On the consistent modeling of shear-thickening polymer solutions

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MODEL DERIVATION

The Hamiltonian of the system: The mechanical part of the system's Hamiltonian is given by[1]

$$H_m = K_{en}(\mathbf{x}) + A(\mathbf{x}), \quad\quad (SM.1)$$

where,

$$K_{en}(\mathbf{x}) = \int \frac{\boldsymbol{M}^2}{2\rho} dV, \qu\quad (SM.2)$$

represents the kinetic energy of the system, $K_{en}(\mathbf{x})$, whereas:

$$A(\mathbf{x}) = \int a(\mathbf{x}) \, dx$$

$$= \frac{nk_B T}{2}\Big[\int [\Phi(I_1) - \ln\det\tilde{\mathbf{c}}] \, dV \quad\quad (SM.3a)$$

$$+ \int [(1-\lambda)\ln(1-\lambda) + \lambda] \, dV\Big],$$

represents the system's Helmholtz free energy with $a(\mathbf{x})$ the Helmholtz free energy density. The potential term $\Phi(I_1)$ in the first integral accounts for contributions to the free energy associated with molecular stretching and is given as

$$\Phi(I_1) = -(b-3)\ln\left(1 - \frac{I_1 - 3}{b-3}\right) \Rightarrow h(I_1) \equiv \frac{\partial\Phi}{\partial I_1} = \frac{b-3}{b-I_1}, \qu\quad (SM.3b)$$

Here, I_1 is the first invariant (the trace) of the tensor $\tilde{\mathbf{c}}$ for which $\tilde{\mathbf{c}}_{\text{eq}} = \mathbf{I}$, and $h(I_1)$ is the spring force law. Note the correction presented in Eq. (SM.3b) relative to Eq. (7a) of Stephanou et al.[2] Also, n is the number density of polymer chains, k_B the Boltzmann constant, and T the temperature. The number density, n, and the mass density are related via $n = (\rho/M)N_{Av}$, where ρ denotes the segment molecular weight of each chain (i.e., a strictly monodisperse system is considered) and N_{Av} is Avogadro's constant. The second integral in Eq. (SM.3) indicates the ideal entropy of mixing for polymer segments that are not associated with the network with an extra term added to ensure that the mixing free energy maximizes under no flow conditions, i.e., when $\lambda = 0$.[3,4] This term can be obtained by substituting λ with $1 - \lambda$ in the ideal entropy of mixing term in Eq. (5) of Stephanou and Georgiou.[4]

The Poisson and dissipation brackets: For a system described by an unconstrained conformation tensor $\mathbf{c}$, the expression for the Poisson bracket is well known (see, e.g., Refs.[1] and [5]):

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

$$- \int c_{\gamma a} \left[\frac{\delta G}{\delta c_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta F}{\delta M_\beta} \right) - \frac{\delta F}{\delta c_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta G}{\delta M_\beta} \right) \right] dV \qquad \text{(SM.4a)}$$

$$- \int c_{\gamma\beta} \left[\frac{\delta G}{\delta c_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta F}{\delta M_\alpha} \right) - \frac{\delta F}{\delta c_{\alpha\beta}} \nabla_\gamma \left(\frac{\delta G}{\delta M_\alpha} \right) \right] dV.$$

Note that here, and throughout this SI, Einstein's summation convention for repeated Greek indices is employed. Furthermore, the following expression for the Poisson bracket associated with the scalar structural variable λ is considered:[3–5]

$$\{F, G\}_\lambda = -\int \left[\frac{\delta F}{\delta \lambda} \nabla_\gamma \left(\lambda \frac{\delta G}{\delta M_\gamma} \right) - \frac{\delta G}{\delta \lambda} \nabla_\gamma \left(\lambda \frac{\delta F}{\delta M_\gamma} \right) \right] dV \qquad \text{(SM.4b)}$$

$$-\int g_{\alpha\beta}\left[\frac{\delta G}{\delta\lambda}\nabla_\beta\left(\frac{\delta F}{\delta M_a}\right)-\frac{\delta F}{\delta\lambda}\nabla_\beta\left(\frac{\delta G}{\delta M_a}\right)\right]dV.$$

The last integral in Eq. (SM.4b) introduces a general coupling between the scalar structural variable and the velocity gradient through the tensor $\mathbf{g}$.[5] As the Poisson bracket has to fulfill the Jacobi identity, certain restrictions have to be imposed on it. Ottinger[5] considered the most general expression for $\mathbf{g}$ according to the Cayley-Hamilton theorem, $\mathbf{g}=g_1\tilde{\mathbf{c}}+g_1\mathbf{I}+g_1\tilde{\mathbf{c}}^{-1}$. Here, in general, $g_k=g_k(\lambda,I_1,I_2,I_3),k=\{1,2,3\}$ and $I_1=\mathrm{tr}\tilde{\mathbf{c}},I_2=\mathrm{lndet}\tilde{\mathbf{c}}$, and $I_3=-\mathrm{tr}\tilde{\mathbf{c}}^{-1}$ are the three invariants of the dimensionless conformation tensor. Then, the following constraints should hold:

$$g_1\frac{\partial g_2}{\partial\lambda}-g_2\frac{\partial g_1}{\partial\lambda}=2\left(\frac{\partial g_1}{\partial I_2}-\frac{\partial g_2}{\partial I_1}\right),$$

$$g_1\frac{\partial g_3}{\partial\lambda}-g_3\frac{\partial g_1}{\partial\lambda}=2\left(\frac{\partial g_1}{\partial I_3}-\frac{\partial g_3}{\partial I_1}\right), \tag{SM.4c}$$

$$g_2\frac{\partial g_3}{\partial\lambda}-g_3\frac{\partial g_2}{\partial\lambda}=2\left(\frac{\partial g_2}{\partial I_3}-\frac{\partial g_3}{\partial I_1}\right),$$

Note that a check whether the Poisson bracket fulfills the Jacobi identity can also be performed using a computer-assisted method.[6] The complete Poisson bracket is then simply given as:

$$\{F,G\}=-\int\left[\frac{\delta F}{\delta M_\gamma}\nabla_\beta\left(M_\gamma\frac{\delta G}{\delta M_\beta}\right)-\frac{\delta G}{\delta M_\gamma}\nabla_\beta\left(M_\gamma\frac{\delta F}{\delta M_\beta}\right)\right]dV$$

$$+\{F,G\}_c+\{F,G\}_\lambda. \tag{SM.4d}$$

Next, for the dissipative bracket, we again choose a form that is frequently employed for a conformation tensor $\mathbf{c}$,

$$[F,G]_c=-\int\frac{\delta F}{\delta c_{\alpha\beta}}\Lambda^c_{\alpha\beta\gamma\varepsilon}\frac{\delta G}{\delta c_{\gamma\varepsilon}}dV. \tag{SM.5a}$$

which accounts for relaxation effects and is proportional to a fourth–rank relaxation tensor. Finally, the complete dissipation bracket is given as

$$[F, G]_{nec} = -\int \frac{\delta F}{\delta \lambda} \Lambda^\lambda \frac{\delta G}{\delta \lambda} dV - \int \nabla_\alpha \left(\frac{\delta G}{\delta M_\beta} \right) Q_{\alpha\beta\gamma\varepsilon} \nabla_\gamma \left(\frac{\delta G}{\delta M_\varepsilon} \right) dV \quad \text{(SM.5b)}$$

$$+[F, G]_c.$$

The first integral on the right-hand side accounts for relaxation effects for the scalar structural variable, whereas the last integral, proportional to the fourth–rank tensor **Q**, aims to add a Newtonian-like rheological behavior to the stress tensor that accounts for the solvent's contribution. Note that the subscript "nec", meaning "no entropy production correction," is added to the dissipation bracket to indicate that this dissipation bracket is without terms involving Volterra derivatives with respect to the entropy density, which can be omitted when one considers (as we do here) isothermal systems.[1] Then,

$$\dot{c}_{\alpha\beta,[1]} = -\Lambda^c_{\alpha\beta\gamma\varepsilon} \frac{\delta H_m}{\delta c_{\gamma\varepsilon}}, \quad \text{(SM.6a)}$$

