right)_G + \frac{C_{\alpha\beta}^k}{\rho_k} \frac{\delta F}{\delta C_{\alpha\beta}^{k''}} \right) \right) \right)
\end{aligned}
$$

- It duly satisfies Onsager’s reciprocity relations
- It does not affect the overall momentum equation
- It redistributes among the products the excess momentum and conformation

* to within an entropy correction term, not needed for isothermal processes

NET Implementation for Homogeneous Micellar System

Breakage & reformation kinetics

Approach: Extension of chemical reaction kinetics in (Beris & Edwards, Thermodynamics of Flowing Systems, 1994) to viscoelastic systems

Stoichiometric equation

$$\mathrm{A} \underset{c_B}{\overset{c_A}{\rightleftharpoons}} 2\,\mathrm{B}$$

Flux: $$J^{\mp} = k \exp\left(-\frac{A^{\mp}}{RT}\right)$$

Affinity: $$A^{\mp} = -\Sigma_k \gamma_k^{\mp} M_k \left(\underbrace{\frac{\delta H}{\delta \rho_k}}_{\rho_k\text{-transfer}} + \underbrace{\frac{C^k_{\alpha\beta}}{\rho_k}\,\frac{\delta H}{\delta C^k_{\alpha\beta}}}_{C^k_{\alpha\beta}\text{-transfer}} \right) \qquad (k = \mathrm{A}, \mathrm{B})$$

Key Element: Dissipation Induced by the Reaction

Dissipation bracket

$$
\begin{aligned}
[F,H] = \int_\Omega J^- \Bigg(-\Sigma_k \gamma_k^- M_k \Bigg(& \frac{\delta F}{\delta \rho_k} + \frac{C^k_{\alpha\beta}}{\rho_k} \frac{\delta F}{\delta C^k_{\alpha\beta}} \\
& - \frac{1}{\Sigma_{k'} \gamma^+_{k'} M_{k'}} \Sigma_{k''} \gamma^+_{k''} M_{k''} \left(\frac{\delta F}{\delta \rho_{k''}} + \frac{C^k_{\alpha\beta}}{\rho_k} \frac{\delta F}{\delta C^{k''}_{\alpha\beta}} \right) \Bigg) \Bigg) \, \mathrm{d}^3 x \\
+ \int_\Omega J^+ \Bigg(-\Sigma_k \gamma_k^+ M_k \Bigg(& \frac{\delta F}{\delta \rho_k} + \frac{C^k_{\alpha\beta}}{\rho_k} \frac{\delta F}{\delta C^k_{\alpha\beta}} \\
& - \frac{1}{\Sigma_{k'} \gamma^-_{k'} M_{k'}} \Sigma_{k''} \gamma^-_{k''} M_{k''} \left(\frac{\delta F}{\delta \rho_{k''}} + \frac{C^k_{\alpha\beta}}{\rho_k} \frac{\delta F}{\delta C^{k''}_{\alpha\beta}} \right) \Bigg) \Bigg) \, \mathrm{d}^3 x
\end{aligned}
$$

$(k = \mathrm{A}, \mathrm{B}; k' = \mathrm{A}, \mathrm{B}; k'' = \mathrm{A}, \mathrm{B})$

Transfer of properties

🟥 donor

🟩 receiver

Final Equations

Model (without momentum & stress equations)

$$\frac{\partial n_{\mathrm{A}}}{\partial t} = -\nabla_\alpha\left(v_\alpha n_{\mathrm{A}}\right) - c_{\mathrm{A}} n_{\mathrm{A}} + \frac{1}{2} c_{\mathrm{B}} n_{\mathrm{B}}^2$$

$$\frac{\partial n_{\mathrm{B}}}{\partial t} = -\nabla_\alpha\left(v_\alpha n_{\mathrm{B}}\right) + 2 c_{\mathrm{A}} n_{\mathrm{A}} - c_{\mathrm{B}} n_{\mathrm{B}}^2$$

$$\frac{\partial C^{\mathrm{A}}_{\alpha\beta}}{\partial t} = -\nabla_\gamma\left(v_\gamma C^{\mathrm{A}}_{\alpha\beta}\right) + C^{\mathrm{A}}_{\gamma\alpha}\nabla_\gamma v_\beta + C^{\mathrm{A}}_{\gamma\beta}\nabla_\gamma v_\alpha - \frac{1}{\lambda_{\mathrm{A}}}\left(C^{\mathrm{A}}_{\alpha\beta} - \frac{n_{\mathrm{A}} k_{\mathrm{B}} T}{K_{\mathrm{A}}}\delta_{\alpha\beta}\right) - c_{\mathrm{A}} C^{\mathrm{A}}_{\alpha\beta} + c_{\mathrm{B}} n_{\mathrm{B}} C^{\mathrm{B}}_{\alpha\beta}$$

$$\frac{\partial C^{\mathrm{B}}_{\alpha\beta}}{\partial t} = -\nabla_\gamma\left(v_\gamma C^{\mathrm{B}}_{\alpha\beta}\right) + C^{\mathrm{B}}_{\gamma\alpha}\nabla_\gamma v_\beta + C^{\mathrm{B}}_{\gamma\beta}\nabla_\gamma v_\alpha - \frac{1}{\lambda_{\mathrm{B}}}\left(C^{\mathrm{B}}_{\alpha\beta} - \frac{n_{\mathrm{B}} k_{\mathrm{B}} T}{K_{\mathrm{B}}}\delta_{\alpha\beta}\right) + c_{\mathrm{A}} C^{\mathrm{A}}_{\alpha\beta} - c_{\mathrm{B}} n_{\mathrm{B}} C^{\mathrm{B}}_{\alpha\beta}$$

$$c_{\mathrm{A}} = c_{\mathrm{Aeq}} \frac{\exp\left(\frac{\mathrm{tr}\,\sigma^{\mathrm{A}}}{2 n_{\mathrm{A}} k_{\mathrm{B}} T}\right)}{\sqrt{\det\left(\frac{K_{\mathrm{A}} \mathbf{C}^{\mathrm{A}}}{n_{\mathrm{A}} k_{\mathrm{B}} T}\right)}} \qquad c_{\mathrm{B}} = c_{\mathrm{Beq}} \frac{\exp\left(\frac{\mathrm{tr}\,\sigma^{\mathrm{B}}}{n_{\mathrm{B}} k_{\mathrm{B}} T}\right)}{\det\left(\frac{K_{\mathrm{B}} \mathbf{C}^{\mathrm{B}}}{n_{\mathrm{B}} k_{\mathrm{B}} T}\right)}$$

Parameters

Dissipative terms:

breakage

reformation

relaxation

Model Non-Dimensionalization & Parameters

Non-dimensionalization

Time: $\widetilde{t} = t/\lambda_{\text{eff}}$ Length: $\widetilde{x}_\alpha = x_\alpha/H$ Pressure: $\widetilde{p} = p/G_0$

Number density: $\widetilde{n}_k = n_k/n_{\text{Aeq}}\ (k = \text{A}, \text{B})$

Conformation: $\widetilde{c}^k_{\alpha\beta} = (K_\text{A}/(k_\text{B}T)\, c^k_{\alpha\beta}\ (k = \text{A}, \text{B})$

Stress: $\widetilde{\sigma}^k_{\alpha\beta} = \sigma^k_{\alpha\beta}/G_0\ (k = \text{A}, \text{B}, \text{total}, \text{solvent})$

Dimensionless numbers

Reynolds number: $Re = \rho H^2/\left(\lambda^2_{\text{eff}} G_0\right)$

Deborah number: $De = \lambda_{\text{eff}} V/H$

Viscosity ratio: $\beta = \eta_s/\eta_0$ Relaxation time ratio: $\varepsilon = \lambda_\text{B}/\lambda_\text{A}$

Reaction rate: $\widetilde{c}_{\text{Aeq}} = \lambda_\text{A} c_{\text{Aeq}}$

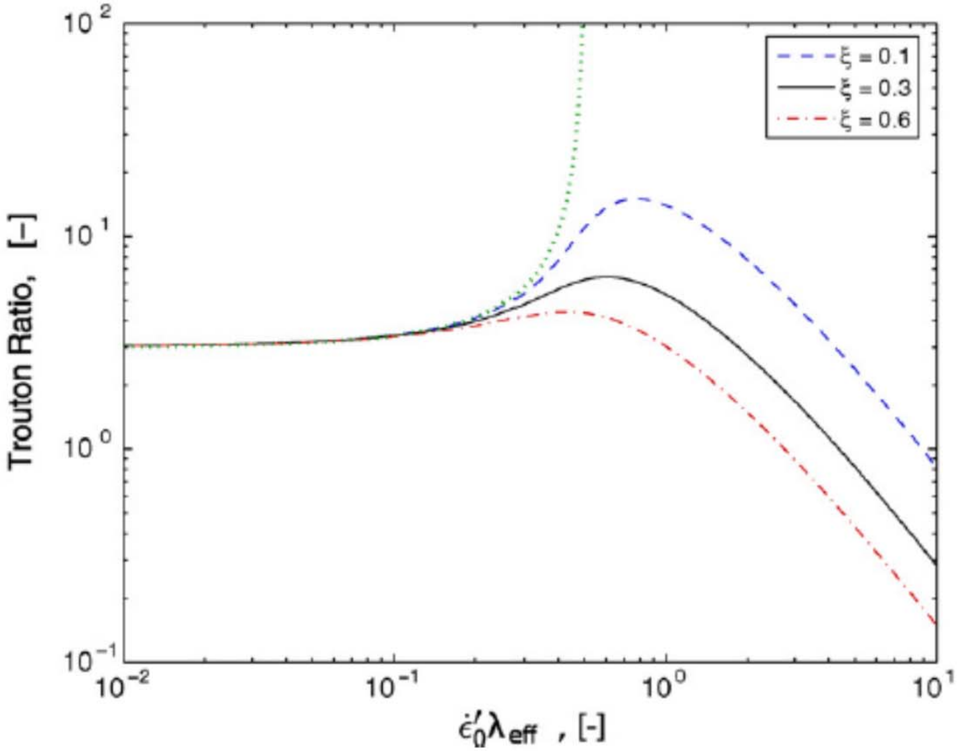
Reformation rate: $\widetilde{c}_{\text{Beq}} = \lambda_\text{A} c_{\text{Beq}} n_{\text{Aeq}}$

