Electronic Supplementary Material (ESI) for Soft Matter.
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Supporting Information

The C36 Laves phase in diblock polymer melts

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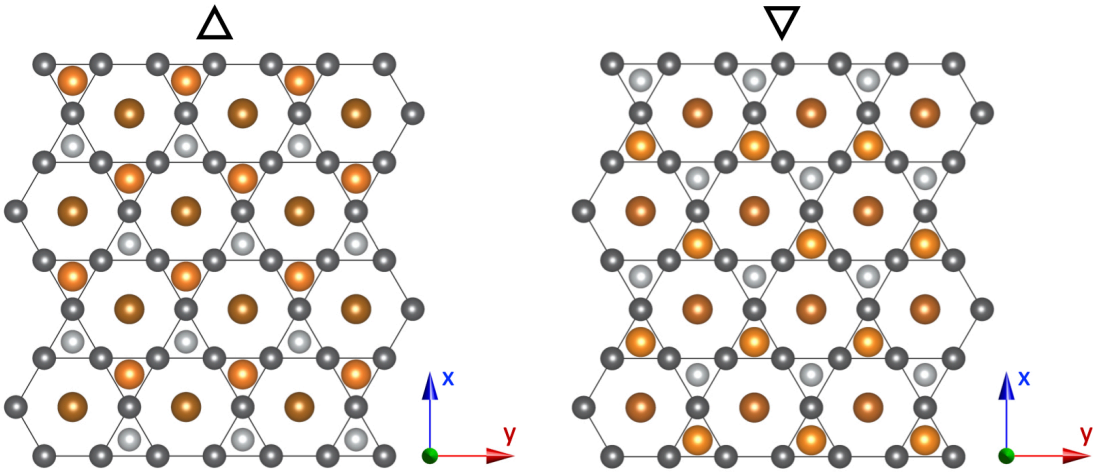

Fig. S1: The two different layer types in a Laves phase with AB_2 stoichiometry, where A sites are shown as orange spheres and B as gray spheres, shown in a top-down view (looking down the [0001] vector of the C14 or C36 unit cell). Lines indicate the kagomé net at the base of the layer. Cartesian x, y, and z directions are defined such that z is perpendicular to the Laves phase layers, and y is parallel to an arbitrarily chosen line in the kagomé net (meaning that x is not), consistent with Figure 1 in the main text. Particles that are darkened (burnt orange or dark gray) are further from the viewer. Figure generated using VESTA.[S1]

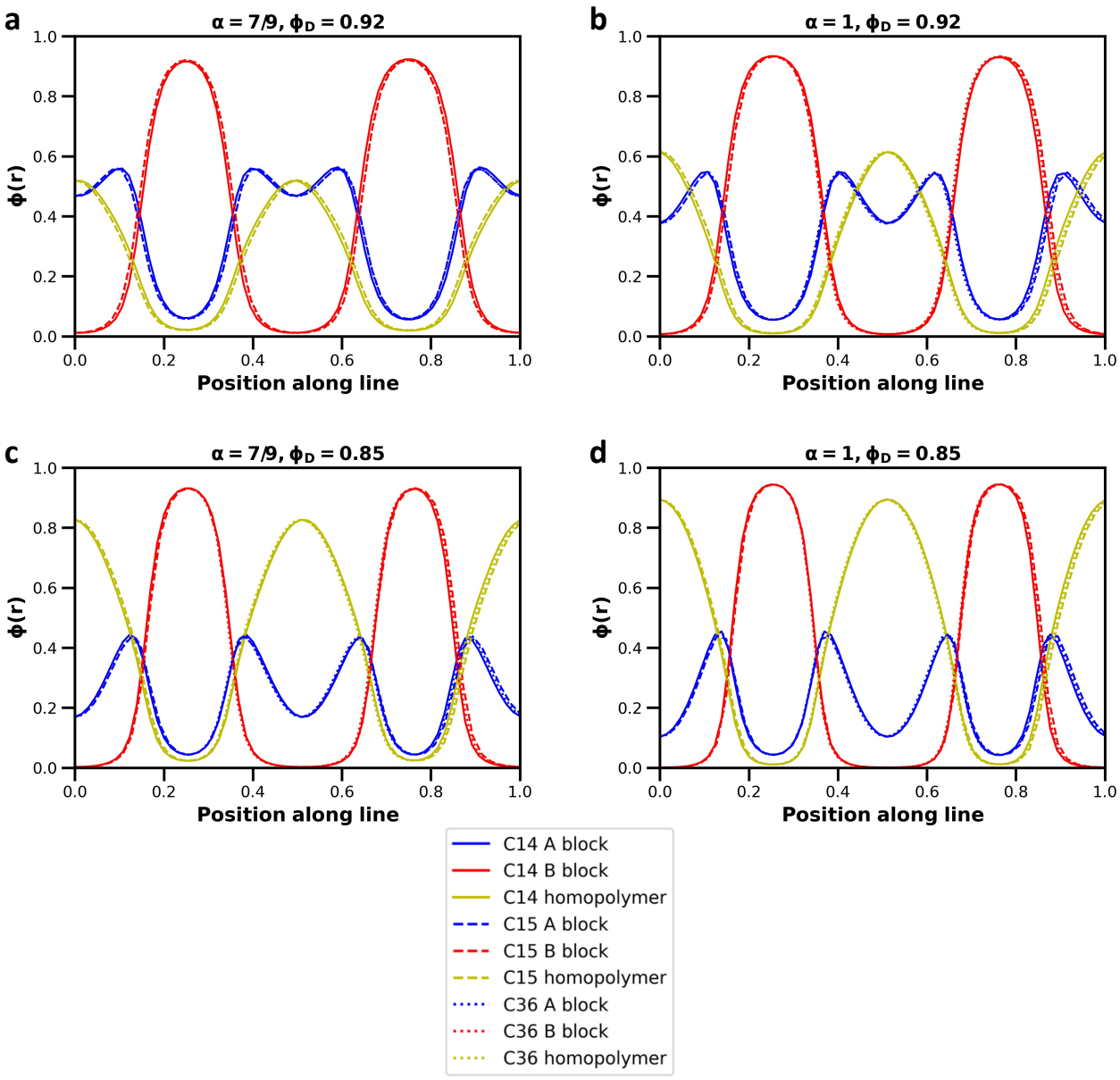

Fig. S2: Local volume fraction $\phi(\mathbf{r})$ of each species in a blend of AB diblock polymers and A homopolymers (where A forms the micelle core), plotted as a function of position along a line that travels through 3 particles in a kagomé net within a single Laves phase layer, as shown visually in the lower-right panel of Figure 2 of the main text. Data were calculated using SCFT at $\chi N = 25, \epsilon = b_A/b_B = 1.31$, and $f_A = 0.18$. The volume fraction of the A block is shown in blue, the B block is shown in red, and the A homopolymer is shown in yellow; data for the C14 mesophase are shown as a solid line, C15 is shown as a dashed line, and C36 is shown as a dotted line. Data are shown for the wet-brush regime ($\alpha = 7/9$, where $\alpha = N_H/N_A$) and the dry-brush regime ($\alpha = 1$), and at bulk diblock polymer volume fractions $\phi_D = 0.92$ and 0.85, as indicated by the title of each subplot.

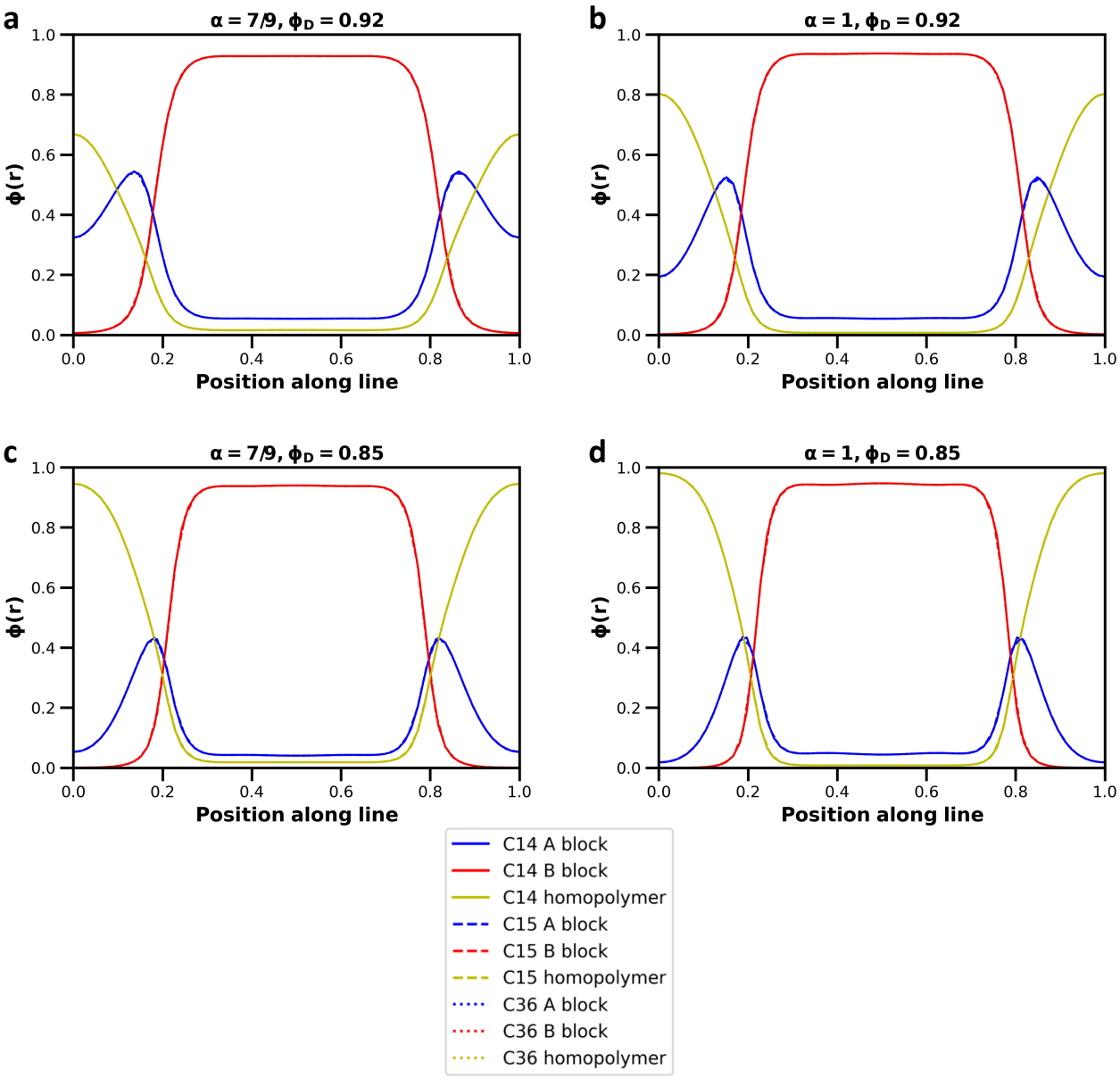

Fig. S3: Local volume fraction $\phi(\mathbf{r})$ of each species in a blend of AB diblock polymers and A homopolymers (where A forms the micelle core), plotted as a function of position along a line that travels between 2 particles in a triangulated layer of the larger particles within a single Laves phase layer, as shown visually in the lower-right panel of Figure 2 of the main text. Data were calculated using SCFT at $\chi N = 25, \epsilon = b_A/b_B = 1.31$, and $f_A = 0.18$. The volume fraction of the A block is shown in blue, the B block is shown in red, and the A homopolymer is shown in yellow; data for the C14 mesophase are shown as a solid line, C15 is shown as a dashed line, and C36 is shown as a dotted line. Data are shown for the wet-brush regime ($\alpha = 7/9$, where $\alpha = N_H/N_A$) and the dry-brush regime ($\alpha = 1$), and at bulk diblock polymer volume fractions $\phi_D = 0.92$ and 0.85, as indicated by the title of each subplot.

