Supplementary Information (SI) for Soft Matter.

Equilibrium Scaling of Phase Separated Elastin-Like Polypeptides for Engineered Condensates

Supplemental Information

Adam Quintana, Gabriel Lopez, Nick Carroll

1 Critical Temperature Chain Length Dependence

The question for wheather the interaction parameter in Flory-Huggins theory (i.e. χ) should depend on the polymer length (i.e. N) can be ascribed to the exact form of the polymer length dependence of the critical temperature (i.e. $T_c(N)$). We show in this section that only a specific form of $T_c(N)$ provides a chain length invariant χ. This then implies that a general form of $T_c(N)$ necessitates the functional dependence $\chi(N,T)$.

As described in the main manuscript, the generalized form for the interaction parameter is given as:

$$\chi(N,T) = \frac{1}{2} + \psi(N)w(T) \tag{S1}$$

Where

$$w(T) = 1 - \frac{T_\theta}{T} + \alpha \ln \frac{T_\theta}{T} \tag{S2}$$

As (S1) is valid for all temperatures, it should stand that this equation applied to the critical temperature $T_c(N)$ would satisfy the critical interaction parameter $\chi_c(N)$ from Flory[1]. Re-arrangement of (S1) applied to the critical condition allows us to determine the functional form for $\psi(N)$.

$$\psi(N) = \frac{\chi_c(N) - \frac{1}{2}}{w(T_c(N))} \tag{S3}$$

Hence, (S3) is generally valid for any form of $T_c(N)$. However, if we were to demand that χ be invariant to N, and thus $\partial\chi/\partial N = 0$, then $\partial\psi/\partial N = 0$. After rearrangement of (S1) applied at the critical condition we arrive at the following equation which is transcendental in T_θ/T_c.

$$\frac{T_\theta}{T_c} - \alpha \ln \frac{T_\theta}{T_c} = 1 - \frac{\chi_c(N) - \frac{1}{2}}{\psi} \tag{S4}$$

This equation will provide the appropriate form for $T_c(N)$ which satisfies a chain length invariant χ so long as ψ is a constant. Yet, the transcendental nature of (S4) requires use of Lambert W-function[2] to solve for T_c. With a few more algebraic steps, (S4) is equivalent to:

$$-\frac{T_\theta}{\alpha T_c} + \ln \frac{T_\theta}{\alpha T_c} = -\left(\frac{\psi - \chi_c(N) + \frac{1}{2}}{\alpha\psi} + \ln\alpha\right) \tag{S5}$$

Taking an exponential and negating gives:

$$-\frac{T_\theta}{\alpha T_c} e^{-\left(\frac{T_\theta}{\alpha T_c}\right)} = -\left(\frac{1}{\alpha}\right) e^{\left(\frac{\chi_c(N) - \frac{1}{2} - \psi}{\alpha\psi}\right)} \tag{S6}$$

Analysis of (S1) and (S2) reveals that χ has a maximum value when $T = T_\theta/\alpha$. Therefore, $T_c < T_\theta/\alpha$, otherwise $\chi < \chi_c$ and phase separation would not occur. Use of the Lambert W-function to (S6) must then be through the negative branch or W_{-1}[2]. Solving for T_c we find:

$$T_c(N) = -\frac{T_\theta}{\alpha}\left(W_{-1}\left(-\left(\frac{1}{\alpha}\right) e^{\left(\frac{\chi_c(N) - \frac{1}{2} - \psi}{\alpha\psi}\right)}\right)\right)^{-1} \tag{S7}$$

Although (S7) is the exact expression, which would guarantee a chain length invariant χ, it is not expressible in basic mathematical functions, which is analytically inhibiting. Hence, we can make a few approximations to generate a simpler form for analysis. Assuming $1 - \frac{T_\theta}{T_c} << 1$, which is equivalent to $T_c - T_\theta << T_c$, we can use a first-order Taylor series on the ln term.

$$\ln \frac{T_\theta}{T_c} \approx \frac{T_\theta}{T_c} - 1 \tag{S8}$$

This allows us to solve for T_c directly in (S4).

$$T_c \approx T_\theta \frac{1}{1 - \frac{\chi_c(N) - \frac{1}{2}}{\psi(1-\alpha)}} \tag{S9}$$

The same assumption used in (S8) allows us to approximate (S9) using a first-order Taylor series.

$$T_c \approx T_\theta + \frac{T_\theta}{2\psi(1-\alpha)} \left(\frac{2}{\sqrt{N}} + \frac{1}{N} \right) \tag{S10}$$