Comparison with the VCM Model

Impact of parameter ξ in extension (Vasquez *et al.*, JNNFM, 2007)

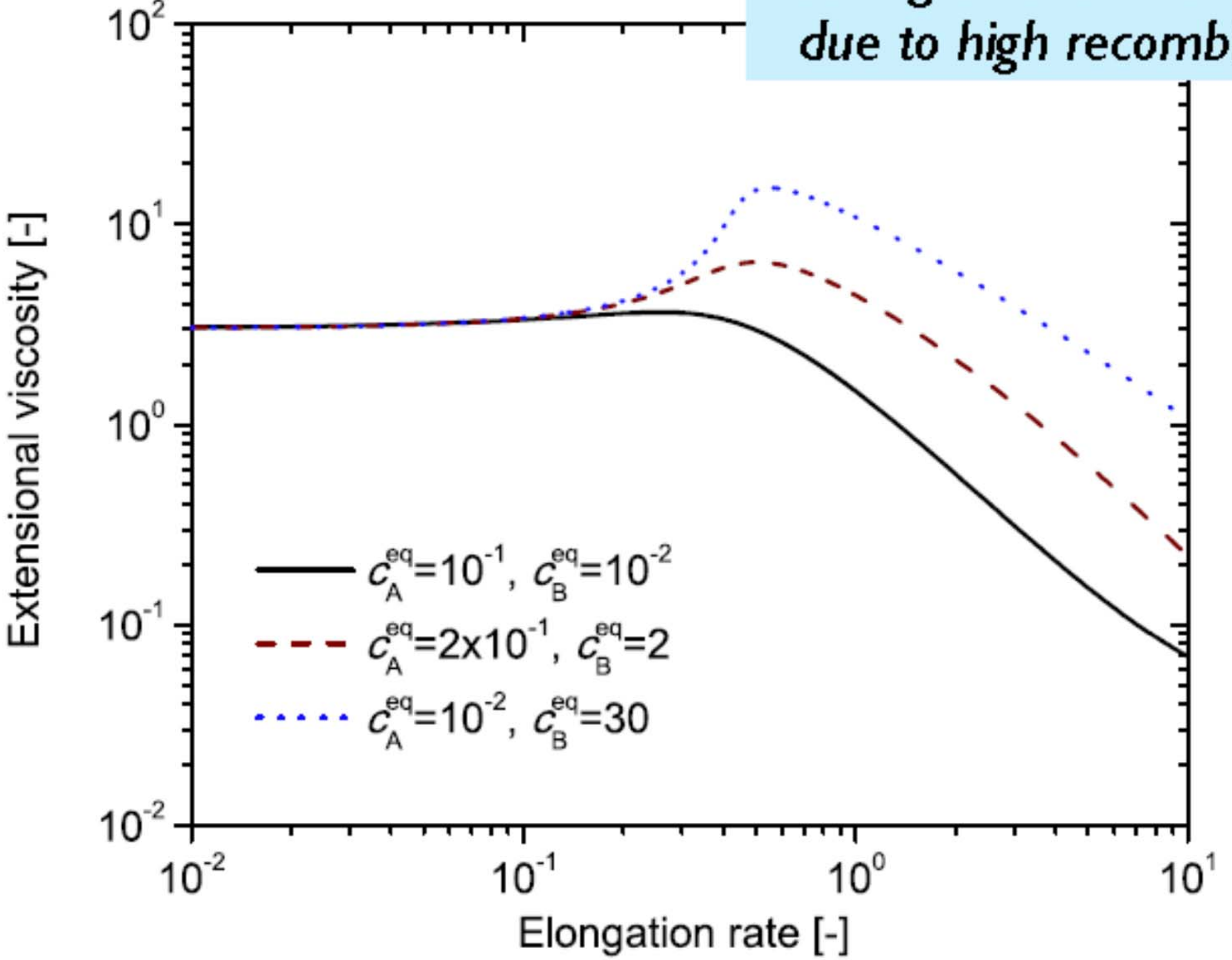
additional parameter

$$c_{\mathrm{A}} = c_{\mathrm{Aeq}} + \frac{1}{3}\xi\left(\nabla\mathbf{v} + \nabla\mathbf{v}^{\mathrm{T}}\right) : \frac{\mathbf{C}^{A}}{n_{A}} \qquad c_{\mathrm{B}} = c_{\mathrm{Beq}}$$