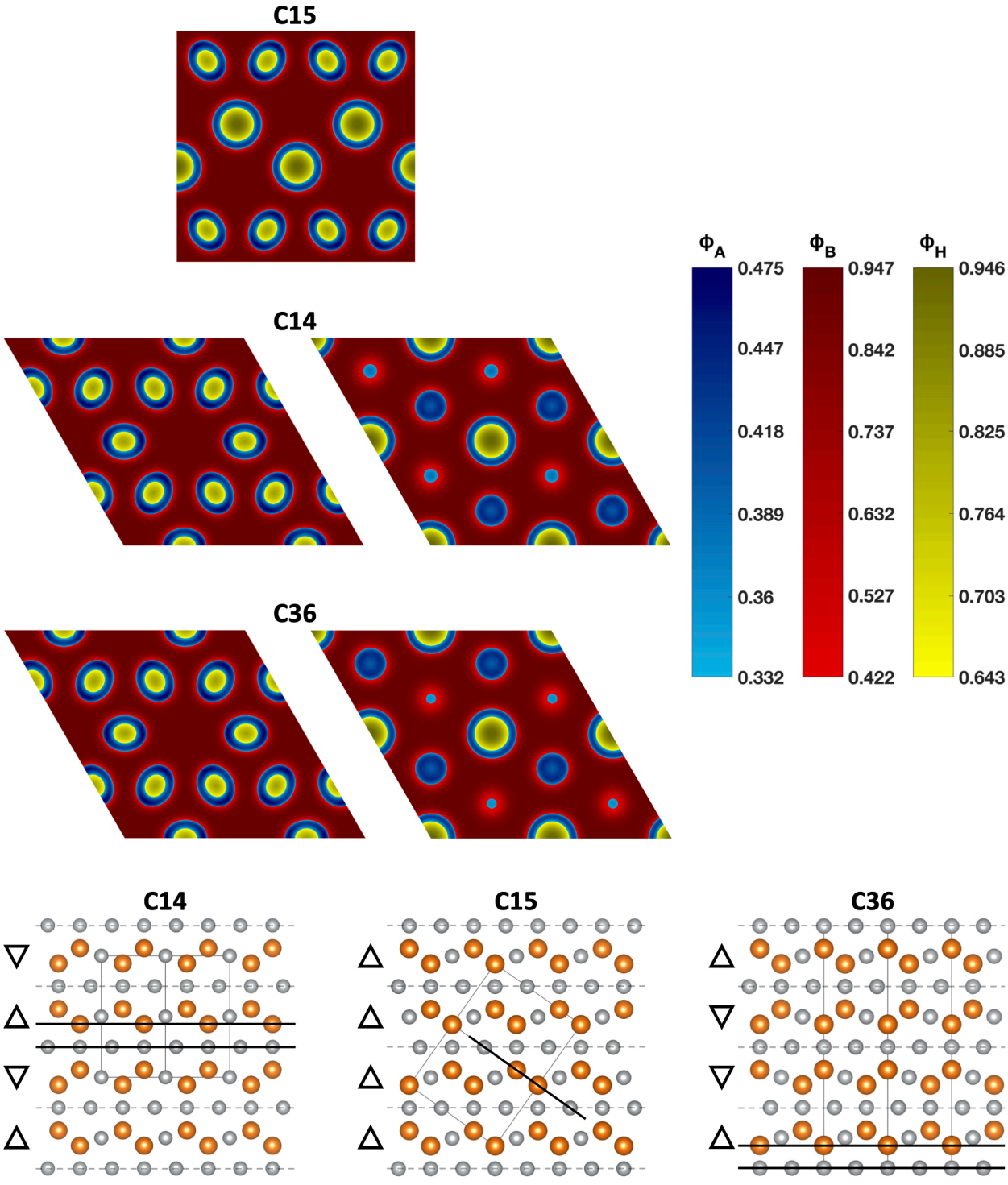

Fig. S4: 2D contour plots showing the local volume fraction $\phi(\mathbf{r})$ of the different species in a blend of AB diblock polymers and A homopolymers (where A forms the micelle core), showing small and large particles in each Laves phase, where color indicates volume fraction as indicated by the colorbars. Figs. 1d-f from the main text are also reproduced, with solid black lines added to indicate the location of the planes that are shown in the contour plots. The volume fraction of the A block is shown in blue, the B block is shown in red, and the A homopolymer is shown in

yellow. Data are shown for the wet-brush regime ($\alpha = 7/9$, where $\alpha = N_{\mathrm{H}}/N_{\mathrm{A}}$) at bulk diblock polymer volume fraction $\phi_{\mathrm{D}} = 0.85$, calculated using SCFT at $\chi N = 25, \epsilon = b_{\mathrm{A}}/b_{\mathrm{B}} = 1.31$, and $f_{\mathrm{A}} = 0.18$.

