

**Leermakers *et al.* Reply:** In our Letter we showed that by fixing the chemical potential of the solvent (or, almost equivalently, fix the concentration of the solvent in the bulk, i.e., outside the droplets), a structurally symmetric interface obtains a nonzero Tolman length (equivalent with  $J_0 \neq 0$ ). Because of this we advised (possibly too strongly) against the use of symmetry arguments in a Helfrich analysis. The preceding Comment [1] by van Male and Blokhuis does not dispute our self-consistent field results for the semigrand canonical ensemble. However, they insist that there are possible thermodynamic paths to curve the interface such that the spontaneous curvature does remain zero. The key new insight is that one can distinguish thermodynamic constraints that yield  $J = 0$  and others that do not. As a result of this Comment we now can more clearly (precisely) specify our concerns regarding the use of symmetry arguments in a Helfrich analysis.

It is instructive to consider the Gibbs equation at fixed temperature:  $d\gamma = -\sum_i \Gamma_i d\mu_i$ . Taking the mean curvature  $J$  as our control parameter and combining the Gibbs equation with the Laplace equation  $\Delta P = \gamma J$  [valid at the surface of tension (SOT)], the Tolman length  $\delta = -k_c J_0 / \gamma(0)$  of the three-component interface is given by

$$\delta = -\Gamma_S \left( \frac{\partial \mu_S}{\partial \Delta P} - \frac{1}{2N} \left[ \frac{\partial \mu_A}{\partial \Delta P} + \frac{\partial \mu_B}{\partial \Delta P} \right] \right)_{T, J \rightarrow 0}, \quad (1)$$

where the excess amount of solvent  $\Gamma_S$  is evaluated at the SOT. In this equation we used the fact that for a structurally symmetric interface in the limit  $J \rightarrow 0$  the SOT is halfway in between the two Gibbs planes and thus  $\Gamma_A = \Gamma_B = \frac{-1}{2N} \Gamma_S$ . Equation (1) is numerically fully consistent with results presented in our Letter and, as we will argue now, is also consistent with the Comment. It indicates that there are two independent ways to find a zero Tolman length. One way is to carefully tune the interactions  $\chi_{AS}$  and  $\chi_{BS}$  such that the adsorption of solvent  $\Gamma_S$  exactly vanishes. This is a trivial case which we will not further elaborate on. The second route is to make sure that upon curving the interface  $\mu_S - \frac{1}{2N}(\mu_A + \mu_B)$  remains constant. The three-component system can be reduced to an effective two-component system. In this case the solvent is seen as some effective medium. For this system we can introduce effective chemical potentials  $\tilde{\mu}_A = \mu_A - N\mu_S$  and  $\tilde{\mu}_B = \mu_B - N\mu_S$  [2]. In line with the Comment we therefore find that the spontaneous curvature vanishes when the sum  $\tilde{\mu}_A + \tilde{\mu}_B$  remains constant. While keeping  $\mu_S = \text{const}$

(as in our Letter), it is impossible to obey to this complex constraint because of a Gibbs-Duhem relation which couples the chemical potentials in the system. It is of interest to know that the Tolman length apparently also vanishes in a canonical ensemble when the composition is taken to be symmetric.

In addition, the Comment elaborates on the fact that a nonzero  $J_0$  leads to a discontinuous first derivative of the surface tension as a function of curvature. We insist on the observation that in a semigrand canonical ensemble (as used in our Letter) this fact is not disputed. In the Comment it is shown that this discontinuity is the natural consequence of our constraints. We agree with the authors that other constraints can be envisioned in which this discontinuity disappears. We hasten to mention that this discussion is a bit academic because systems with a finite surface tension will minimize their Helmholtz energy: they can do this by minimizing the surface area. As a result the flat interface remains the ground state. The Helmholtz energy is continuous around  $J = 0$ , irrespective which bending constraint is present.

In summary, the Comment is valid and a useful scientific contribution. When it comes to the application of symmetry arguments in a Helfrich analysis we stress (in line with our Letter) that structural symmetry of the interface is insufficient to judge whether the spontaneous curvature is finite or not. One should also (new insight from the Comment) consider the thermodynamic constraints that are imposed while curving the interface.

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- [1] F. A. M. Leermakers, P. A. Barneveld, J. Sprakel, and N. A. M. Besseling, preceding Comment, *Phys. Rev. Lett.* **98**, 039601 (2007).
- [2] In the Comment, the authors use  $\tilde{\mu}$  without the tilde notation.