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Comment on “Symmetric Liquid-liquid Interface with a Nonzero Spontaneous Curvature”

The Letter [1] demonstrates that a planar liquid-liquid interface with symmetric concentration profiles may have a nonzero spontaneous curvature J_0 . It is furthermore argued that the symmetric nature of the system combined with a nonzero J_0 leads to a discontinuous first derivative of the surface tension as a function of curvature. Our main goal in this Comment is to show that the surface tension remains continuous and differentiable, however. In addition, we show that one may still have $J_0 = 0$, depending on the thermodynamic path chosen to bend the interface.

The system considered in the Letter consists of two polymers A and B of equal length N , in an athermal solvent S , that interact through a Flory parameter χ . If χ is above critical, this system phase separates into a phase rich in polymer A and a phase rich in polymer B .

The Letter discusses bending the interface at a constant solvent volume fraction ϕ_S . Upon bending, ϕ_S will be different in- and outside the droplets formed. If the solvent constraint is located in the B -rich phase ($\phi_S(B) = \text{const}$) then we obtain the results indicated by circles in Fig. 1.

As Fig. 1. shows, a nonzero spontaneous curvature (derivative of $\Delta\gamma(J)$ in $J = 0$) is found, equal to the value reported in the Letter. The reason that $J_0 \neq 0$ can be understood from the observation that the constraint used is *not* symmetric; if we were to fix ϕ_S in the A -rich phase instead, we obtain the dashed curve in Fig. 1, which is the mirror image of the $\phi_S(B) = \text{const}$ curve.

In the Letter, ϕ_S is always fixed in the bulk phase outside the droplet. Hence, the constraint *changes* from $\phi_S(B) = \text{const}$ for $J > 0$ to $\phi_S(A) = \text{const}$ for $J < 0$, leading to an apparent discontinuous derivative of the surface tension at $J = 0$. This is problematic since it would imply that the spontaneous curvature is undefined.

The incompressibility condition, $\phi_A + \phi_B + \phi_S = 1$, makes the densities mutually dependent. For fixed N and χ , the thermodynamic state of the system is determined by *two* state variables, say the polymer chemical potentials μ_A and μ_B . Care should be taken to incorporate the pressure into the chemical potential expressions by treating the solvent as free volume.

The resulting phase diagram is shown in the inset of Fig. 1. The line $\mu_A = \mu_B$ corresponds to a planar interface. To the right of this line ($\mu_A > \mu_B$), spherically or cylindrically curved droplets of the A -rich phase may be present in a bulk of the B -rich phase.

The system is symmetric with regard to the interchanging polymer A and B . A zero spontaneous curvature is obtained only if the planar interface is approached along a path that *does not* violate the A/B symmetry. One such path corresponds to the condition $\mu_A + \mu_B = \text{const}$, which gives the result indicated by the open squares in

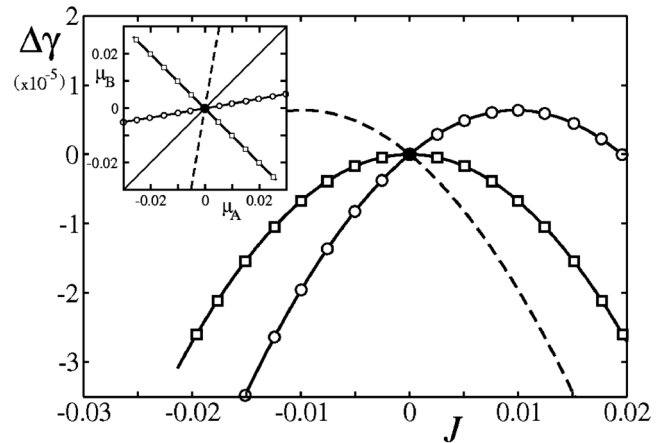


FIG. 1. The (reduced) surface tension for a cylindrically shaped interface as a function of curvature J ; parameters are equal to those in Fig. 2 of the Letter [1]. Positive curvature is defined as curving towards the A -rich phase. Circles are the results for constant $\phi_S(B)$ and squares for constant $\mu_A + \mu_B$. The dashed line is the result for constant $\phi_S(A)$. The inset shows the corresponding paths in the phase diagram.

Fig. 1. Indeed, one finds $J_0 = 0$ as dictated by symmetry. The condition $\phi_S(A) + \phi_S(B) = \text{const}$ or a canonical system with equal amounts of A and B , also both yield $J_0 = 0$ (results not shown).

In general, one needs to specify in what way the interface is bent to determine the sign and magnitude of J_0 . This is simply inherent to the definition of the spontaneous curvature as (minus) the derivative of the surface tension with respect to curvature. For multicomponent systems, this is especially relevant due to the increasing dimensionality of the phase diagram. But even for a one-component system this is already an issue since one has the option to bend the interface at constant temperature or at constant chemical potential [2].

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