[pex59] Lamellar spacing in micro-phase-separated diblock polymer melt

Consider a diblock copolymer with degree of polymerization N and monomeric length a in a lamellar micro-phase-separated state. The size d of the lamellar spacing is governed by two free-energy contributions (per polymer): $\Delta\bar{F} = \Delta\bar{F}_{\rm str} + \Delta\bar{F}_{\rm int}$. Determine both contributions and then calculate the dependence of d on T and on N from the extremum condition applied to $\Delta\bar{F}$.
(i) The first contribution is entropic in nature, $\Delta\bar{F}_{\rm str} = -T\Delta\bar{S}$, due to the stretching of a polymer segment from a random-walk coil conformation into a straightened out segment. Use the Gaussian probability distribution of mean-square end-to-end distances predicted by the FJC model: $P \sim \exp(-d^2/Na^2)$ and the relation $\Delta\bar{S} \sim k_{\rm B} \ln P$.
(ii) The second contribution is enthalpic in nature, $\Delta\bar{F}_{\rm int} = \Delta\bar{H}$, representing the interfacial energy. Assume that the interfacial energy density (energy per area) γ is given. The total interfacial area is inversely proportional to the lamellar spacing. Therefore, we can write $\Delta\tilde{F}_{\rm int} \sim \gamma/d$ for the free energy per volume. This relation must be converted into $\Delta\bar{F}_{\rm int}$ (per polymer) by using the following dependence of the volume on the number $N_{\rm p}$ of polymers: $V = N_{\rm p} N a^3$, assuming that monomers are compact.

Solution: