

# NonEquilibrium Thermodynamics of Flowing Systems: 2

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## Schedule:

1. 4/13/07, 9:30 am Introduction. One mode viscoelasticity.
2. 4/13/07, 10:15 am **Coupled transport: Two-fluid model\*.**
3. 4/14/07, 2:00 pm Modeling under constraints: Liquid crystals.
4. 4/14/07, 3:00 am Non-homogeneous systems: Surface effects.

\*Following the development in "Beris and Edwards, 1994, Section 9.2"

# Coupled Transport 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

# Single Fluid Model: Variables



- For an incompressible, inhomogeneous (variable polymer concentration,  $n$ =chain number density is variable) system we have
  - $\rho_1$ , 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,  $\mathbf{c} = k_B T / K$  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:

$$A = \int_V \left( \frac{1}{2} \rho v^2 + a_e + a_m \right) dV$$

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

$$a_e = \frac{1}{2} \left( K \operatorname{tr} \mathbf{C} - nk_B T \log \left( \det \left( \frac{(K\mathbf{C})}{(nk_B T)} \right) \right) \right)$$

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  $\varphi$  is the polymer volume fraction:

$$\varphi = \frac{(nN)}{(nN + n_s)}$$

# 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:

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

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

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

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

# Single Fluid: Dissipation Structure



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

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

# Single Fluid: Final Equations



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

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

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

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

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



# 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 with 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: $\mathbf{D} = -1/2\mathbf{E} = 1/4\mathbf{B} = \mathbf{D}\delta$



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

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

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

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

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

# Two- Fluid Model: Variables



- For an incompressible, inhomogeneous (variable polymer concentration,  $n$ =chain number density is variable) system we have (keeping  $\rho = \rho_1 + \rho_2 = \text{constant}$ )
  - $\rho_1$ , the polymer density ( $n = N_A \rho_1 / MW_1$ );  $\rho_2$ , 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
    - $\mathbf{C} = \langle \mathbf{R}\mathbf{R} \rangle$  (second moment of the end-to-end distribution function) =  $n\mathbf{c}$
- At equilibrium,  $\mathbf{c} = k_B T / K$  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:

$$A = \int_V \left( \frac{1}{2} \rho_1 v_1^2 + \frac{1}{2} \rho_2 v_2^2 + a_e + a_m \right) dV$$

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

$$a_e = \frac{1}{2} \left( K \operatorname{tr} \mathbf{C} - nk_B T \log \left( \frac{\det \left( \frac{(K\mathbf{C})}{(nk_B T)} \right)}{(nk_B T)} \right) \right)$$

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  $\varphi$  is the polymer volume fraction:

$$\varphi = \frac{(nN)}{(nN + n_s)}$$

# 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

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

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

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

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

# Transformation of Variables



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

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

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

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

$$\nabla \cdot \mathbf{v} = 0 \quad \frac{\partial \rho_-}{\partial t} + v_\alpha \nabla_\alpha \rho_- + \nabla_\alpha \left( (1 - \varphi) \Delta v_\alpha \rho_- \right) = 0$$

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

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

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

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

# Two-Fluid: Dissipation Structure

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

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

# Two- Fluid: Final Momentum and Conformation Equations



$$\frac{\partial \mathbf{g}_{+\alpha}}{\partial t} + \nabla_{\beta} (v_{1\beta} \mathbf{g}_{1\alpha} + v_{2\beta} \mathbf{g}_{2\alpha}) + \mathbf{g}_{1\beta} \nabla_{\alpha} v_{1\beta} + \mathbf{g}_{2\beta} \nabla_{\alpha} v_{2\beta} =$$

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

$$\frac{\partial \mathbf{g}_{-\alpha}}{\partial t} + (1 - \varphi) \nabla_{\beta} (v_{1\beta} \mathbf{g}_{1\alpha}) - \varphi \nabla_{\beta} (v_{2\beta} \mathbf{g}_{2\alpha}) + (1 - \varphi) \mathbf{g}_{1\beta} \nabla_{\alpha} v_{1\beta} - \varphi \mathbf{g}_{2\beta} \nabla_{\alpha} v_{2\beta} =$$

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

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



# 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:

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

# 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

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- **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)