[pex14] Polymer gel free-energy density of mixing

A dry gel of volume fraction ϕ_0 and volume V_g swells, when immersed in a solvent, to volume $V_g \lambda_1 \lambda_2 \lambda_3$. Hence its volume fraction decreases to the value $\phi = \phi_0/\lambda_1 \lambda_2 \lambda_3$. From [pln47] we pull the expression for the free-energy density of a polymers solution and set $N \to \infty$ in the first term on account of the cross-linking, yielding the expression

$$f_{\text{sol}}(\phi) = \frac{k_B T}{v_c} \Big[(1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi) \Big].$$

From these ingredients derive the following expression for the free-energy density of mixing:

$$f_{\text{mix}}(\lambda_1, \lambda_2, \lambda_3) = \frac{\phi_0}{\phi} \big[f_{\text{sol}}(\phi) - f_{\text{sol}}(0) \big] - \big[f_{\text{sol}}(\phi_0) - f_{\text{sol}}(0) \big] \rightsquigarrow \frac{\phi_0}{\phi} f_{\text{sol}}(\phi),$$

where the simplified expression to be used in [pln65] disregards terms that are not affected by swelling and uses $f_{\text{sol}}(0)$ as a reference value.

[adapted from Doi 2013]

Solution: