# Supporting information for: Tunable conformational asymmetry in particle-forming diblock copolymer alloys

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## S1 Self-Consistent Field Theory

Calculations in this work are performed using the C++ implementation of the Polymer Self-Consistent Field (PSCFpp) software package.<sup>S1</sup> In this section, we present the formulation of the block copolymer self-consistent mean field theory (SCFT) implemented in PSCFpp. Our discussion here closely follows the formalism presented alongside PSCFpp's Fortran-based predecessor,  $S^{2,S3}$  although the present discussion is specific to the diblock alloy system. More generalized discussions of SCFT are available elsewhere.  $S^{4-S6}$ 

Using PSCFpp, we consider a system of incompressible, continuous Gaussian chain polymers composed of three unique monomer types  $i \in \{A, B, C\}$ , with statistical segment lengths  $b_i$ . These monomers are coarse-grained and occupy the common monomer reference volume v. The interaction strength between two monomers i and  $j \neq i$  is given by the Flory-Huggins parameter  $\chi_{ij}$ ; self-interaction of a monomer *i* with itself is thermodynamically neutral with  $\chi_{ii} = 0$ . We consider a blend of two diblock polymer chains  $k \in \{AB, B'C\}$  with total chain degrees of polymerization  $N_{AB}$  for the AB chain and  $N_{B'C}$  for the B'C chain. These total degrees of polymerization represent the sum of the degrees of polymerization of their constituent blocks such that  $N_{AB} = N_A + N_B$  is the sum of  $N_A$  A-monomers and  $N_B$  B-monomers while  $N_{\rm B'C} = N_{\rm B'} + N_{\rm C}$  is the sum of  $N_{\rm B'}$  B-monomers and  $N_{\rm C}$  C-monomers. In the blend, the overall volume fractions of the AB and B'C polymers are  $\phi_{AB}$  and  $\phi_{B'C} = 1 - \phi_{AB}$ , respectively. The requirement of a uniform coarse-grained monomer volume v yields an equivalence between volume and degree of polymerization such that the volume fraction of a block within a polymer chain is given by its degree of polymerization:  $f_{\rm A} = N_{\rm A}/N_{\rm AB}$  for the A-block in the AB chain and  $f_{\rm C} = N_{\rm C}/N_{\rm B'C}$  for the C-block in the B'C chain. SCFT calculations in PSCFpp are performed on a single unit-cell with periodic boundary conditions to represent the structure throughout a macroscopic volume. This unit cell has volume V and contains n = V/v monomers.

It is useful to note that, in the context of SCFT calculations in PSCFpp, a "monomer" acts as a bookkeeping device and there is far more flexibility in its definition than would be appropriate in a synthetic or experimental context. In the SCFT formalism, a "monomer" need not represent a single chemical repeat unit, as is typical in a synthetic context, but instead represents the molar mass of polymer chain occupying one monomer reference volume, v.<sup>S3</sup> In our calculations, v is chosen such that  $N_{\rm AB} = 1$  which produces two convenient outcomes. First, chain length asymmetry,  $N_{\rm B'C}/N_{\rm AB}$ , becomes numerically equivalent to  $N_{\rm B'C}$ . Second, energies can be easily reported on a per-chain basis because the number of monomers in the system, n, can be interpreted as the number of chains of length  $N_{\rm AB}$ . Sinturel et al.<sup>S7</sup> offer a helpful discussion about mapping the SCFT parameters to those of real polymers.

In SCFT, the many-body particle-particle interactions of the polymer melt are replaced by a spatially varying chemical potential field acting on a representative set of non-interacting polymer chains in the saddle-point approximation that is relevant as a mean-field description. The potential field acting on monomer i at spatial position  $\mathbf{r}$  is denoted by  $\omega_i(\mathbf{r})$  and given for each monomer by

$$\omega_{\rm A}(\mathbf{r}) = \chi_{\rm AB}\rho_{\rm B}(\mathbf{r}) + \chi_{\rm AC}\rho_{\rm C}(\mathbf{r}) + \xi(\mathbf{r}) \tag{S1}$$

$$\omega_{\rm B}(\mathbf{r}) = \chi_{\rm AB} \rho_{\rm A}(\mathbf{r}) + \chi_{\rm BC} \rho_{\rm C}(\mathbf{r}) + \xi(\mathbf{r}) \tag{S2}$$

