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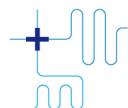
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ABSTRACT

A stable region of the double primitive (DP) network structure formed by the AB-type comb-shaped block copolymer (A-g-B CSBCP) melts is identified using self-consistent field theory. The formation mechanism of the DP network is systematically investigated. In the mean-field limit, the transition in the A-g-B CSBCP melts between the DP network and its spherical counterpart, the metastable body-centered cubic (BCC) spheres, can be either continuous or discontinuous, distinct from the typical order-order transitions (OOTs) observed in conventional block copolymer melts. We further determine the critical point at which the discontinuity vanishes. Our results demonstrate that the stability of the DP phase and the continuous OOT primarily originate from the unique chain architecture of the A-g-B CSBCP.

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I. INTRODUCTION

In the last three decades, extensive experimental and theoretical studies have led to significant progress in understanding and predicting the microphase behavior of block copolymers (BCPs).^{1,2} Four generic types of microstructures have been observed in BCP melts: lamellar, bicontinuous network, cylindrical, and spherical phases.³ Among these ordered structures, tubular network morphologies, owing to their interconnected channels and high volumetric surface areas,⁴ hold great promise for the development of various functional materials.^{5–8} To date, although 349 distinct network phases have been generated using artificial intelligence,⁹ only two network nanostructures, the double gyroid (DG)³ and the O^{70} (*Fddd*) phases,^{10,11} have been predicted to be equilibrium phases in diblock-copolymer (DBC) melts using self-consistent field theory (SCFT). Beyond simple DBCs, theoretical studies predict that double-diamond (DD) and double-primitive (DP) networks can be

stabilized through blending¹² or chain-architecture design.¹³ Takagi *et al.* successfully obtained the DD network in ternary blends of diblock copolymers containing polyisoprene blocks of different chain lengths.¹⁴ Thermodynamically stable DD networks have been found in syndiotactic polypropylene-block-polystyrene¹⁵ and isotactic polypropylene-block-polystyrene melts.¹⁶ The stability of the DD phase arises from the release of packing frustration within the minority block, achieved through either blending or the introduction of helical segments. Recently, Lee *et al.* reported that a stable DP network nanostructure can be obtained by linking small functional groups to the ends of diblock-copolymer chains.¹⁷

The DG and O^{70} networks^{3,10} occupy the region of the phase diagram between the lamellar and cylindrical phases, whereas the stable region of the DP network is located near the spherical phases.^{13,18} This proximity indicates that adjusting system parameters (e.g., temperature) might induce a sphere-network transformation. Such a transformation is closely related to topological

defects (e.g., broken struts) in network structures formed by BCPs, which affect the performance of the materials.^{19,20} It is noteworthy that tubular network nanostructures have spherical counterparts. For example, BCC spheres and DP networks possess the same space group, with the nodes in the DP network corresponding to the spheres in the BCC phase. Therefore, the topology of the DP network can be considered as a direct linking of neighboring sphere centers. In a recent study, Chang *et al.* kinetically trapped a double-network structure sharing the same space group as the Frank-Kasper (FK) A15 phase ($Pm\bar{3}n$) via solution casting.²¹ Unlike the DP network, the FK-like network phase is built from the bisectors of the spheres, with its nodes in every single network alternating periodically between three-strut and four-strut connections. We focus on the DP network in this work because of its simpler topological structure and richer foundational literature, in contrast to the newly discovered FK-like network. Although hexagonal-network,²² network-network,^{23,24} and DG-FK-A15 transformations²⁵ have been investigated, to the best of our knowledge, studies of the DP-sphere transformation have been lacking.

In this work, we revisit the self-assembly behavior of AB-type comb-shaped block-copolymer (A-g-B CSBCP) melts, which was previously investigated by Lin and co-workers,²⁶ by considering a broader set of candidate nanostructures than in the earlier study. The A-g-B CSBCP can adopt loop-bridge-dangle conformations²⁷ to accommodate the local geometries of the nodes and struts in tubular networks, making it possible to stabilize the DD and DP phases. The mechanism by which the chain architecture stabilizes the DD and DP phases through macromolecular conformations has been discussed previously.¹³ We first construct a phase diagram for A-g-B CSBCP melts, in which stable regions of the DD and DP networks are found. To gain insight into the formation mechanism, we systematically investigate the effects of immiscibility between the A and B blocks and chain architecture on the stability of the DP phase. We further investigate the phase transition between the DP and BCC phases, revealing that it can be either continuous or discontinuous depending on the chain architecture.