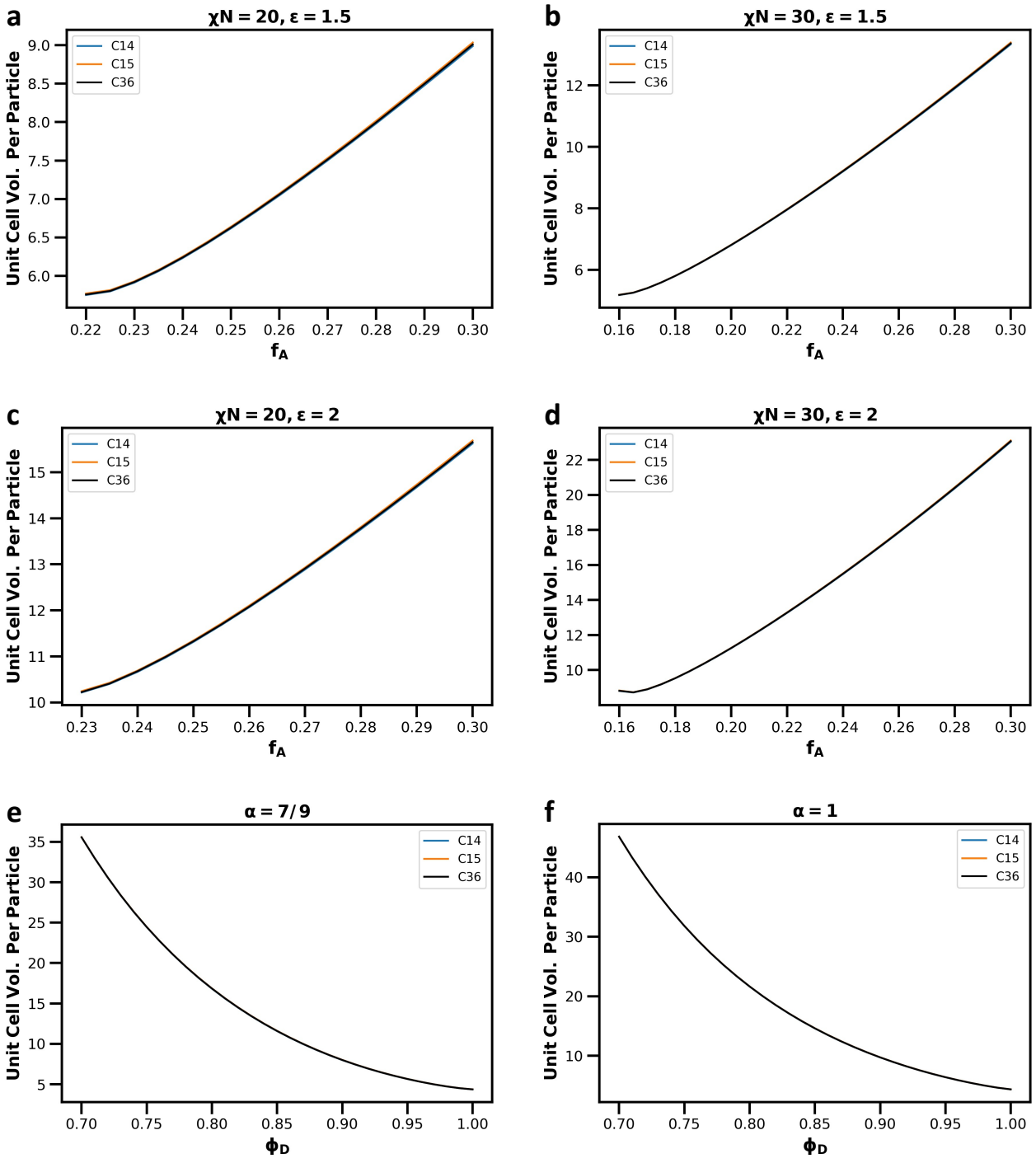

Fig. S5: Unit cell volume per particle for all conditions tested, computed using optimized unit cell parameters determined by self-consistent field theory. The lengths are made dimensionless using the length $\sqrt{N}b_{\mathrm{B}}$. Panels (a-d) show data for neat AB diblock polymer melts at the indicated values of χN and $\epsilon = b_{\mathrm{A}}/b_{\mathrm{B}}$, as a function of polymer composition f_{A}. Panels (e-f) show data for blends of AB diblock polymers and A homopolymers (where A forms the micelle core), at $\chi N = 25, \epsilon = 1.31, f_{\mathrm{A}} = 0.18$, and $\alpha = 7/9$ or 1 (where $\alpha = N_{\mathrm{H}}/N_{\mathrm{A}}$), as a function of diblock polymer volume fraction ϕ_{D}.

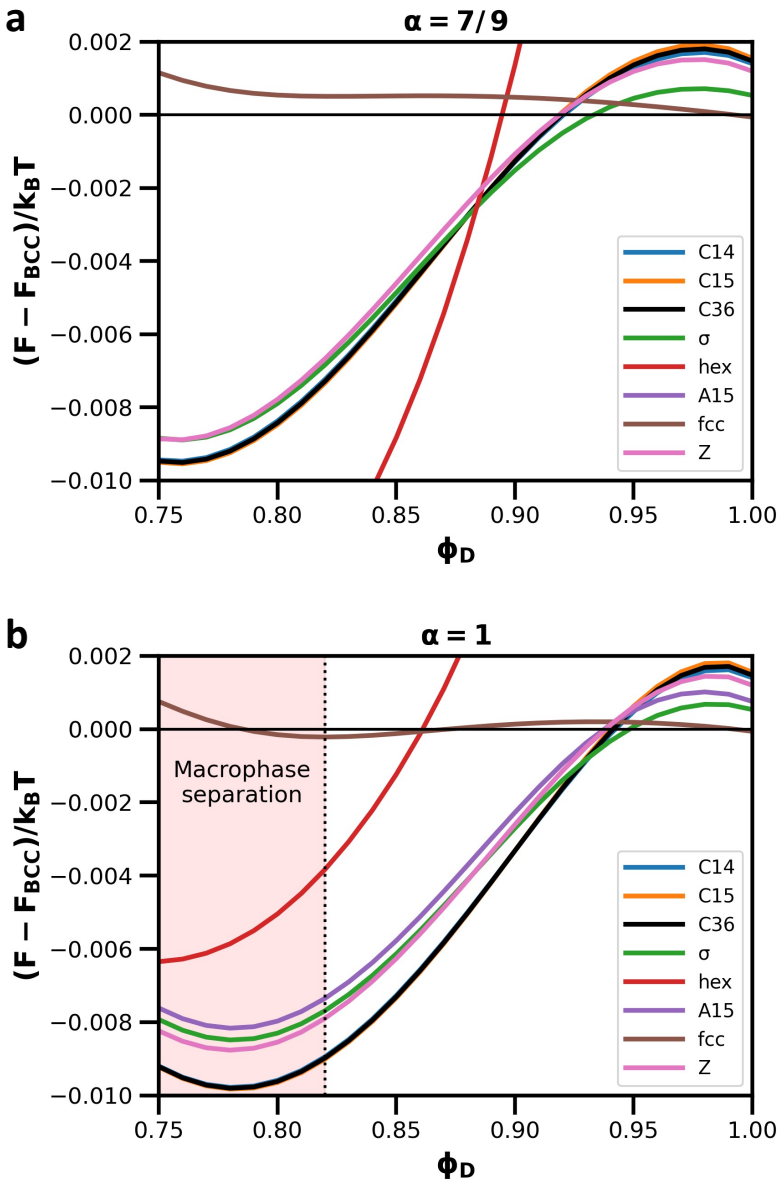

Fig. S6: Identical to Fig. 3 in the main text, but now including the fcc, Z, and A15 mesophases, which were excluded from the main text figure for clarity. Helmholtz free energy per chain in a blend of AB diblock polymers and A homopolymers (where A forms the micelle core) relative to the free energy of the bcc mesophase, calculated using SCFT at $\chi N = 25, \epsilon = b_A/b_B = 1.31$, and $f_A = 0.18$ as a function of AB diblock polymer volume fraction ϕ_D. Data are shown for (a) the wet-brush regime ($\alpha = 7/9$, where $\alpha = N_H/N_A$) and (b) the dry-brush regime ($\alpha = 1$).