$$\omega_{\rm C}(\mathbf{r}) = \chi_{\rm AC} \rho_{\rm A}(\mathbf{r}) + \chi_{\rm BC} \rho_{\rm B}(\mathbf{r}) + \xi(\mathbf{r})$$
(S3)

where  $\rho_i(\mathbf{r})$  is the average local volume fraction of monomer *i* at position  $\mathbf{r}$  and  $\xi(\mathbf{r})$  is a Lagrange multiplier enforcing the incompressibility constraint,

$$\rho_{\rm A}(\mathbf{r}) + \rho_{\rm B}(\mathbf{r}) + \rho_{\rm C}(\mathbf{r}) = 1 \tag{S4}$$

Running an SCFT calculation requires that the user first provide an initial guess for  $\omega_A$ ,  $\omega_B$ , and  $\omega_C$ . These initial values are used to compute the partition function of each polymer

k according to

$$Q_k = \frac{1}{V} \int_V d\mathbf{r} \, q_k(\mathbf{r}, N_k) \tag{S5}$$

where the forward propagator  $q_k(\mathbf{r}, N_k)$  represents the solution of the modified diffusion initial value problem for chain type k,

$$\frac{\partial q_k\left(\mathbf{r},s\right)}{\partial s} = \left[\frac{b_{i(s)}^2}{6}\nabla^2 - \omega_{i(s)}(\mathbf{r})\right] q_k(\mathbf{r},s), \qquad q_k(\mathbf{r},0) = 1$$
(S6)

where  $s \in [0, N_k]$  is the coordinate along the chain contour. The subscript i(s) on  $b_{i(s)}$  and  $\omega_{i(s)}$  indicate that the statistical segment length and chemical potential field will be those corresponding to the monomer type at contour position s. More explicitly: when k = AB, we use  $b_A$  and  $\omega_A(\mathbf{r})$  when integrating over the region  $s \in [0, N_A]$  and we use  $b_B$  and  $\omega_B(\mathbf{r})$ for integration over  $s \in [N_A, N_{AB}]$ ; when k = B'C, we use  $b_C$  and  $\omega_C(\mathbf{r})$  for integration over  $s \in [0, N_C]$  and we use  $b_B$  and  $\omega_B(\mathbf{r})$  for integration over  $s \in [N_C, N_{B'C}]$ .

The forward propagator  $q_k(\mathbf{r}, s)$  is a normalized partition function for the portion of chain k on [0, s] when the chain contour segment s is constrained to position  $\mathbf{r}$ . Under the same positional constraint of segment s, the normalized partition function for the remainder of chain k,  $[s, N_k]$ , is given by the backward propagator  $q_k^{\dagger}(\mathbf{r}, s)$  which is the solution of the modified diffusion initial value problem

$$-\frac{\partial q_k^{\dagger}(\mathbf{r},s)}{\partial s} = \left[\frac{b_{i(s)}^2}{6}\nabla^2 - \omega_{i(s)}(\mathbf{r})\right] q_k^{\dagger}(\mathbf{r},s), \qquad q_k^{\dagger}(\mathbf{r},N_k) = 1$$
(S7)

The product of the forward and backward propagators,  $q_k(\mathbf{r}, s)q_k^{\dagger}(\mathbf{r}, s)$ , is proportional to the probability of finding chain contour segment s at position  $\mathbf{r}$ .<sup>S4</sup> This proportionality can then be used to compute the average local volume fractions of each monomer,  $\rho_i(\mathbf{r})$ , which in turn can be used to compute the potential field for each monomer  $\omega_i(\mathbf{r})$ . Details of the local monomer volume fractions differ between the canonical and grand canonical ensembles, and are given below in Equations S8-S9 and S13-S14 respectively. The circular dependence of Equations S1-S3 on Equations S8-S10 (or Equations S13-S15) via Equations S4-S7 means that the SCFT calculation must iterate on  $\omega_i(\mathbf{r})$  from the user-provided initial guess until these equations become self-consistent within a specified tolerance. In our calculations, we measure error using the relative residual norm described by Matsen<sup>S8</sup> and converge calculations to a tolerance of  $1 \times 10^{-6}$ . Iterations are done according to an Anderson Mixing scheme<sup>S8-S10</sup> which optimizes unit cell parameters simultaneously with the field<sup>S10,S11</sup> to minimize stress and obtain an accurate free energy.

#### S1.1 Canonical Ensemble

In the canonical ensemble, system composition is specified for the system by declaring  $\phi_{AB}$ and  $\phi_{B'C}$  in the input file. Using these values, and the partition functions above, the local volume fractions of each monomer are calculated with <sup>S6</sup>

$$\rho_{\rm A}(\mathbf{r}) = \frac{\phi_{\rm AB}}{Q_{\rm AB}N_{\rm AB}} \int_0^{N_{\rm A}} ds \, q_{\rm AB}(\mathbf{r}, s) q_{\rm AB}^{\dagger}(\mathbf{r}, s) \tag{S8}$$

$$\rho_{\rm B}(\mathbf{r}) = \frac{\phi_{\rm AB}}{Q_{\rm AB}N_{\rm AB}} \int_{N_{\rm A}}^{N_{\rm AB}} ds \, q_{\rm AB}(\mathbf{r},s) q_{\rm AB}^{\dagger}(\mathbf{r},s) + \frac{\phi_{\rm B'C}}{Q_{\rm B'C}N_{\rm B'C}} \int_{N_{\rm C}}^{N_{\rm B'C}} ds \, q_{\rm B'C}(\mathbf{r},s) q_{\rm B'C}^{\dagger}(\mathbf{r},s)$$
(S9)

$$\rho_{\rm C}(\mathbf{r}) = \frac{\phi_{\rm B'C}}{Q_{\rm B'C} N_{\rm B'C}} \int_0^{N_{\rm C}} ds \, q_{\rm B'C}(\mathbf{r}, s) q_{\rm B'C}^{\dagger}(\mathbf{r}, s) \tag{S10}$$

After these equations are solved self-consistently with those in Equations S1-S7, the Helmholtz free energy per monomer is given by  $S^{2}$ 

$$\frac{F}{nk_BT} = \frac{1}{V} \int d\mathbf{r} \left[ \left( \chi_{AB} \rho_A \rho_B + \chi_{AC} \rho_A \rho_C + \chi_{BC} \rho_B \rho_C \right) - \left( \omega_A \rho_A + \omega_B \rho_B + \omega_C \rho_C \right) \right] + \frac{\phi_{AB}}{N_{AB}} \left( \ln \frac{\phi_{AB}}{Q_{AB}} - 1 \right) + \frac{\phi_{B'C}}{N_{B'C}} \left( \ln \frac{\phi_{B'C}}{Q_{B'C}} - 1 \right)$$
(S11)

where  $k_B T$  is the Boltzmann constant and T is the absolute temperature.

#### S1.2 Grand Canonical Ensemble

Instead of system composition, calculations in the grand canonical ensemble specify the dimensionless chemical potential of the AB and B'C polymers ( $\mu_{AB}/k_BT$  and  $\mu_{B'C}/k_BT$ , respectively). These chemical potentials are related to the overall volume fractions by <sup>S6</sup>

$$\exp\left(\frac{\mu_k}{k_B T}\right)Q_k = \phi_k \tag{S12}$$

This relation, combined with incompressibility of the system, means that  $\mu_{AB}/k_BT$  and  $\mu_{B'C}/k_BT$  are not independent, allowing us to set  $\mu_{AB}/k_BT = 0$  throughout our calculations while varying  $\mu_{B'C}/k_BT$ . The relation in Equation S12 can also be used to compute the local volume fractions of each monomer via substitution into Equations S8-S10, giving

$$\rho_{\rm A}(\mathbf{r}) = \frac{1}{N_{\rm A}} \exp\left(\frac{\mu_{\rm AB}}{k_B T}\right) \int_0^{N_{\rm A}} ds \, q_{\rm AB}(\mathbf{r}, s) q_{\rm AB}^{\dagger}(\mathbf{r}, s) \tag{S13}$$

$$\rho_{\rm B}(\mathbf{r}) = \frac{1}{N_{\rm AB}} \exp\left(\frac{\mu_{\rm AB}}{k_B T}\right) \int_{N_{\rm A}}^{N_{\rm AB}} ds \, q_{\rm AB}(\mathbf{r}, s) q_{\rm AB}^{\dagger}(\mathbf{r}, s) + \frac{1}{N_{\rm B'C}} \exp\left(\frac{\mu_{\rm B'C}}{k_B T}\right) \int_{N_{\rm C}}^{N_{\rm B'C}} ds \, q_{\rm B'C}(\mathbf{r}, s) q_{\rm B'C}^{\dagger}(\mathbf{r}, s)$$
(S14)

$$\rho_{\rm C}(\mathbf{r}) = \frac{1}{N_{\rm B'C}} \exp\left(\frac{\mu_{\rm B'C}}{k_B T}\right) \int_0^{N_{\rm C}} ds \, q_{\rm B'C}(\mathbf{r}, s) q_{\rm B'C}^{\dagger}(\mathbf{r}, s) \tag{S15}$$

After the calculation converges, the grand canonical free energy is given by <sup>S12</sup>

$$F_g = -PV \tag{S16}$$

where P is the system pressure. For our alloy system, the number of AB chains,  $n_{AB}$ , and the number of B'C chains,  $n_{B'C}$ , along with their respective chemical potentials can be used to relate the grand canonical free energy to the Helmholtz free energy with<sup>S6</sup>

$$F_g = F - n_{\rm AB}\mu_{\rm AB} - n_{\rm B'C}\mu_{\rm B'C} \tag{S17}$$

which can be combined with Equation S16 to give

$$PV = -F + n_{\rm AB}\mu_{\rm AB} + n_{\rm B'C}\mu_{\rm B'C} \tag{S18}$$

By noting that  $n_k = n\phi_k/N_k$  and non-dimensionalizing Equation S18 by dividing by  $nk_BT$ , we obtain

$$\frac{Pv}{k_BT} = -\frac{F}{nk_BT} + \frac{\phi_{AB}}{N_{AB}} \left(\frac{\mu_{AB}}{k_BT}\right) + \frac{\phi_{B'C}}{N_{B'C}} \left(\frac{\mu_{B'C}}{k_BT}\right)$$
(S19)

which gives the dimensionless pressure output by PSCFpp in terms of the dimensionless chemical potentials, dimensionless Helmholtz free energy, and overall species volume fractions, all of which are also reported by the program.<sup>S3</sup>

## S2 Phase Coexistence

For two or more phases to be in equilibrium, they must have equal pressure and temperature, and the chemical potential of each species in the system must be the same in all phases. In the SCFT calculations employed here, the temperature of the system is set by the Flory-Huggins parameter  $\chi_{ij}$ ; therefore, the equal temperature condition for equilibrium is met as long as calculations are done at fixed  $\chi_{ij}$ , regardless of the ensemble in which calculations are performed. Establishing the equal-pressure and equal-chemical potential conditions differs by the ensemble selected. The remainder of this section describes the methods for equilibrium determination in the canonical and grand canonical ensembles.

#### S2.1 Canonical Ensemble: Common Tangent

The SCFT calculations performed here assume incompressibility of the polymers. Due to this assumption in the canonical ensemble, the addition of a constant pressure to the system will not change the Helmholtz free energy.<sup>S6</sup> This means that the pressure in the canonical ensemble is arbitrary, and the requirement of constant pressure can always be met. The requirement of equal chemical potential in all phases for each species is established via the common tangent construction.  $^{S13}$ 

To numerically determine a common tangent between phases I and II, the Helmholtz free energy data for each phase, collected at intervals of  $\Delta \phi_{AB} = 0.005$ , is first fit to a cubic spline, giving the energy of each phase as a function of  $\phi_{AB}$ ,  $F^{I}(\phi_{AB})$  and  $F^{II}(\phi_{AB})$ . To ensure fidelity to the underlying data, this spline was computed with a zero smoothing factor, which forces the curve to pass exactly through all data points.<sup>S14</sup> The compositions of the two coexisting phases,  $\phi_{AB}^{I}$  and  $\phi_{AB}^{II}$ , were then calculated numerically by seeking the root of

$$\mathbf{f}(\phi_{AB}^{\mathrm{I}}, \phi_{AB}^{\mathrm{II}}) = \begin{bmatrix} f_1(\phi_{AB}^{\mathrm{I}}, \phi_{AB}^{\mathrm{II}}) \\ f_2(\phi_{AB}^{\mathrm{I}}, \phi_{AB}^{\mathrm{II}}) \end{bmatrix}$$
(S20)

where  $f_1$  and  $f_2$  are given by

$$f_{1}(\phi_{AB}^{I},\phi_{AB}^{II}) = \frac{dF^{I}}{d\phi_{AB}}(\phi_{AB}^{I}) - \frac{F^{I}(\phi_{AB}^{I}) - F^{II}(\phi_{AB}^{II})}{\phi_{AB}^{I} - \phi_{AB}^{II}}$$
(S21)

$$f_2(\phi_{AB}^{I}, \phi_{AB}^{II}) = \frac{dF^{II}}{d\phi_{AB}}(\phi_{AB}^{I}) - \frac{F^{I}(\phi_{AB}^{I}) - F^{II}(\phi_{AB}^{II})}{\phi_{AB}^{I} - \phi_{AB}^{II}}$$
(S22)