II. MODEL SYSTEM AND SELF-CONSISTENT FIELD THEORY (SCFT)

We consider an A-g-B CSBCP melt in a volume V , containing n_c chains at temperature T . Each A-g-B CSBCP (as shown in Fig. 1) consists of N segments with five B-segment side chains grafted onto an A backbone. For simplicity, we set the number of side chains to $m = 5$. Other values, $m = 2, 3, 4$, and 7 , have been considered in previous studies.^{26–28} The length of each side chain is $f_{sc}N$, and the distance between two consecutive grafting points is $f_{bb}N$. We define an architectural parameter $\tau = f_2/(f_1 + f_2)$ to describe the relative position of the side chains along the A backbone, where f_1N and f_2N are the lengths of the A_1 and A_2 blocks, respectively, as illustrated in Fig. 1. This chain architecture may serve as an alternative coarse-grained model for the $L_{n_1}DA_mL_{n_2}$ triblock copolymer, oligo(lactic acid)-block-oligo(2-hydroxytetradecanoic acid)-block-oligo(lactic acid).^{29,30} In this representation, the ester-containing polyester moieties of the L and DA units are combined into an effective A-type backbone, whereas the alkyl substituents of the DA units

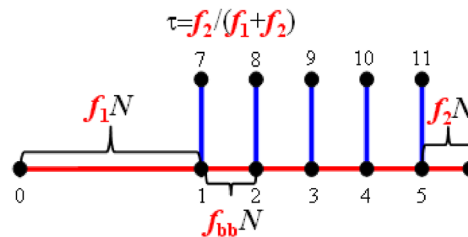


FIG. 1. Illustration of the chain architecture of the A-g-B CSBCP, where the numbers refer to the indices of the junction points.

are modeled as B-type side chains. This mapping reflects the chemical similarity of the L and DA backbones and the immiscibility between the backbone and side chain segments.

We assume that all N segments have the same number density ρ_0 and statistical segment length b and that the grafting density of the side chains is sufficiently low for each block in the A-g-B CSBCP to be modeled as a Gaussian chain. We adopt the “standard” model and self-consistent field theory (SCFT) to describe this system.³¹

Within the mean-field approximation, the Helmholtz free energy per chain is given by

$$\beta f_c = \frac{\chi N}{V} \int d\mathbf{r} \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - \ln Q_c - \frac{1}{V} \sum_{\alpha} \int d\mathbf{r} \omega_{\alpha}(\mathbf{r}) \phi_{\alpha}(\mathbf{r}) + \eta(\mathbf{r}) \left[1 - \sum_{\alpha} \phi_{\alpha}(\mathbf{r}) \right], \quad (2.1)$$

where $\phi_{\alpha}(\mathbf{r})$ and $\omega_{\alpha}(\mathbf{r})$ are the volume-fraction fields and their conjugate potential fields for segments of type $\alpha = A, B$, respectively, and Q_c is the single-chain partition function given by

$$Q_c = \frac{1}{V} \int d\mathbf{r} q_{p,q}(\mathbf{r}, s) q_{q,p}(\mathbf{r}, 1-s). \quad (2.2)$$

Here, $q_{p,q}(\mathbf{r}, s)$ is a propagator satisfying the modified diffusion equation (MDE),

$$\frac{\partial q_{p,q}(\mathbf{r}, s)}{\partial s} = \nabla^2 q_{p,q}(\mathbf{r}, s) - \omega_{\alpha}(\mathbf{r}) q_{p,q}(\mathbf{r}, s), \quad (2.3)$$

starting from vertex p and ending at vertex q (see Fig. 1). Here, $0 \leq s \leq 1$ is the normalized chain-contour variable along a block with vertices p and q as its two ends, and the segment type α depends on the vertices p and q . Table S1 of the supplementary material lists the propagators on an A-g-B CSBCP chain and their corresponding initial conditions. After solving the MDEs, the volume-fraction fields $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ are calculated, and the following SCFT equations are solved iteratively:

$$\begin{cases} \phi_A(\mathbf{r}) = \sum_{\alpha=A} \int_0^1 ds q_{p,q}(\mathbf{r}, s) q_{q,p}(\mathbf{r}, 1-s), \\ \phi_B(\mathbf{r}) = \sum_{\alpha=B} \int_0^1 ds q_{p,q}(\mathbf{r}, s) q_{q,p}(\mathbf{r}, 1-s), \\ \omega_A(\mathbf{r}) = \chi N \phi_B(\mathbf{r}) + \eta(\mathbf{r}), \\ \omega_B(\mathbf{r}) = \chi N \phi_A(\mathbf{r}) + \eta(\mathbf{r}). \end{cases} \quad (2.4)$$

With $f_{bb} = 0.05$, the model contains only three independent parameters: $f_A = 1 - 5f_{sc}$, τ , and χN , where χ is the Flory–Huggins interaction parameter. All SCFT calculations are performed using the open-source software package PSCF+.³²

The density distribution of vertex v is computed as

$$\rho^v(\mathbf{r}) = \frac{1}{Q_c} \prod_p q_{p,v}(\mathbf{r}, 1), \quad (2.5)$$

where the product runs over all branches terminating at vertex $v = 0, \dots, 11$ (see Fig. 1).

III. RESULTS

The phase diagram of our model system is constructed by comparing the dimensionless mean-field Helmholtz free energy per chain, βf_c , of nine candidate ordered phases: lamellae (L), hexagonal cylinders (HEX), the Frank–Kasper (FK) A15 and σ phases, hexagonal close-packed spheres (HCP), double gyroid (DG), double diamond (DD), double primitive (DP), and body-centered cubic (BCC) spheres. A representative phase diagram in the τ – f_A plane at $\chi N = 75$ is shown in Fig. 2. It is interesting to note that the DP structure emerges as a stable phase in the window defined by $0.14 < \tau < 0.23$ and $0.5 < f_A < 0.52$. As τ increases, SCFT predicts the order–order phase-transition sequence HCP $\rightarrow$ DP $\rightarrow$ HEX $\rightarrow$ DD $\rightarrow$ DG. On the one hand, as in the phase diagrams constructed by Li and co-workers,^{13,18} the stable DP network phase in the current model is located near the spherical phase. It is reasonable to speculate that the morphology of the stable DP phase in this system is obtained by deforming the spherical domains of a spherical phase. On the other hand, a conventional network phase (DG or DD) is obtained by varying the cylinders of the HEX phase.²² Figure S1(a) shows the volume-fraction field of the DP phase formed by the A-g-B CSBCP at $f_A = 0.5$, $\tau = 0.16$, and $\chi N = 75$, where we can see that the struts are thinner than those formed by DBC [see Fig. S1(c)]. Previous SCFT studies have shown that the DP phase formed by the DBC melts is metastable.^{3,9,13}

We first investigate the effect of the interaction strength between A and B segments (χN) on the DP morphology. We find that increasing χN leads to a significant enlargement in the cross-sectional dimensions of the network struts. At $\chi N = 120$, the struts in the DP phase formed by the A-g-B CSBCP are almost as thick as those in DBC melts [see Figs. S1(a), S1(b), S2(a), and S2(b)].

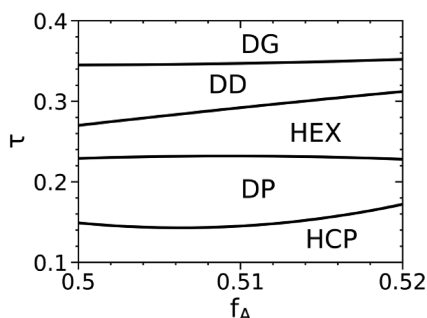


FIG. 2. SCFT phase diagram of the A-g-B CSBCP melts in the τ – f_A plane at $\chi N = 75$.

To understand the morphological evolution of the DP phase, we quantitatively investigate how the strut thickness varies with χN . Figure 3(a) shows the volume-fraction profiles of the A and B segments along the line connecting two neighboring nodal points (or sphere centers), i.e., the segment distribution along the central axis of a strut. We observe that increasing χN enhances the segregation between the A and B segments along the central axis of a strut, resulting in an increase in strut thickness. More importantly, we note a point at $\chi N = 72.675$, when $f_A = 0.5$ and $\tau = 0.16$, where the two volume-fraction profiles are tangent to one another. The struts become “disconnected” if χN falls below this point. We define a connectivity parameter $\Delta \equiv \phi_A(0.5L_0/R_g, 0, 0) - \phi_B(0.5L_0/R_g, 0, 0)$ to quantify the degree of connection between neighboring nodal domains; larger values of Δ indicate stronger connections between these domains. As shown in Fig. 3(b), Δ varies continuously with χN at $f_A = 0.5$ and $\tau = 0.16$. This observation is nontrivial, indicating that the transition between the DP phase and its spherical counterpart, the BCC phase, can be continuous, which will be discussed in detail later.

