Thermodynamics of microdroplet phase in elastic phase separation

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Motivation

We study the thermodynamics of binary mixtures of a gel and a solvent, where the solvent is a minority component. In typical binary systems without elastic interactions only the surface tension determines the phase behaviours. Here, The elastic interactions originating from the gel component and surface tension competes to determine the phases of the system. Using mean-field theory we compute the droplet size as a function of the surface tension, Flory parameter, and elastic moduli of the gel. When the surface tension dominates one observes macroscopic solvent droplet, whereas when elastic interactions become sufficiently strong, the dispersed micro-droplet phase emerges as the most stable one.

Main Objectives

- Thermodynamics of a gel-solvent mixture is determined using mean field theory.
- Competition between elasticity and surface tension leads to a dispersed micro-droplet phase below a critical value of surface tension.
- In the small-surface tension limit, the dispersed micro-droplet phase is the most stable one.
- Below a critical value of the surface tension elasticity dominates and the dispersed micro-droplet phase is stabilised.

Phase separation in binary polymer mixtures

Solvent volume fraction dictates equilibrium morphologies of phase separated binary mixtures.

Planar Interface:

The free-energy density $\mathcal{F}(\phi)$ of the planar configuration is given by,

$$\mathcal{F}(\phi_{in},\phi_{out},f,\lambda) = f\mathcal{F}_b(\phi_{in}) + (1-f)\mathcal{F}_b(\phi_{out}) + \mathcal{F}_s(f) + \lambda\left[\phi_0 - f\phi_{in} - (1-f)\phi_{out}\right],$$

Conditions for thermodynamic equilibrium:

$$\text{Chemical equilibrium:}\quad \mu(\phi_{in}) = \mu(\phi_{out}),$$

$$\text{Mechanical equilibrium:}\quad \Pi(\phi_{in}) = \Pi(\phi_{out}).$$

A spherical Drop:

The free-energy density is given by,

$$\mathcal{F}_d(\phi_{in},\phi_{out},f,\lambda) = f\mathcal{F}_b(\phi_{in}) + (1-f)\mathcal{F}_b(\phi_{out}) + \left(36\pi f^2 N/V\right)^{1/3}\gamma + \lambda\left[\phi_0 - f\phi_{in} - (1-f)\phi_{out}\right].$$

$\phi < \phi_* \rightarrow$ minority phase $\rightarrow$ spherical drop.

Mechanical equilibrium: $\Pi(\phi_{in}) = \Pi(\phi_{out}) + 2\gamma\left(\frac{4\pi N}{3fV}\right)^{\frac{1}{3}}$.

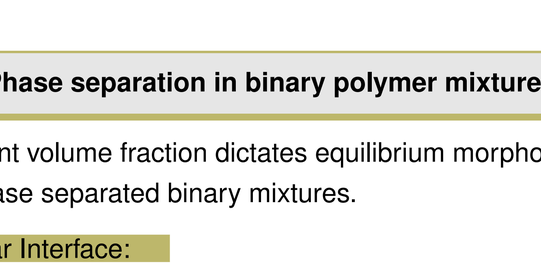

Figure 2: Finite size scaling of equilibrium drop radius $R(L)/L$, of a phase separated binary polymer mixture. Coexistence densities inside and outside the droplet $\tilde{\phi}_{in}$ and $\tilde{\phi}_{out}$ approaches the coexistence values obtained from a common tangent construction as $L \rightarrow \infty$. Inset shows the rate of change of the radius approaches zero as $L \rightarrow \infty$.

$$R = \left(\frac{\phi_0 - \phi_{out}}{\phi_{in} - \phi_{out}}\right)^{1/3} \frac{L}{(4\pi/3)^{1/3}}.$$

Elastic interactions change the equilibrium morphologies of phase separated binary mixtures

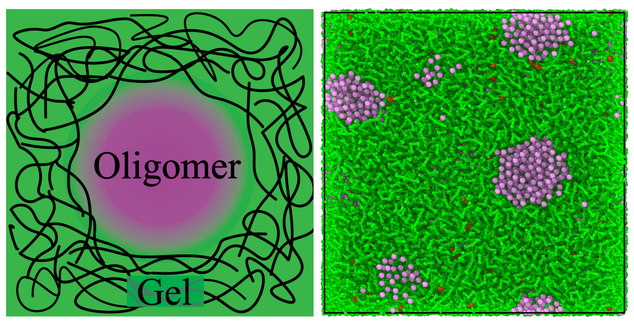

Figure 2: (a) Schematic illustration of the phase separated gel oligomer system. (b) MD simulation snapshot of phase separating gel oligomer system.