The root of  $\mathbf{f}(\phi_{AB}^{I}, \phi_{AB}^{II})$  occurs when the slope of the tangent to each energy curve,  $dF^{i}/d\phi_{AB}$ , is equal to the slope of the line connecting the two tangent points,  $(\phi_{AB}^{I}, F^{I}(\phi_{AB}^{I}))$  and  $(\phi_{AB}^{II}, F^{II}(\phi_{AB}^{II}))$ , which guarantees that the points are co-linear along the common tangent. This construction is depicted in Fig. S1.

Optimization was done with the SciPy root-finding method scipy.optimize.root using the 'hybr' method option, which uses a modified Powell method as implemented in MINPACK.<sup>S15,S16</sup> In general, we find this method to be very robust for common tangent calculations, with most tangent calculations converging when the mid-point of each energy curve is used as the initial guess for the respective  $\phi_{AB}^i$ , which was the default initial guess for our calculations.

When this methodology was used to choose a macrophase separation pairing for com-

parison to the Laves phase, as done in Fig. S2 or Fig. 2 of the main text, phases I and II represent the AB-rich and B'C-rich bcc or fcc phases. This same methodology was used in construction of the phase diagram to determine phase boundaries along the Laves phase field, in which case phases I and II would represent a Laves phase and one of the AB-rich or B'C-rich phases.



Figure S1: Representative illustration of the common tangent calculation method for arbitrary phases I and II, using hypothetical quadratic Helmholtz free energy curves for these phases,  $F^{I}(\phi_{AB})$  and  $F^{II}(\phi_{AB})$  respectively. The method iterates on the values of the coexistence compositions,  $\phi_{AB}^{I}$  (phase I) and  $\phi_{AB}^{II}$  (phase II), to find the root of Equation S20. The solid lines are the tangents to  $F^{I}(\phi_{AB})$  and  $F^{II}(\phi_{AB})$  at the points ( $\phi_{AB}^{I}, F^{I}(\phi_{AB}^{I})$ ) and ( $\phi_{AB}^{II}, F^{II}(\phi_{AB}^{II})$ ), respectively. These tangent points are marked with black dots. The dashed line connects the two tangent points, ( $\phi_{AB}^{I}, F^{I}(\phi_{AB}^{II})$ ) and ( $\phi_{AB}^{II}, F^{II}(\phi_{AB}^{II})$ ). The slopes of the tangent lines and the connector line are indicated on the graph algebraically as they are listed in Equations S21 and S22. When all three slopes are equal, at the root of Equation S20, the tangent points ( $\phi_{AB}^{I}, F^{I}(\phi_{AB}^{II})$ ) and ( $\phi_{AB}^{II}, F^{II}(\phi_{AB}^{II})$ ) will be co-linear along the common tangent.

#### S2.2 Grand Canonical Ensemble

Our approach to phase coexistence in the grand canonical ensemble follows the method described by Matsen<sup>S17</sup> and that used by Magruder et al.<sup>S18</sup> in their work on conformationally symmetric diblock alloys. Due to the incompressibility of the system, the chemical potentials of the AB and B'C chains are not independent, allowing us to choose  $\mu_{AB}/k_BT = 0$  for all calculations. This trivially satisfies the chemical potential criteria for the AB chain. The chemical potential value input to PSCF for the B'C chain,  $\mu_{\rm B'C}/k_BT$ , is then controlled as an independent variable and phases are compared across  $\mu_{B'C}/k_BT$  values (similarly to  $\phi_{AB}$ in the canonical ensemble). By controlling the value of  $\mu_{B'C}/k_BT$ , we thus also meet the chemical potential criterion for B'C. The pressure of each phase as calculated with Eqn. S19 is output by PSCF following convergence of the SCFT calculation. The final equilibrium criterion, equal pressure, is met when the  $Pv/k_BT$  vs  $\mu_{B'C}/k_BT$  curves of the phases intersect. In general, SCFT calculations were run at increments of 0.0005 in  $\mu_{B'C}/k_BT$ . In some cases, however, larger sampling increments were required when large ranges of  $\mu_{B'C}/k_BT$ needed to be sampled to find an intercept. These larger sampling increments were most often needed while resolving the high-temperature regions near the ODT, where the  $P(\mu_{B'C})$ curves of disorder and the AB-rich or B'C-rich fcc phases were nearly parallel. In these cases,  $\mu_{\rm B'C}/k_BT$  needed to be sampled over ranges up to two orders of magnitude larger than was typically required. Regardless of sampling increment, interpolation was used to determine the chemical potential and composition of the phases at equilibrium.

