Supporting Information for

Phase Separation and Ripening in a Viscoelastic Material

Tine Curk\textsuperscript{a}, Erik Luijten\textsuperscript{a,b}

Correspondence: tcurk@jhu.edu, luijten@northwestern.edu

This PDF file includes:
- Supporting text
- Fig. S1
- SI References
We consider a droplet in a viscoelastic medium described by the upper-convected Maxwell model. The constitutive relation of the upper-convected Maxwell model (1) is

\[ T + \lambda_1 T_{(1)} = -\eta_0 \dot{\gamma}, \]  

where \( T \) is the stress tensor and \( \gamma \) the strain tensor, \( \lambda_1 = \eta_0 / G \) the relaxation time with \( \eta_0 \) the zero-shear-rate viscosity and \( G \) the shear modulus. \( T_{(1)} \) is the upper-convected time derivative of the stress tensor

\[ T_{(1)} = \frac{\partial}{\partial t} T + v \cdot \nabla T - (\nabla v)^T \cdot T - T \cdot \nabla v, \]  

with \( v \) the velocity of the medium and \( \nabla v \) the gradient of \( v \); superscript \( \dagger \) denotes the transpose of a tensor. The rate-of-strain tensor is

\[ \dot{\gamma} = (\nabla v)^\dagger + \nabla v. \]  

For an isolated spherical droplet the problem is spherically symmetric. The velocity is radially symmetric, \( v_\theta = v_\phi = 0 \) and \( \partial v_r / \partial \theta = \partial v_r / \partial \phi = 0 \). The velocity gradient in spherical coordinates is

\[ \nabla v = \begin{pmatrix} \frac{\partial v_r}{\partial r} & 0 & 0 \\ 0 & \frac{v_r}{r} & 0 \\ 0 & 0 & \frac{\partial v_r}{\partial \phi} \end{pmatrix}. \]

Due to the absence of rotational deformations both the stress and the strain tensor are diagonal. The convective derivative is also diagonal

\[ v \cdot \nabla T = \begin{pmatrix} v_r \frac{\partial T_{rr}}{\partial r} & 0 & 0 \\ 0 & v_r \frac{\partial T_{rr}}{\partial \theta} & 0 \\ 0 & 0 & v_r \frac{\partial T_{rr}}{\partial \phi} \end{pmatrix}. \]

Thus, the constitutive relation simplifies to only two independent equations,

\[ \frac{T_{rr}}{\lambda_1} + \frac{\partial T_{rr}}{\partial t} + v_r \frac{\partial T_{rr}}{\partial r} = 2 \frac{\partial v_r}{\partial r} (-G + T_{rr}) \]  

and

\[ \frac{T_{\theta\theta}}{\lambda_1} + \frac{\partial T_{\theta\theta}}{\partial t} + v_r \frac{\partial T_{\theta\theta}}{\partial r} = 2 \frac{v_r}{r} (-G + T_{\theta\theta}) \]

while the relation for \( \phi \phi \) components is identical to that for the \( \theta \theta \) components [Eq. (7)].

**A. Small-stress limit.** For small stresses, \( T_{rr} / G \ll 1 \), the last term on the right-hand side of Eq. (6) can be neglected. Furthermore, at small stresses the velocity \( v_r \) also vanishes, \( v_r \rightarrow 0 \) as \( T_{rr} \rightarrow 0 \), so that the last term on the left-hand side can be neglected as well. Since \( T_{rr} \sim T_{\theta\theta} \), the same approximation applies to Eq. (7) and the constitutive relation reduces to

\[ \frac{T_{rr}}{\lambda_1} + \frac{\partial T_{rr}}{\partial t} = -2G \frac{\partial v_r}{\partial r} \]  

and

\[ \frac{T_{\theta\theta}}{\lambda_1} + \frac{\partial T_{\theta\theta}}{\partial t} = -2G \frac{v_r}{r}. \]

These two equations are a spherically symmetric case of the Maxwell model given by

\[ T + \lambda_1 \frac{\partial}{\partial t} T = -\eta_0 \dot{\gamma}. \]

Therefore, in the small-stress limit, the upper-convected Maxwell model reduces to the Maxwell model. While we have focused on the spherically symmetric case, other geometries and approximations to the upper-convected derivative are discussed in Ref. (1).

**B. Model generalizations.** The upper-convected Maxwell model considers elasticity and relaxation due to the material viscosity of the polymers. To include effects of the solvent viscosity we need the Oldroyd B-model,

\[ T + \lambda_1 T_{(1)} = -\eta_0 (\dot{\gamma} + \lambda_2 \gamma_{(2)}), \]

where \( \gamma_{(2)} \) is the second rate-of-strain tensor and \( \lambda_2 \) the retardation time that is determined by the solvent viscosity (1). For the case of coarsening droplets, the observation of viscoelastic ripening requires the relaxation time \( \lambda_2 \) to be at least a few orders of magnitude larger than the retardation time, \( \lambda_2 / \lambda_1 \sim 0 \). In this case the Oldroyd B-model reduces to the upper-convected Maxwell model [Eq. (1)]. In addition, the viscoelastic ripening exponent is determined in the small-stress limit, where all nonlinear generalizations of the Oldroyd B-model, such as the Giesekus model, the White–Metzner model or the Oldroyd 8-constant model, reduce to the Maxwell model with \( \lambda_2 / \lambda_1 \sim 0 \). Thus, we expect the viscoelastic ripening exponent calculated using the Maxwell model to apply to any constitutive relation that reduces to the Maxwell model in the small-stress limit.
2. Comparison of strain-stiffening models

The elastic pressure for a spherical droplet with an expansion ratio \( \lambda \) is defined as

\[
p_{el}(\lambda) = \frac{E_Y}{6} \left( 5 - 4\lambda^{-1} - \lambda^{-4} \right) + E_c E_Y (\lambda - 1)^2. \quad [12]
\]

For the data shown in the main text, we chose the exponent \( \beta = 2 \) as the lowest even exponent to describe strain stiffening. Here we investigate the effect of strain stiffening by comparing the ripening results for \( \beta = 4 \) and for the Mooney–Rivlin model \((2)\), where the elastic pressure is given by

\[
p_{MR}(\lambda) = n \frac{E_Y}{6} \left( 5 - 4\lambda^{-1} - \lambda^{-4} \right) + (1 - n) \frac{E_Y}{3} \left( 2\lambda - 1 - \lambda^{-2} \right), \quad [13]
\]

with \( n \) the strain stiffening parameter. For \( n = 1 \), the Mooney–Rivlin model reduces to the Gent model, whereas for large expansion ratios \( \lambda \to \infty \) and \( n < 1 \), Mooney–Rivlin would approach Eq. \((12)\) with \( \beta = 1 \) and \( E_c = 2(1 - n)/3 \). Thus, of the three models, Mooney–Rivlin exhibits the weakest strain-stiffening effect.

Comparing these strain-stiffening models we observe that all models exhibit three distinct ripening regimes (Fig. S1). Differences appear when the initial stress is large, \( \gamma > E_Y \tau_0 \), in which case the Mooney–Rivlin model allows substantially larger initial cavity expansion (Fig. S1a). However, all models exhibit a viscoelastic ripening exponent of \( \alpha \approx 1 \) at very large relaxation time (Fig. S1b). Moreover, at sufficiently small initial stress, \( \gamma < E_Y \tau_0 \), all three models converge even in the initial elastic response (Fig. S1c,d). In the limit \( \gamma \ll E_Y \tau_0 \) (and thus \( \lambda \sim 1 \)), all three models reduce to the linear elastic model.

---

**Fig. S1.** Viscoelastic ripening comparison of different models for strain stiffening: \( \beta = 2 \) (black line), \( \beta = 4 \) (blue line) using Eq. \((12)\), and Mooney–Rivlin with \( n = 0.5 \) (red line) using Eq. \((13)\). a) Reference \((\gamma = 3.06 k_B T / r_0^2, E_Y = k_B T / r_0^2, \) cf. main-text Fig. 3 at \( \tau_r / \tau = 10^3 \), b) slower relaxation \( \tau_r / \tau = 10^{12} \), c) lower surface tension \((\gamma = k_B T / r_0^2)\), d) stiffer gel \((E_Y = 10 k_B T / r_0^2)\). All other parameters are the same as those used in Figure 3 in the main text. The dotted line is the Ostwald ripening prediction [Eq. (5) in the main text], while the dashed line is the low-stress viscoelastic ripening prediction [Eq. (9) in the main text].

---

**References**

1. RB Bird, RC Armstrong, O Hassager, CF Curtiss, *Differential constitutive equations*. (Wiley, New York), pp. 341–423 (1987).
2. M. Kothari, T Cohen, Effect of elasticity on phase separation in heterogeneous systems. *J. Mech. Phys. Solids* 145, 104153 (2020).