Total free energy of the gel-solvent system,

$$\mathcal{F}_{tot}(\phi) = \mathcal{F}_b(\phi) + \mathcal{F}_{el}(f) + \mathcal{F}_{surf}(f).$$

Where,

$$\mathcal{F}_b(\phi) = \phi\ln\phi + \frac{1}{N_B}(1-\phi)\ln(1-\phi) + \chi(T)\phi(1-\phi),$$

$$\mathcal{F}_{el}(f) = \frac{4\pi N(R^3 - R_0^3)}{(1-f)V}\int_1^{R/R_0}\frac{\lambda^2 W(\lambda)}{(\lambda^3-1)^2}d\lambda.$$

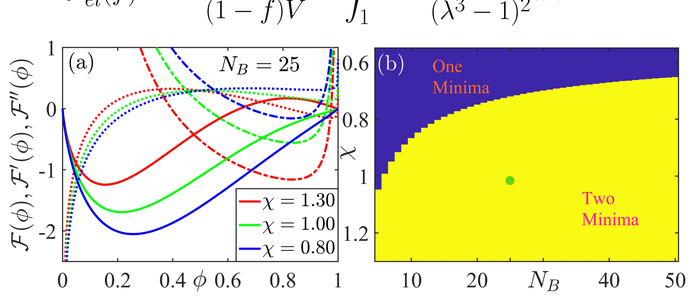

Figure 3: Panel (a) shows $\mathcal{F}_b(\phi)$ for $N_B = 25$ and $\chi = 0.8, 1.0$and1.3. At high temperature, or lower values of χ, the unstable region where $\mathcal{F}_b''(\phi) < 0$ disappears and thus $\mathcal{F}_b(\phi)$ becomes a function with a single minima and this thus implies the mixed phase is the only stable phase. The present calculation has been done for parameter values which supports two minimas in $\mathcal{F}_b(\phi)$. Panel (b) shows the demarcation between the one minima and the two-minima region in the $\chi - N_B$ plane (note that χ increases in the downward direction).

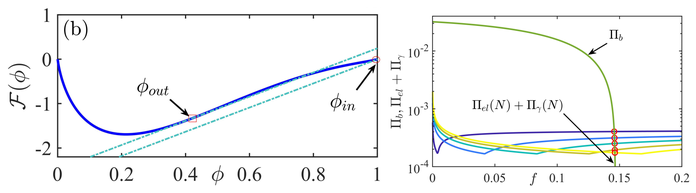

Figure 4: (a) The parallel tangent construction of the bulk free-energy, $\mathcal{F}_b(\phi)$ when one has a high but finite N_B. (b) The solution of the equation, $\Pi_b(\phi_{in}) - \Pi_b(\phi_{out}) = 2\gamma\left(\frac{4\pi N}{3fV}\right)^{1/3} + (1-f)F_{el}'(f) - F_{el}(f)$.

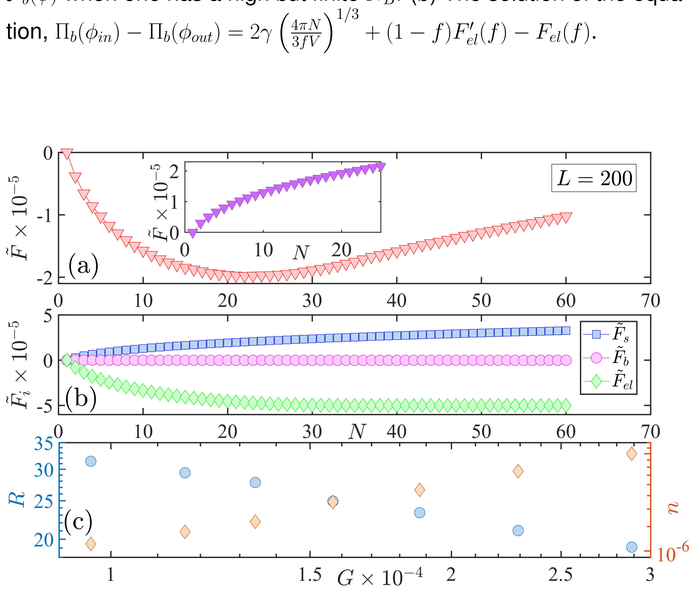

Figure 5: Total free energy, (a), as a function of the number of droplets N showing a minimum at $N_m \approx 23$ for $L = 200$. In the inset, Free energy of binary mixture is shown, where $N = 1$ is the lowest energy state. Surface energy F_s, increases, the elastic energy F_{el}, decreases, whereas, the bulk free energy $\mathcal{F}_b(\phi)$is almost independent of N as shown in (b). Panel (c) shows the dependence of the droplet radius R and the number density of the droplets n and the shear modulus of the gel G.