# S3 Impact of Conformational Asymmetry

As discussed in the main text, we evaluated the impact of conformational asymmetry in each of the Laves particles by simultaneously varying the chain length asymmetry and the conformational asymmetries. At each condition conformational asymmetry and chain length asymmetry, we ran canonical ensemble SCFT calculations at a variety of blend fractions for the Laves phases and a set of AB-rich and B'C-rich macrophase separation competitors. We used the common tangent construction to determine which set of AB-rich and B'C-rich phases made the most competitive macrophase separation pair, and compared the Laves phase energy to this macrophase separation tangent. The results of this analysis at  $\chi N = 28.0$ were reported in Figure 2 of the main text. Figure S2 reports the results of this analysis at  $\chi N = 25.0$ . Unlike at  $\chi N = 28$ , where bcc-bcc coexistence dominated the macrophase separation reference, here both fcc and bcc appear frequently on both ends of the macrophase separation tangent. Aside from the more frequent appearance of fcc phases, the trends seen here are quite similar to those reported in the main text.



Figure S2: Minimum free energy of the C14 Laves phase relative to the macrophase separation tangent line at various conformational asymmetries for (a) the AB diblock, (b) the B'C diblock, or (c) both the AB and B'C diblocks for  $\chi_{AB}N_{AB} = \chi_{BC}N_{B'C} = 25.0$ ,  $\chi_{AC}N_{AB} = 50.0$ , and  $f_A = f_C = 0.20$ . Shaded regions indicate those in which one or both of the AB-rich and B'C-rich fcc phases are used in the macrophase separation tangent (in place of the corresponding bcc phase) at one or more of the conformational asymmetries studied here.

# S4 Candidate Phases

In order to generate the phase diagrams reported in the main text, we needed to consider a variety of competitor phases in addition to the Laves phases and macrophase separation candidates. Table S1 lists the phases considered during construction of phase diagrams. The table contains crystallographic information, SCFT spatial discretization, and information on the number of particles and assignment of particles as AB or B'C micelles. As stated in the main text, the phases considered in this work are inspired by the work of Xie et al.<sup>S19</sup> and match the candidate set employed by Magruder et al.<sup>S18</sup> In constructing our phase diagram, we have chosen to omit hexagonally close-packed spheres (hcp) from the set of candidate phases. The hcp phase is nearly degenerate with fcc, <sup>S19,S20</sup> and any changes (if any) it would produce in the phase diagram would be negligible; fcc is taken to be representative of both close-packed sphere phases.

Several of the candidate phases listed here (specifically ReO<sub>3</sub>, TiO<sub>2</sub>, CaF<sub>2</sub>, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) proved particularly difficult to converge in many regions of the phase diagram, as noted previously by Magruder et al.,<sup>S18</sup> and are therefore missing from many of the canonical ensemble calculation sets. Among these phases, ReO<sub>3</sub> proved the most problematic, as we were unable to achieve convergence of an initial field at the desired conformational asymmetry for either of the phase diagrams reported in this work (Figures 4 and 5 of the main text). In the case of  $\epsilon_{BC} = 1.5$ , we were unable to converge an initial field for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Finally, we were unable to obtain initial fields for either TiO<sub>2</sub> or CaF<sub>2</sub> for  $\epsilon_{AB} = \epsilon_{BC} = 1.5$ . In all cases, if we were unable to obtain an initial field at the desired conformational asymmetry, we assume the phase is highly unfavorable at the conditions being considered, and omit it from the analysis.