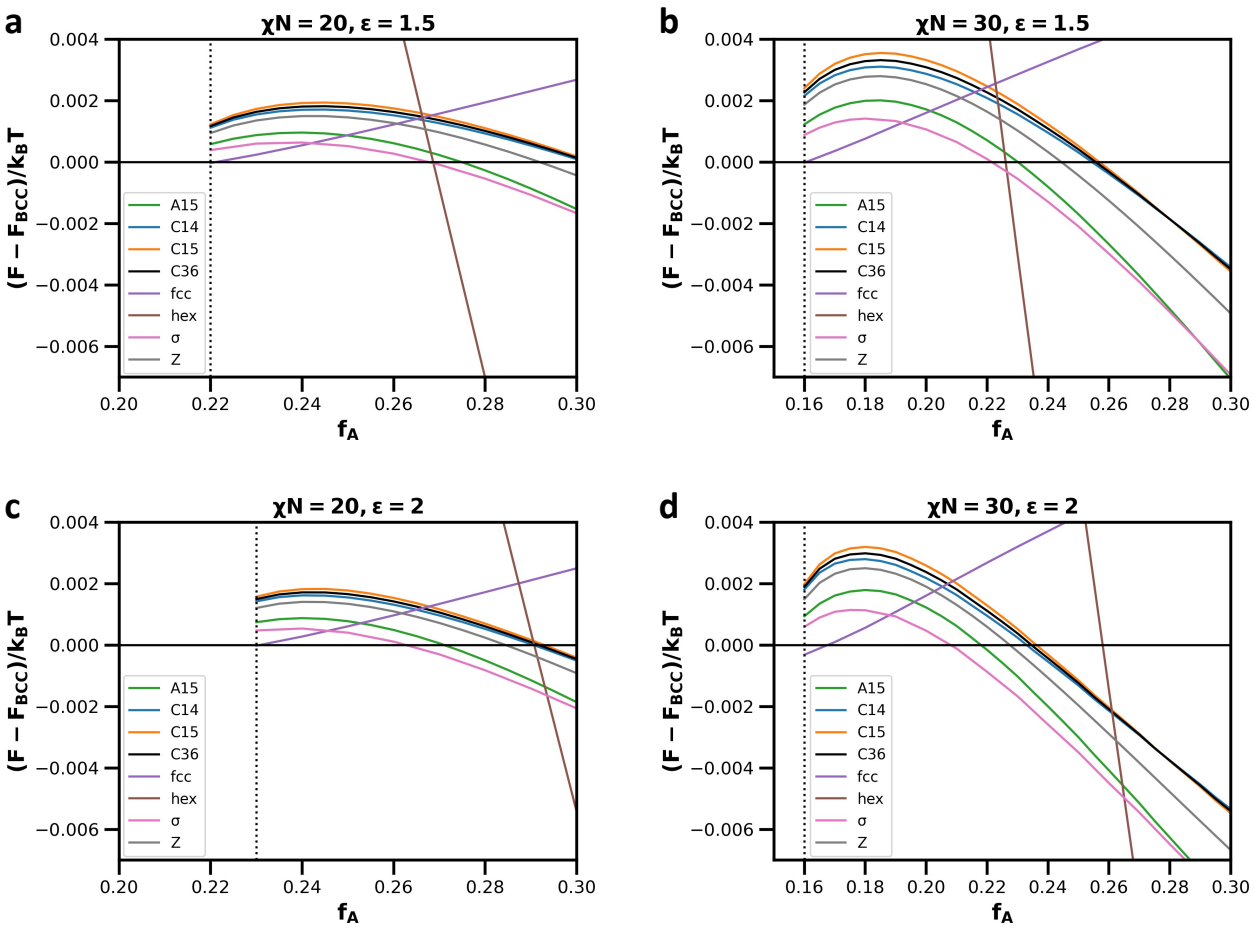

Fig S7: Helmholtz free energy per chain in a neat melt of AB diblock polymers relative to the free energy of the bcc mesophase, calculated using SCFT at the indicated values of χN and $\epsilon = b_{\mathrm{A}}/b_{\mathrm{B}}$, as a function of polymer composition f_{A}, for all candidate mesophases. Compositions to the left of the vertical dotted lines correspond to the disordered regime. Data for the fcc, hex, and σ mesophases are reproduced from Kim et al.,[S2] while all other data were calculated anew for this work.