New Model Predictions

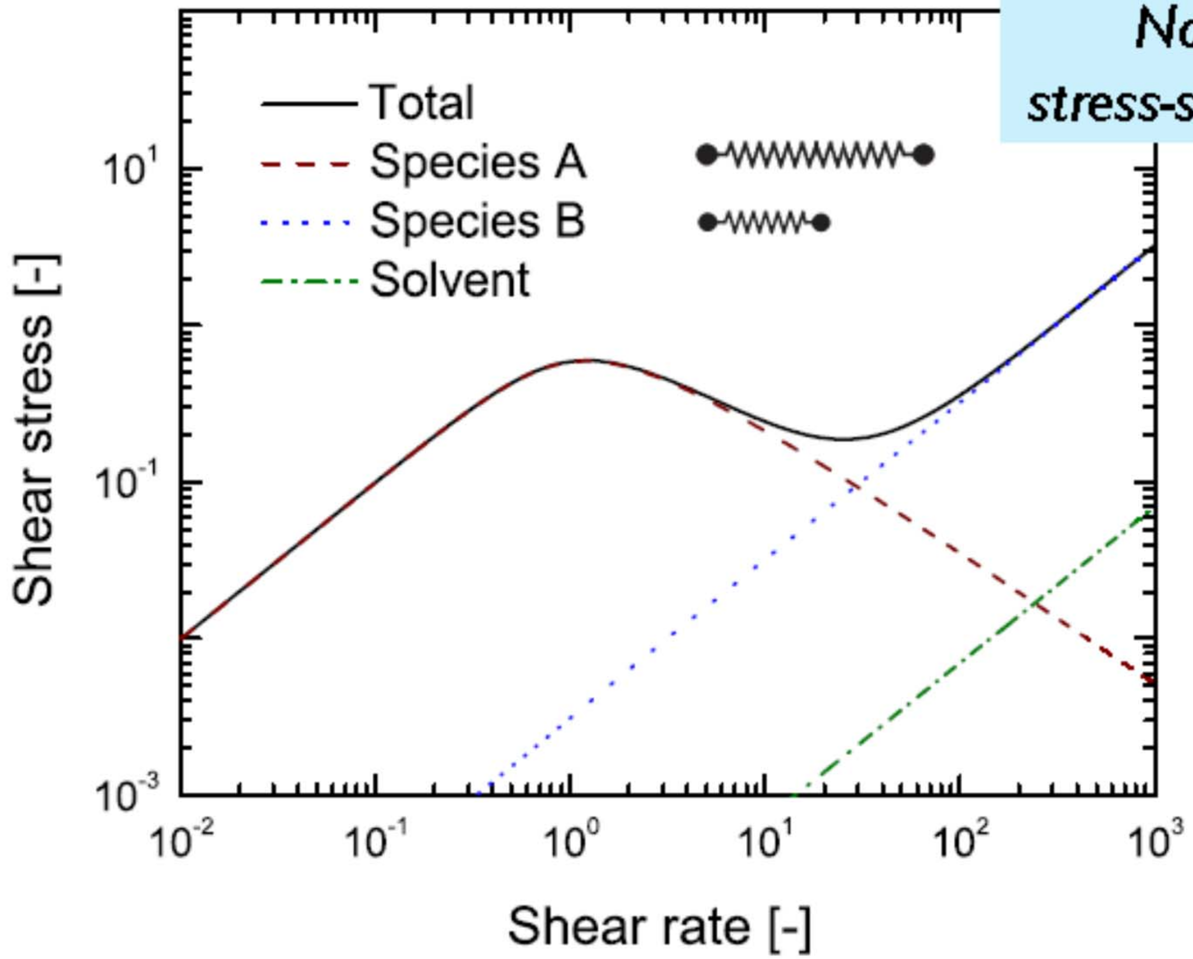
Parameters: $\beta = 7 \times 10^{-5}$; $\varepsilon = 10^{-4}$



Strong extension thickening due to high recombination!