Table S1: Complete list of phases considered during generation of the phase diagrams. Table includes the name of the phase (Phase name); the label used to identify the phase in figures (Label Name); The crystal system and space group of the phase; the spatial discretization used in SCFT calculations for the phase (SCFT grid size); the number of nominally spherical particles in a unit cell of the phase (Particles per unit cell); the ratio of the number of particles composed of AB chains to the number of particles composed of B'C chains (AB:B'C particle ratio).

	Label name	Crystal system	Space group	SCFT grid size	Particles	AB:B'C
Phase name					per unit	particle
					$\mathbf{cell}$	ratio
MgZn <sub>2</sub>	C14	Hexagonal	$P6_3/mmc$	64x64x104	12	2:1
MgCu <sub>2</sub>	C15	Cubic	$Fd\overline{3}m$	96x96x96	24	2:1
W	bcc	Cubic	Im <del>3</del> m	48x48x48	2	$0 \text{ or } 1^*$
CsCl	alt-bcc	Cubic	$Pm\overline{3}m$	64x64x64	2	1:1
Cu	fcc	Cubic	$Fm\overline{3}m$	48x48x48	4	$0 \text{ or } 1^*$
Hexagonally	hov	Hoverenel	n6mm	18×18	N / A	$0 \text{ or } 1^*$
packed cylinders	nex	Tiexagonai	pomm	40X40	$\mathbf{N}/\mathbf{A}$	0 01 1
Alternating hex	alt-hex	Hexagonal	p6mm	48x48	N/A	2:1
Inverted alt-hex	$(alt-hex)_i$	Hexagonal	p6mm	48x48	N/A	1:2
Nb <sub>3</sub> Sn	A15	Cubic	$Pm\overline{3}n$	64x64x64	8	1:3
$AlB_2$	$AlB_2$	Hexagonal	P6/mmm	64x64x64	3	2:1
sapphire ( $\alpha$ -BN)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Trigonal	$R\overline{3}c$	64x64x64	10	3:2
$\alpha$ -BN	$\alpha$ -BN	Hexagonal	$P6_3/mmc$	48x48x64	4	1:1
$CaF_2$	$CaF_2$	Cubic	$Fm\overline{3}m$	64x64x64	12	2:1
Li <sub>3</sub> Bi	Li <sub>3</sub> Bi	Cubic	$\mathrm{Fm}\overline{3}\mathrm{m}$	64x64x64	16	3:1
Inverted Li <sub>3</sub> Bi	$(Li_3Bi)_i$	Cubic	$Fm\overline{3}m$	64x64x64	16	3:1
rocksalt	NaCl	Cubic	$Fm\overline{3}m$	64x64x64	8	1:1
$\mathrm{ReO}_3$	$\mathrm{ReO}_3$	Cubic	$Pm\overline{3}m$	64x64x64	4	3:1
$\sigma$ -FeCr	σ	Tetragonal	$P4_2/mnm$	128x128x64	30	1:2**
TiO <sub>2</sub>	$\mathrm{TiO}_2$	Tetragonal	$P4_2/mnm$	64x64x42	6	1:2
ZnS	ZnS	Cubic	$F\overline{4}3m$	64x64x64	8	1:1

\*These structures represent the AB-rich and B'C-rich morphologies considered for macrophase separation. All particles are composed of the majority species, with the minority located in interstitial sites.

\*\*Particle assignment for  $\sigma$  is not trivial given the complexity of the structure. Here, B'C is placed in particles with volume above the number-averaged particle volume for the phase (Wyckoff positions 4f, 8i', and 8j) while AB is placed in particles with volumes below this average (Wyckoff Positions 2b, and 8i), according to the volumes computed by Reddy et al. using the diblock foam model.<sup>S21</sup> This "above average" vs "below average" criteria was chosen for consistency with the Laves phases, in which B'C was assigned to the larger particles.

# S5 Laves Phase Degeneracy

The main text reports that choice of Laves phase to use in the analysis would have little impact on the results because the Laves phases are found here to be nearly degenerate in free energy. To support this claim, Figure S3 shows the free energy of the C15 Laves phase relative to C14 based on the canonical ensemble SCFT calculations used to generate the phase diagram in Figure S4. We have chosen to use the C14 phase as the representative Laves phase in our analysis because our data show that it is, within the Laves phase field, more stable than C15. However, within this range, the total difference in the Laves phase free energies never exceeds  $1 \times 10^{-4}$  k<sub>B</sub>T per chain of length  $N_{AB}$ . It is interesting to note that, over a brief composition window at lower  $\phi_{AB}$  than the Laves phase field, C15 is briefly more stable than C14; regardless, it still remains metastable relative to macrophase separation.