To examine the microscopic details of the structural evolution as χN increases, we investigate the spatial distributions of the chain vertices. At $\chi N = 72$, the A_1 block forms the core of each sphere, whereas the remaining A segments accumulate outside the core to form a shell (see Fig. S3). At $\chi N = 73$, a similar core–shell-like distribution is observed, but the shells of neighboring nodes are connected to form the network (see Fig. S4). The vertex-density distributions at both values of χN show that vertices 3–6 are concentrated in the

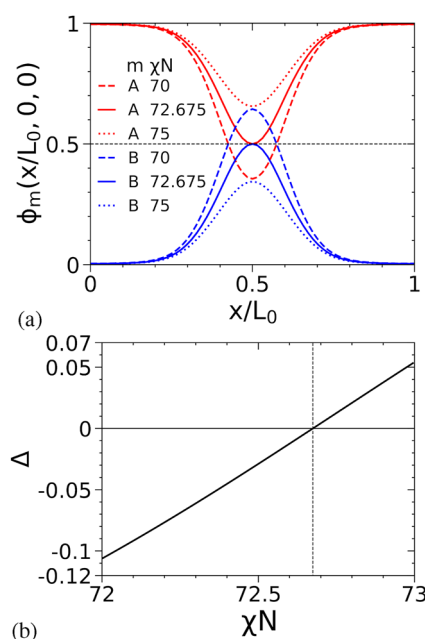


FIG. 3. (a) Volume-fraction profiles of the A and B segments, $\phi_m(xL_0/R_g, 0, 0)$, along the line connecting two neighboring nodal points (i.e., sphere centers) at $\chi N = 70$, 72.675 , and 75 , respectively, where L_0/R_g is the natural period of the cubic unit cell in units of the radius of gyration, $R_g \equiv \sqrt{N/6} b$. (b) Connectivity parameter Δ as a function of χN . The dashed vertical line marks $\chi N = 72.675$, where $\Delta = 0$, $f_A = 0.5$, and $\tau = 0.16$.

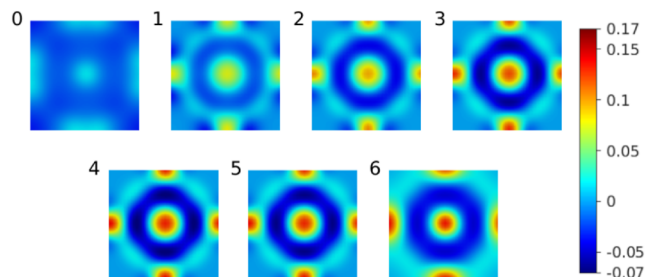


FIG. 4. Variations of the vertex density distributions as χN increases from 72 to 73, $\rho_{\chi N=73}^v(\mathbf{r}) - \rho_{\chi N=72}^v(\mathbf{r})$, with $\rho_{\chi N}^v(\mathbf{r})$ being the density distribution of vertex v ($v = 0-6$). $f_A = 0.5$ and $\tau = 0.16$.

region between neighboring nodes. A similar core-shell-like network structure has been reported previously.¹³ Furthermore, Fig. 4 shows that the vertices undergo different degrees of displacement as χN increases from 72 to 73. The side chain grafting points (vertices 1–5), and particularly the free end of the A_2 block (vertex 6), are displaced more significantly than the free end of the A_1 block (vertex 0). In other words, the segments forming the shells exhibit greater spatial variation than those forming the cores. These results indicate that formation of the DP network is driven primarily by anisotropic swelling of the shell regions. Videos S1 and S2 show the corresponding evolution of isosurfaces viewed along the [001] direction. In Video S1, χN increases from 50 to 100 at $f_A = 0.5$ and $\tau = 0.16$; in Video S2, it increases from 60 to 90 at $f_A = 0.52$ and $\tau = 0.14375$.