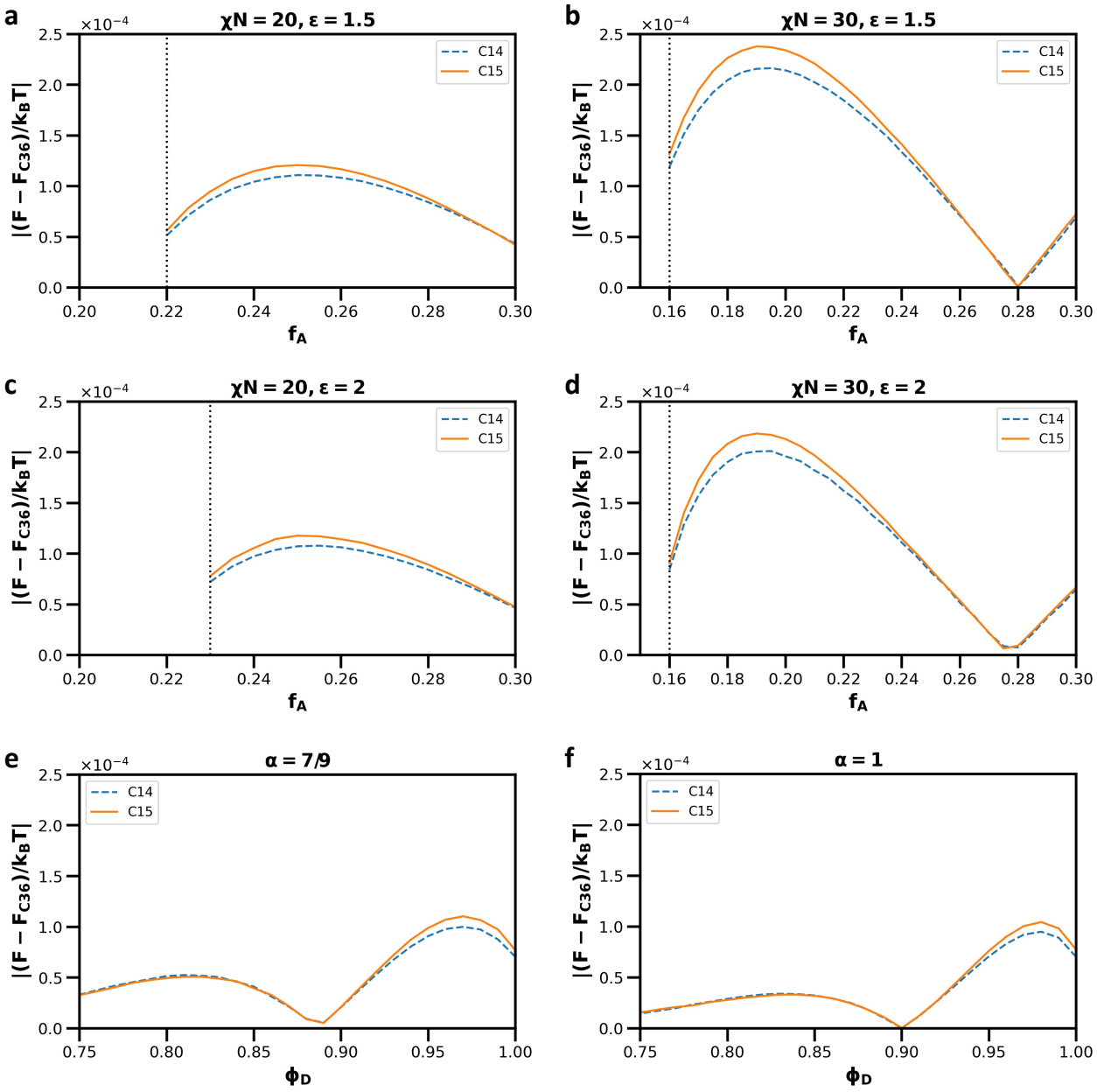

Fig S8: Identical to Figs. 4 and 5 of the main text, but the absolute values are shown rather than the true values. In all cases, the lines plotted are the absolute value of the free energy per chain of the C14 and C15 mesophases relative to the C36 mesophase, calculated using SCFT. Panels (a-d) correspond to Fig. 5 of the main text, showing data for neat AB diblock polymer melts at the indicated values of χN and $\epsilon = b_A/b_B$, as a function of polymer composition f_A. Panels (e-f) correspond to Fig. 4 of the main text, showing data for blends of AB diblock polymers and A homopolymers (where A forms the micelle core), at $\chi N = 25, \epsilon = 1.31, f_A = 0.18$, and $\alpha = 7/9$ or 1 (where $\alpha = N_H/N_A$), as a function of diblock polymer volume fraction ϕ_D.

References:

(S1) K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272-1276.

(S2) K. Kim, M. W. Schulze, A. Arora, R. M. Lewis, M. A. Hillmyer, K. D. Dorfman and F. S. Bates, *Science*, 2017, **356**, 520-523.