Figure S3: The energy of the C15 Laves phase relative to that of C14 from canonical ensemble SCFT data used to generate the phase diagram in Fig. 4 of the main text and Figure S4 here. The vertical dotted lines represent the bounds (in  $\phi_{AB}$ ) of Figure S4b and Fig. 4b, and serve as a guide for the range relevant to the Laves phase field reported in this work.

## S6 Phase Diagram

In this work, most of the calculations have been done in the canonical ensemble, with the grand-canonical ensemble reserved for resolving 3-phase coexistence and the region near the ODT. In the canonical ensemble, system composition is specified directly via blend fractions, which are bound on [0,1]. This naturally-bounded domain allows energy profiles (sweeps in blend fraction with other parameters fixed, such that common tangent calculations can be completed) to be computed in parallel at a variety of conditions without concern that the resultant data will miss the coexistence region. In contrast, the chemical potential in the grand-canonical ensemble is specified rather than the blend fraction. The chemical potential is not similarly bounded, and the numerical range in which coexistence would be observed is not known a priori. It is also not known how far the chemical potential at coexistence may shift with changes in, for example, segregation strength or chain length. By running canonical ensemble calculations in parallel at the desired parameter ranges (in our case, segregation strength) we can quickly obtain results over the desired range. When additional accuracy is needed, these initial results can then act as a guide to estimate chemical potential values when refining three-phase coexistence or the regions near disorder.

Construction of the phase diagram reported in Figure 4 for an alloy with  $N_{B'C}/N_{AB} = 1.0$ and  $\epsilon_{BC} = 1.5$  started with initial sets of canonical ensemble SCFT calculations followed by common tangent constructions at  $\chi N = 23.5$  (the lowest value at which the Laves phases converged) and integer values of  $\chi N$  from 24.0 to 40.0 to obtain a coarse map of the phase boundaries. Subsequent canonical ensemble, common-tangent calculations were then performed at increments of 0.5 in  $\chi N$  around the AB-rich and B'C-rich coexistence transitions points (such as where the AB-rich phase in coexistence with the Laves phase field changes from fcc to bcc, or from bcc to hex). These first two rounds of calculation considered only the Laves phases and the macrophase separation competitors. A third round of canonical ensemble calculations added the remaining competitors at a selection of segregation strengths. Below the transition to Laves-hex<sub>AB</sub> coexistence, competing phases were run at all sampled segregation strengths. Above this transition, we noticed that the AB-rich hex phase quickly out-competes the Laves phases and suspected that it would similarly outcompete the other sphere-forming morphologies. We chose to run the remaining competitors only at  $\chi N = 30$ ,  $\chi N = 40$ , and at odd values of  $\chi N$  from 31 to 39 finding that, indeed, all competitors are similarly outcompeted by AB-rich hex with increasing  $\chi N$ . On the basis of this result, we chose not to run the competing phases at the remaining  $\chi N$  values. Finally, grand canonical ensemble calculations were used to refine the position of invariant points and map the region near the ODT.

Here, Figure S4 reports the same phase diagram as Fig. 4 of the main text, but includes the particular points used to generate the diagram. Each dot in Figure S4 represents a point at which we have collected SCFT data. Data were collected at the highest density near invariant points where grand canonical ensemble was used to resolve the three-phase coexistence conditions. The reported data show that the splines used to draw the phase boundaries introduce no anomalous shapes and broadly reflect the collected data.



Figure S4: (a) Phase diagram for an AB/B'C alloy with  $N_{\rm B'C}/N_{\rm AB} = 1.0$ ,  $f_{\rm A} = f_{\rm C} = 0.20$ ,  $\epsilon_{\rm AB} = 1.0$ ,  $\epsilon_{\rm BC} = 1.5$ , and assuming purely enthalpic  $\chi$  values such that  $\chi_{\rm AC}N_{\rm AB} = 2(\chi N)$  at all T and (b) a detailed view of the Laves phase field within that phase diagram. Points indicate conditions at which we collected SCFT data. The reference temperature,  $T_0$ , was chosen to correspond to  $\chi N = 30$ . Non-linear segments of the phase diagram are drawn using cubic splines fit to the sampled data.

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