This form for $T_c(N)$ will ensure that $\partial\chi/\partial N \approx 0$ when ψ is a constant. It should be noted that (S10) only approximates (S7) and does not capture the existence of poles which may exist due to the factor of $1/W_{-1}$ at low N. Therefore, the approximation is mostly valid for large N. The critical temperature dependence chosen in the main manuscript was a more general form given in equation (11), written here for convenience.

$$T_c = T_\theta + \delta_T N^{-\gamma} \tag{S11}$$

The generalized form (S11) will functionally deviate from the specific form (S10) when N is small, as they both tend toward T_θ for large N. We can compare this generalized form with the approximation of the chain length invariant form and find where the two will be functionally equivalent. With a substitution of the dependent variable to $y = 1/\sqrt{N}$, we can approximate (S11) with a second-order Taylor series about $y = 1$ which is the lowest value of pertinence (i.e. $N = 1$).

$$T_c \approx T_\theta + \delta_T \left(1 + 2\gamma \left(\frac{1}{\sqrt{N}} - 1 \right) + 2\gamma(2\gamma - 1) \left(\frac{1}{\sqrt{N}} - 1 \right)^2 \right) \tag{S12}$$

Expanding and collecting like terms, we find that the generalized form for $T_c(N)$ will analytically approximate the specific form of (S10) when

$$\gamma = \frac{5}{8} \tag{S13}$$

and

$$\delta_T = \frac{T_\theta}{\gamma\psi(1-\alpha)}. \tag{S14}$$

However, T_θ will be shifted by $1.9375\delta_T$.

Therefore, only under the specific form for the critical temperature as given by (S7) and approximated by (S10) for large N will the interaction parameter of (S1) and (S2) be invariant to chain length N. The generalized form given by (S11) will approximate the specific form of (S10) when $\gamma = 5/8$. This implies this value of γ will give the approximate form necessary to make χ invariant to N, valid at large N. Any other value of γ, or any other generalized form for $T_c(N)$, will necessitate that χ vary with N according to (S3).

2 Physical meaning of α

The parameter α is newly introduced in the temperature dependence of the classical Flory-Huggins interaction parameter. This term was derived as being related to the mixing contribution to the heat capacity C_m.

$$C_m = \alpha k_B \langle \phi(1-\phi) \rangle \tag{S15}$$

If we suppose that the total heat capacity is a sum of individual contributions scaled with polymer volume fraction ϕ [3], we obtain:

$$C = C_p\phi_0 + C_s(1-\phi_0) + C_m \tag{S16}$$

Where C_p and C_s are the pure polymeric and pure solvent heat capacities respectively, and ϕ_0 is the system polymer volume fraction. Thus the parameter α scales the mixing contribution to heat capacity which is weighted by the term $\langle\phi(1-\phi)\rangle$ conferring dependence on polymer concentration and phase state. The assumption that $\partial\alpha/\partial\beta = 0$, where $\beta = 1/k_BT$ implies that the thermal variance of C_m lies solely on $\langle\phi(1-\phi)\rangle$. This term can be further expanded:

$$\langle\phi(1-\phi)\rangle = \phi_0 - \langle\phi^2\rangle \tag{S17}$$

Here we make use of the conservation of volume fraction to obtain $\langle\phi\rangle = \phi_0$. The second term can be further expanded in terms of the coacervate volume ratio p and the dense and dilute volume fractions, ϕ'' and ϕ' respectively.

$$\langle\phi^2\rangle = \left(\phi''^2 - \phi'^2\right)p + \phi'^2 = (\phi_0 - \phi')(\phi'' + \phi') + \phi''^2 \tag{S18}$$

Here we substitute p as determined through a volume conservation constraint. As both ϕ'' and ϕ' depend sensitively on T and N, $\langle\phi^2\rangle$ and thus C_m will be likewise dependent. If $\partial\alpha/\partial\beta \neq 0$, then C_m will inherit the specific thermal dependencies of $\alpha(T)$, yet without experimental measurements of heat capacities such thermal dependencies cannot be determined. It should be noted that this form for $\langle\phi^2\rangle$ is only valid when $\chi > \chi_c(N)$, otherwise the solution is homogeneous and $\langle\phi^2\rangle = \phi_0^2$.

References

[1] P. J. Flory. *Principles of polymer chemistry.* Cornell University Press, 1953.

[2] NIST:DLMF. Nist digital library of mathematical functions, 4.13 lambert w-function.

[3] A. S. Teja. Simple method for the calculation of heat capacities of liquid mixtures. *J. Chem. Eng. Data*, 28(1):83–85, 1983.