Homogeneous Shear Flow Predictions -1

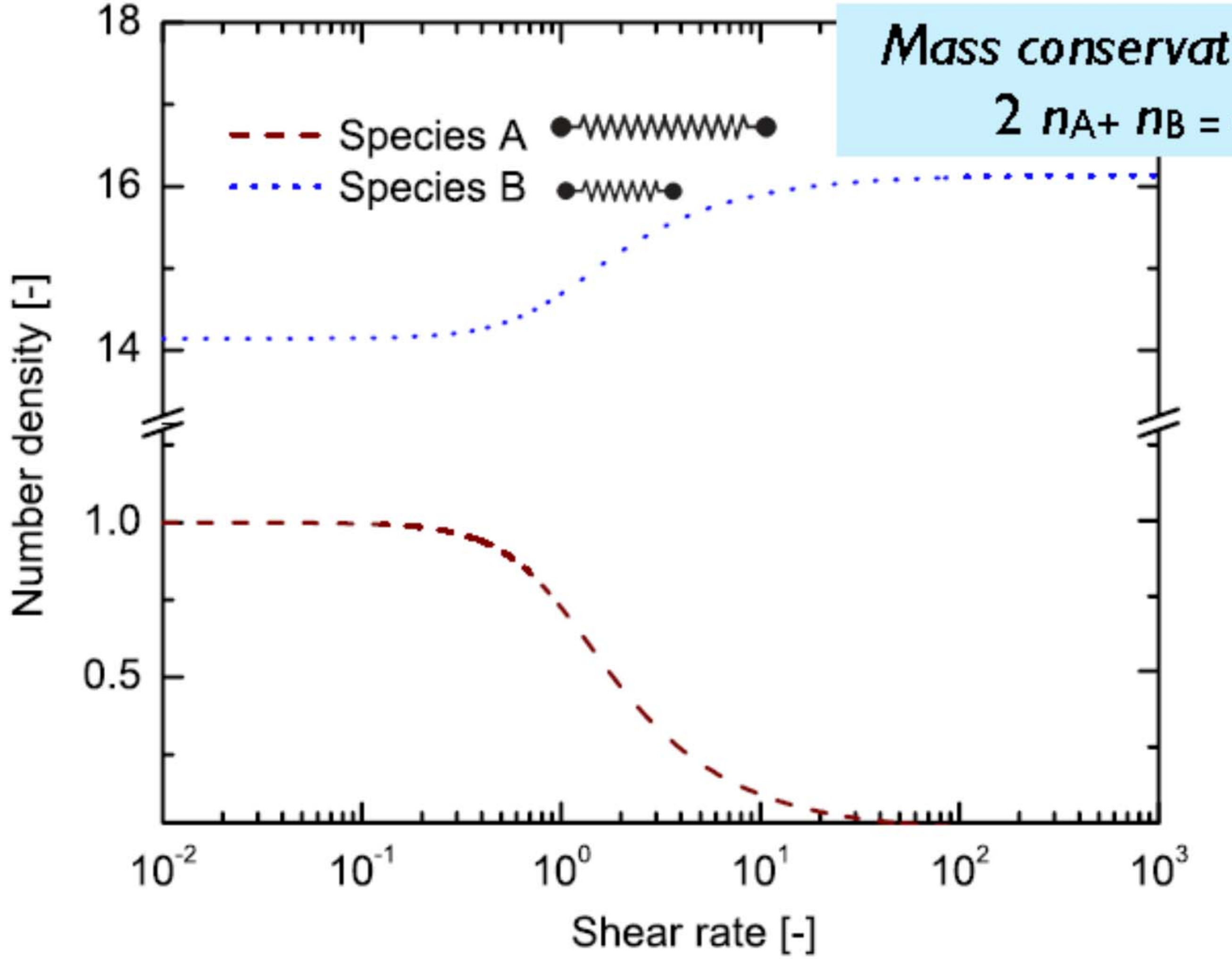
Parameters: $\beta = 7 \times 10^{-5}\,;\, \varepsilon = 10^{-4}\,;\, \widetilde{c}_{\mathrm{Aeq}} = 1\,;\, \widetilde{c}_{\mathrm{Beq}} = 10^{-2}$



Non-monotone stress-stain relationship!

Homogeneous Shear Flow Predictions -2

Parameters: $\beta = 7 \times 10^{-5}\,;\ \varepsilon = 10^{-4}\,;\ \widetilde{c}_{\mathrm{Aeq}} = 1\,;\ \widetilde{c}_{\mathrm{Beq}} = 10^{-2}$