$$\frac{D\lambda}{Dt} \equiv \frac{\partial \lambda}{\partial t} + \mathbf{u} \cdot \nabla \lambda = -\Lambda^\lambda \frac{\delta H_m}{\delta \lambda} + \boldsymbol{\kappa} : \mathbf{g}, \quad \text{(SM.6b)}$$

where we have defined the upper-convected time derivative:

$$\dot{c}_{\alpha\beta,[1]} \equiv \frac{\partial c_{\alpha\beta}}{\partial t} + u_\gamma \nabla_\gamma c_{\alpha\beta} - c_{\alpha\gamma} \nabla_\gamma u_\beta - \nabla_\gamma u_\alpha c_{\gamma\beta}, \quad \text{(SM.6c)}$$

the material time derivative defined in Eq. (SM.6c), and $\boldsymbol{\kappa} = (\nabla \mathbf{u})^T$ is the transposed velocity gradient. Finally, the stress tensor is given as,

$$\sigma_{\alpha\beta} = 2c_{\alpha\gamma} \frac{\delta A}{\delta c_{\beta\gamma}} + g_{\alpha\beta} \frac{\delta A}{\delta \lambda} + Q_{\alpha\beta\gamma\varepsilon} \nabla_\gamma u_\varepsilon, \quad \text{(SM.7)}$$

In the following, we make the choice $\mathbf{g} = (\lambda_\infty - \lambda)\tilde{\mathbf{c}}$ which duly satisfies the constraints imposed by Eq. (SI.4c).[5] This choice aims to closely match the corresponding term in the fluidity evolution equation, see Eq. (4a). Then, we consider the following choice for the **Q** tensor:[3,7–9]

$$Q_{\alpha\beta\gamma\varepsilon} = \eta_s (\delta_{\alpha\gamma}\delta_{\beta\varepsilon} + \delta_{\alpha\varepsilon}\delta_{\beta\gamma}). \quad \text{(SM.8)}$$

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Finally, for the relaxation tensor and Λ^λ, we consider the simplest possible expressions:[3,7,8]

$$\Lambda^c_{\alpha\beta\gamma\varepsilon} = \frac{1-\lambda}{2nk_BT\tau_R}\big[\tilde{c}_{\alpha\gamma}\delta_{\beta\varepsilon} + \tilde{c}_{\alpha\varepsilon}\delta_{\beta\gamma} + \tilde{c}_{\beta\gamma}\delta_{\alpha\varepsilon} + \tilde{c}_{\beta\varepsilon}\delta_{\alpha\gamma}$$

$$+ 2\alpha\big(\tilde{c}_{\alpha\gamma}\tilde{c}_{\beta\varepsilon} + \tilde{c}_{\alpha\varepsilon}\tilde{c}_{\beta\gamma}\big)\big], \tag{SM.9}$$

$$\Lambda^\lambda = \frac{1}{nk_BT\tau_\lambda}.$$

THERMODYNAMIC ADMISSIBILITY

Any thermodynamic system must obey the restriction of a non-negative total rate of entropy production. When the fluid studied is isothermal and incompressible, the entropy production results from the degradation of mechanical energy leading to $dH_m/dt = [H_m, H_m] \leq 0.$[1] For this to be satisfied in our model, it can be shown that the following condition must hold:

$$-[H_m, H_m] = \int \nabla_\alpha\left(\frac{\delta H_m}{\delta M_\beta}\right)Q_{\alpha\beta\gamma\varepsilon}\nabla_\gamma\left(\frac{\delta H_m}{\delta M_\varepsilon}\right)dV + \int \Lambda^\lambda\left(\frac{\delta H_m}{\delta\lambda}\right)^2 dV$$

$$+ \int \frac{\delta H_m}{\delta c_{\alpha\beta}}\Lambda^c_{\alpha\beta\gamma\varepsilon}\frac{\delta H_m}{\delta c_{\gamma\varepsilon}}dV \geq 0. \tag{SM.10}$$