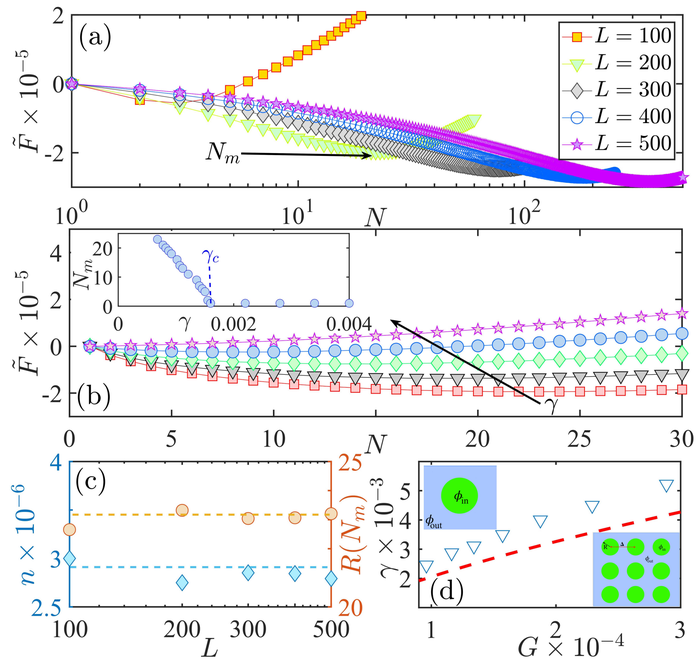

Figure 6: Free energy of the micro-droplet phase $\tilde{F}(N)$ vs. number of droplets, N for different system sizes $L = 100, 200, \ldots 500$ (panel (a)), and surface tension, $\gamma = 0.0025, \ldots 0.004$ (panel (b)). Inset of (b), shows a stable micro-droplet phase for $\gamma < \gamma_c \approx 4.0 \times 10^{-3}$ for $G = 1.9 \times 10^{-4} k_B T/a^3$ and box size $L = 200$. The number density and droplet radii n, and R as a function of system size L is shown in (c), and a phase boundary demarcating regions of stable macrodroplet and multiple micro-droplet phase is shown in (d). The symbols denote the phase boundary computed via mean-field theory ($N_B = 25$) and the dashed line is that via scaling arguments.

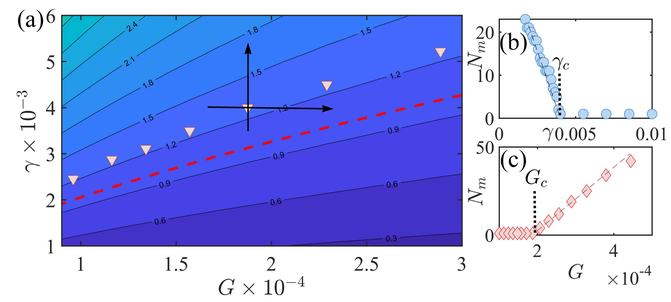

Figure 7: Panel (a) shows the contour plot of the dimensionless ratio h/α in the γ-G plane, where α is equal to 2.5. The inverted triangles denotes the phase-boundary between the macro-droplet and the dispersed micro-droplet phases computed from our mean-field theory. Panel (b) and (c) shows the macro-droplet to dispersed micro-droplet transition as one crosses the phase boundary along the two principal directions.

Summary

- ☐ A competition between surface tension and network elasticity decides the phase of the mixture.
- ☐ The dispersed micro-droplet phase is indeed a thermodynamic minimum for a gel-solvent mixture with high enough elastic constant.
- ☐ Once the surface-tension exceeds a critical value, a single macroscopic droplet is the stable thermodynamic phase.
- ☐ Our framework can be generalised to any other bulk free energy which is bistable in nature.

References

[1] S. Biswas,B. Mukherjee& B. Chakrabarti,*arXiv:2104.00651,(2021)*.

[2] K.A. Rosowski, *et al. Nat. phys.* **16(4)**, 422–425 (2020).

[3] R.W. Style, *et al. Phys. Rev. X.* **8(1)**, 011028 (2018).

[4] B. Mukherjee, & B. Chakrabarti *Polymers*. **12(7)**, 1576 (2020).

[5] M. Kothari *et al. J Mech. Phys. Solids.* **145**, 104153 (2020).

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