Mass conservation requires

$2\ n_{A} + n_{B} = \text{const.}$

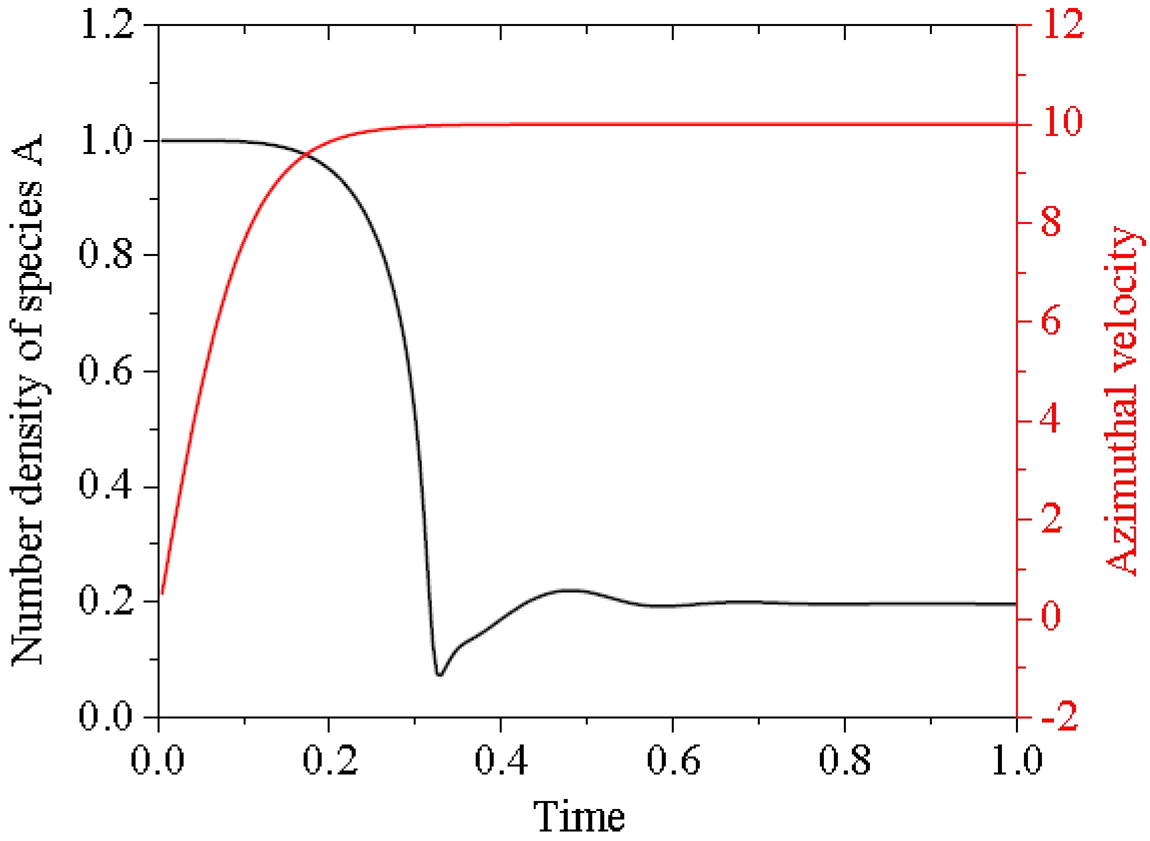
Start-up of Couette Flow Predictions -1

$p = 0.1,\ E^{-1} = 10^{-2},\ \epsilon = 4.5 \times 10^{-4},\ \tilde{c}_{\mathrm{Aeq}} = 4.7,\ \tilde{c}_{\mathrm{Beq}} = 7.3,\ \beta = 7 \times 10^{-5}$

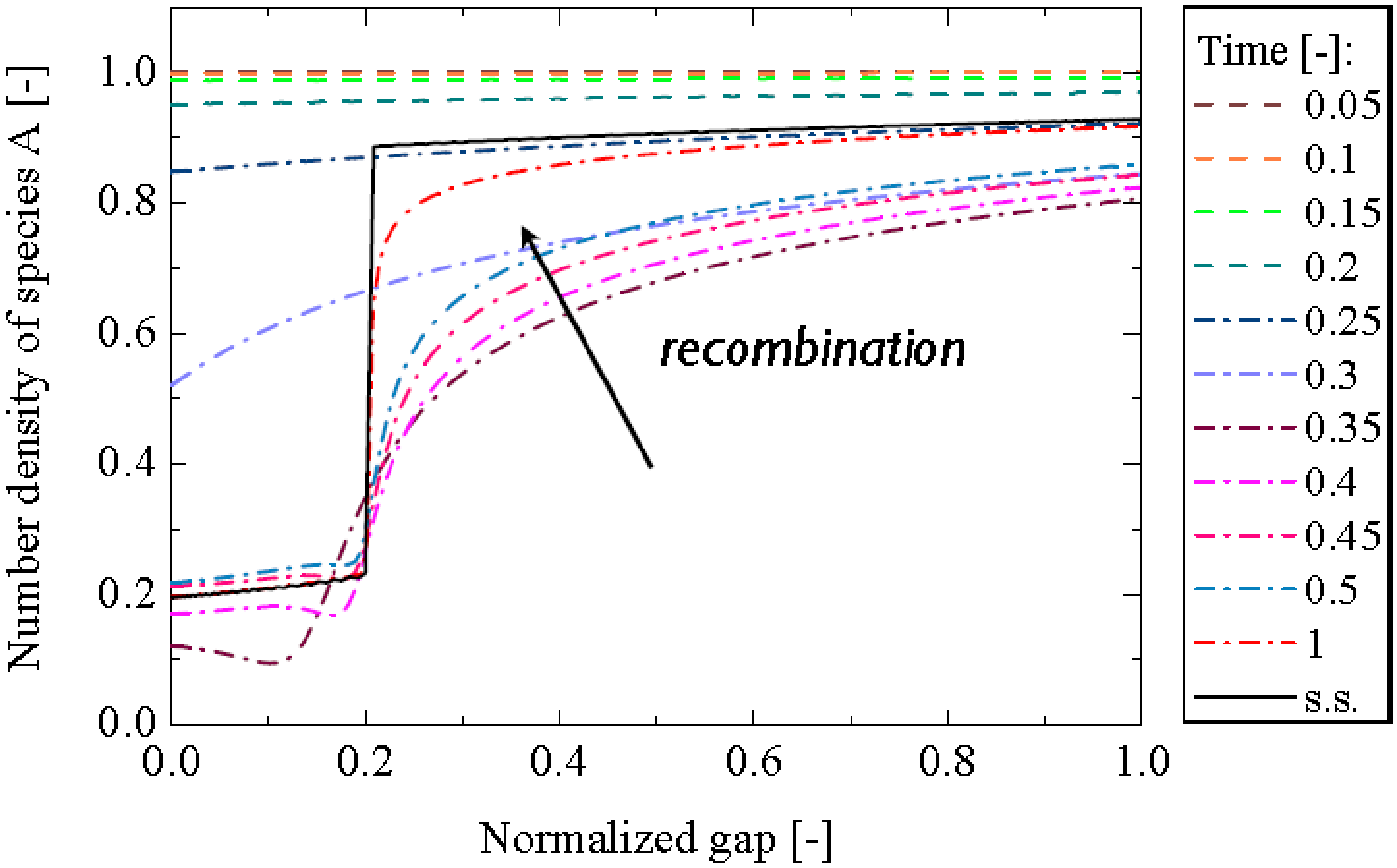
(Zhou *et al.*., SIAM J. Appl. Math 2012)

<u>Ramp-up experiment:</u> $v_i = De\,\tanh(10t),\ v_o = 0$

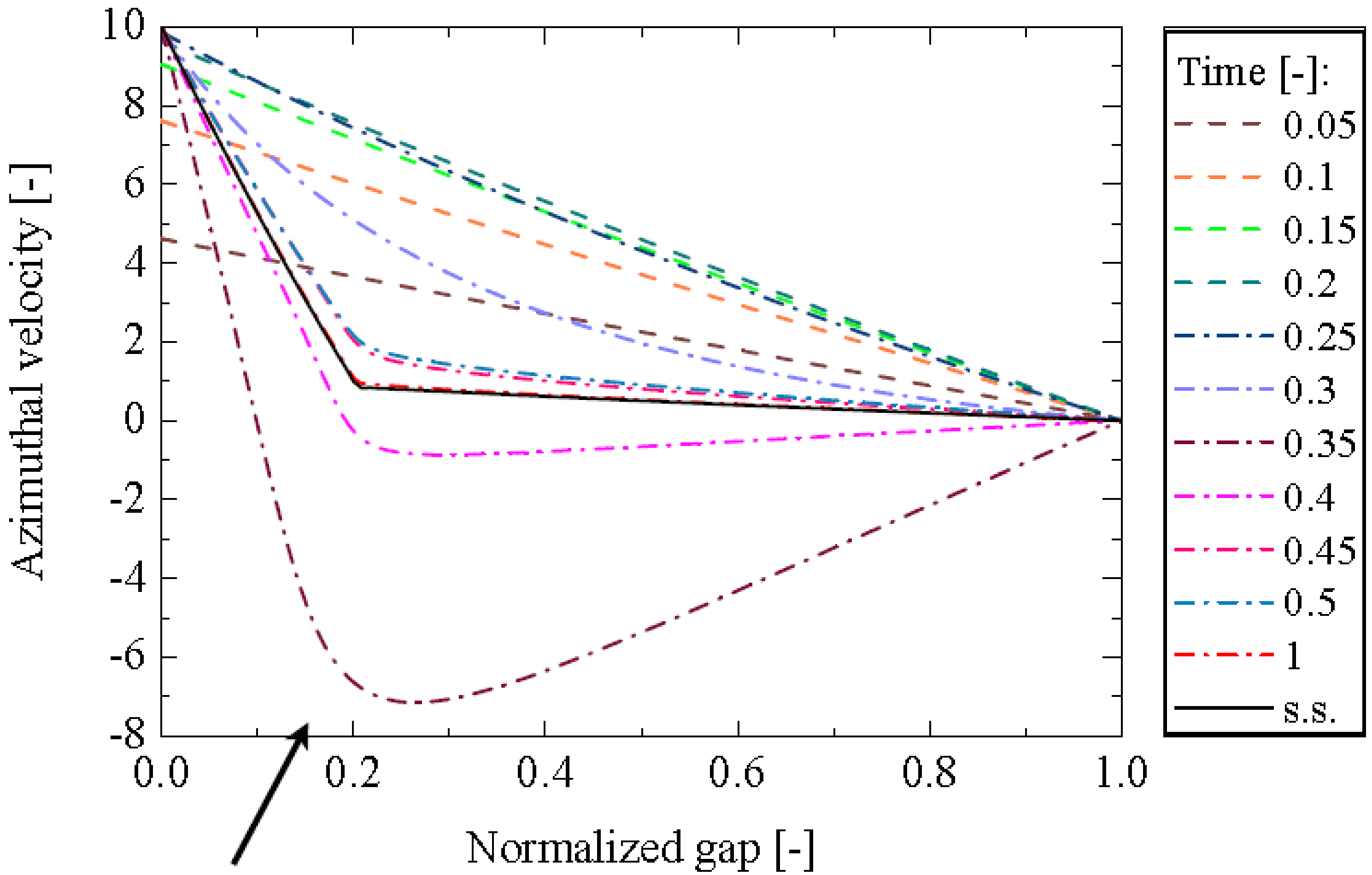
Dynamics at the inner wall:



Start-up of Couette Flow Predictions -2



Start-up of Couette Flow Predictions -3

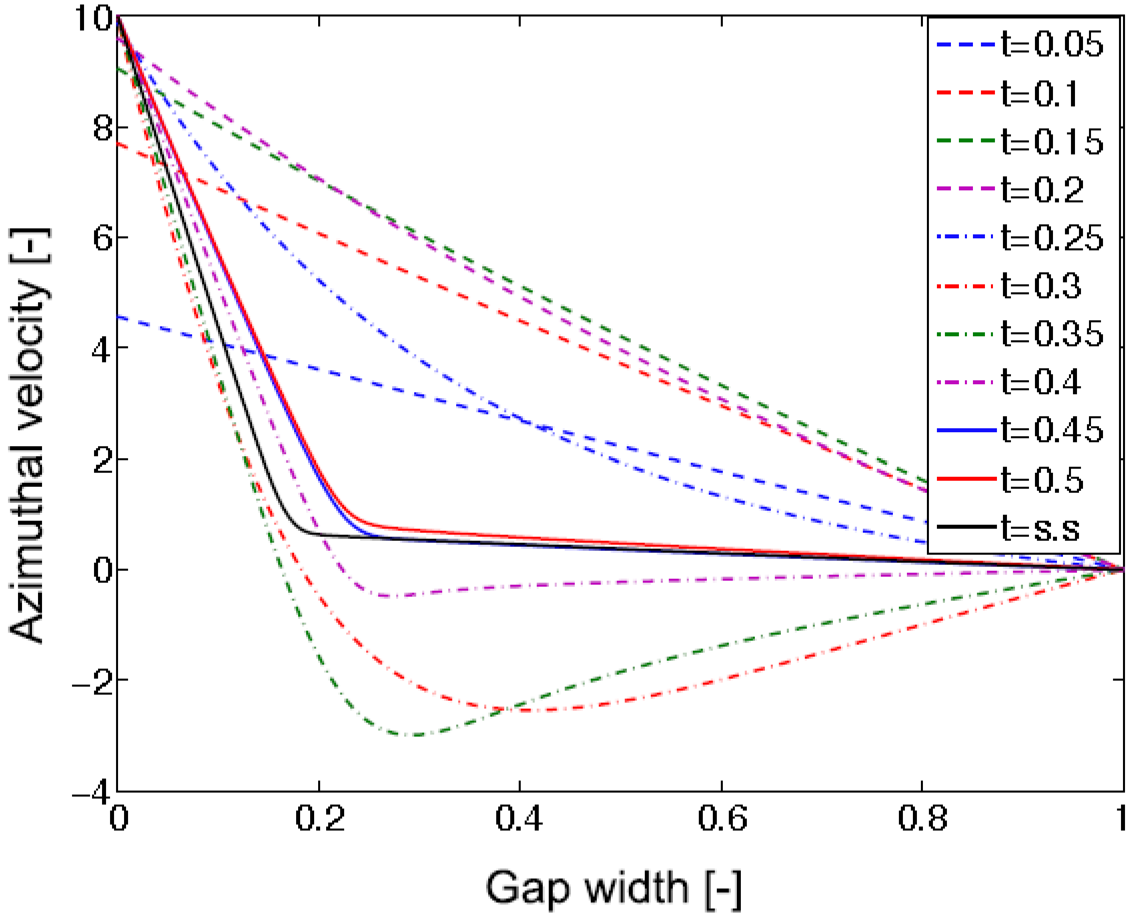


strong elastic recoil

Ark *et al.* (2012) Langmuir

VCM Predictions

$p = 0.1,\ \delta = \times 10^{-3},\ E^{-1} = 0,\ \varepsilon = 1.5 \times 10^{-3},\ \tilde{c}_{\mathrm{Aeq}} = 0.9,\ \tilde{c}_{\mathrm{Beq}} = 1.4,\ \beta = 7 \times 10^{-5},\ \xi = 0.7$



Zhou *et al.* (2012) SIAM J. Appl. Math

Rodlike Shear-Banding Micelles: Conclusions

- We have corrected and significantly extended the description within NET that first appeared in our previous work [Beris and Edwards, 1994] of chemical reactions taking into account momentum and (for systems with internal structure) conformation transfers during each elementary reaction

- The new description allows for reaction rates that are conformation-dependent:
  - This can explain some very recent experiments on DNA scission under extension [Muller et al., ICR Lisbon, 2012]
  - The new description has been applied to the modeling of a system of concentrated rodlike micelles:
    - The new model produces very similar, non-monotonic shear stress vs. shear rate, predictions for homogeneous shear flows, while being thermodynamically consistent and requiring fewer parameters
    - The new model shows much more significant recoil than the VCM in the cylindrical Couette flow

- More recent work: Extension of the model to account for mass diffusion, along the lines of the two-fluid approach: Presentation at 14:00 today