The first is easily shown to be:

$$\int \nabla_\alpha\left(\frac{\delta H_m}{\delta M_\beta}\right)Q_{\alpha\beta\gamma\varepsilon}\nabla_\gamma\left(\frac{\delta H_m}{\delta M_\varepsilon}\right)dV = \eta_s\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}} \geq 0. \tag{SM.11a}$$

which holds when $\eta_s \geq 0$. The second is always non-negative provided $\Lambda^\lambda \geq 0$, which from Eq. (SM.10) holds provided that $\tau_\lambda \geq 0$. Then, the third expression reads:

$$\frac{\delta H_m}{\delta c_{\alpha\beta}} \Lambda^c_{\alpha\beta\gamma\varepsilon} \frac{\delta H_m}{\delta c_{\gamma\varepsilon}}$$

$$= \frac{nk_B T(1-\lambda)}{2\tau_R}[\alpha h^3 \text{tr}\tilde{\mathbf{c}}^2 + h^2(1-3a)\text{tr}\tilde{\mathbf{c}} \qquad \text{(SM.11b)}$$

$$- 3h(2-3a) + (1-a)\text{tr}\tilde{\mathbf{c}}^{-1}] \geq 0,$$

This can be written in the following form using the eigenvalues of the conformation tensor, $\mu_j, \{j = 1,2,3\}$,

$$\frac{\delta H_m}{\delta C_{\alpha\beta}} \Lambda^C_{\alpha\beta\gamma\varepsilon} \frac{\delta H_m}{\delta C_{\gamma\varepsilon}} = \frac{nk_B T(1-\lambda)}{2\tau_R} \sum_{k=1}^{3} \frac{(h\mu_k - 1)^2}{\mu_k}[1 - \alpha + \alpha h\mu_k] \geq 0, \quad \text{(SM.11b)}$$

Thus, since $0 \leq \lambda \leq 1$ this is non-negative provided $0 \leq \alpha \leq 1$ and $\tau_R \geq 0$. Overall, it is proven that $dH_m/dt = [H_m, H_m] \leq 0$ when $\eta_s, \tau_\lambda, \tau_R$ are non-negative and $0 \leq \alpha \leq 1$.

References:

[1] A.N. Beris and B.J. Edwards, "Thermodynamics of Flowing Systems: With Internal Microstructure,"*Thermodynamics of Flowing Systems: With Internal Microstructure* (Oxford University Press, New York, 1994).

[2] P.S. Stephanou, I.C. Tsimouri, and V.G. Mavrantzas, "Simple, Accurate and User-Friendly Differential Constitutive Model for the Rheology of Entangled Polymer Melts and Solutions from Nonequilibrium Thermodynamics,"Materials (Basel). **13**, 2867 (2020).

[3] P.S. Stephanou, "A Constitutive Hemorheological Model Addressing Both the Deformability and Aggregation of Red Blood Cells,"Phys. Fluids **32**, 103103 (2020).

[4] P.S. Stephanou and G.G. Georgiou, "A Nonequilibrium Thermodynamics Perspective of Thixotropy,"J. Chem. Phys. **149**, 244902 (2018).

[5] H.C. Öttinger, "Beyond Equilibrium Thermodynamics,"*Beyond Equilibrium*

Thermodynamics (John Wiley and Sons, 2005).

[6] M. Kröger and M. Hütter, "Automated Symbolic Calculations in Nonequilibrium Thermodynamics,"Comput. Phys. Commun. **181**, (2010).

[7] P.S. Stephanou and I.C. Tsimouri, "A Constitutive Hemorheological Model Addressing the Deformability of Red Blood Cells in Ringer Solutions,"Soft Matter **16**, 7585 (2020).

[8] P.S. Stephanou, V.G. Mavrantzas, and G.C. Georgiou, "Continuum Model for the Phase Behavior, Microstructure, and Rheology of Unentangled Polymer Nanocomposite Melts,"Macromolecules **47**, 4493 (2014).

[9] P.S. Stephanou, "The Rheology of Drilling Fluids from a Non-Equilibrium Thermodynamics Perspective,"J. Pet. Sci. Eng. **165**, 1010 (2018).