To gain deeper insight into the phase transition between DP and BCC phases, we investigate how τ affects the transition. As shown in Fig. 5, for relatively large values of τ , the connectivity parameter Δ varies continuously with χN . By contrast, when τ falls below a threshold value, Δ exhibits a discontinuous jump as χN is varied. An analogous behavior is observed in the free energy. The free energy curves for BCC and DP at $\tau = 0.125$ are shown in Fig. S5. The first derivatives of free energy with respect to χN change continuously at large τ but become discontinuous below a particular value [see Fig. S5(b)]. These observations indicate that the DP–BCC phase

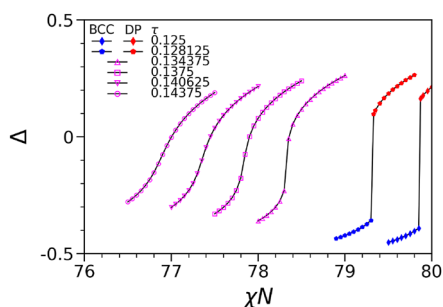


FIG. 5. Connectivity parameter Δ as a function of χN for the BCC and DP mesophases at various values of τ . $f_A = 0.52$.

transition may be either continuous or discontinuous, depending on τ . Although Δ is a local measure of morphology, it can nevertheless describe the morphological evolution across the DP–BCC phase transition.

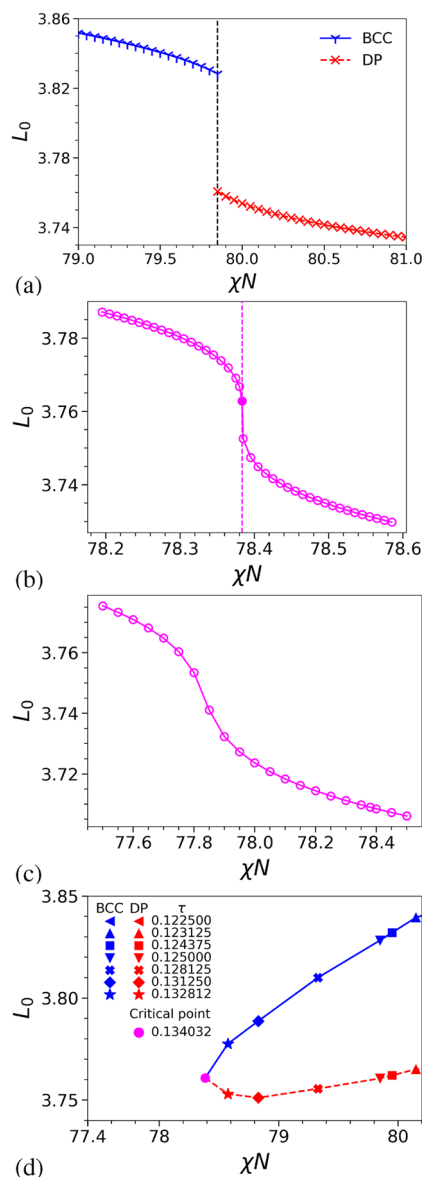


FIG. 6. Natural period, L_0 , of the BCC and DP mesophases as functions of χN at (a) $\tau = 0.125$, (b) $\tau = 0.134032$, and (c) $\tau = 0.1375$. The dashed vertical lines in (a) and (b) mark $\chi N = 79.850$ and 78.3835 , respectively. The solid circle in (b), at $L_0 = 3.762795$, marks the natural period at the critical point. (d) Natural period of the BCC and DP phases along the coexistence line shown in Fig. 8; blue and red symbols denote the BCC and DP phases, respectively. The markers in (d) correspond to the coexistence points ($\tau, \chi N$) as follows: $\blacktriangleleft$, (0.122500, 80.280); $\blacktriangle$, (0.123125, 80.150); $\blacksquare$, (0.124375, 79.950); $\blacktriangledown$, (0.125000, 79.850); $\times$, (0.128125, 79.330); $\blacklozenge$, (0.131250, 78.830); $\star$, (0.1328125, 78.575); and a pink colored circle, (0.134032, 78.3835), denoting the critical point.

Because the DP–BCC transition is isosymmetric, a discontinuous transition is accompanied by a jump in the natural period.^{33–36} We, therefore, examine how τ affects the natural period. As shown in Fig. 6(a), at $\tau = 0.125$, the natural period exhibits a discontinuous

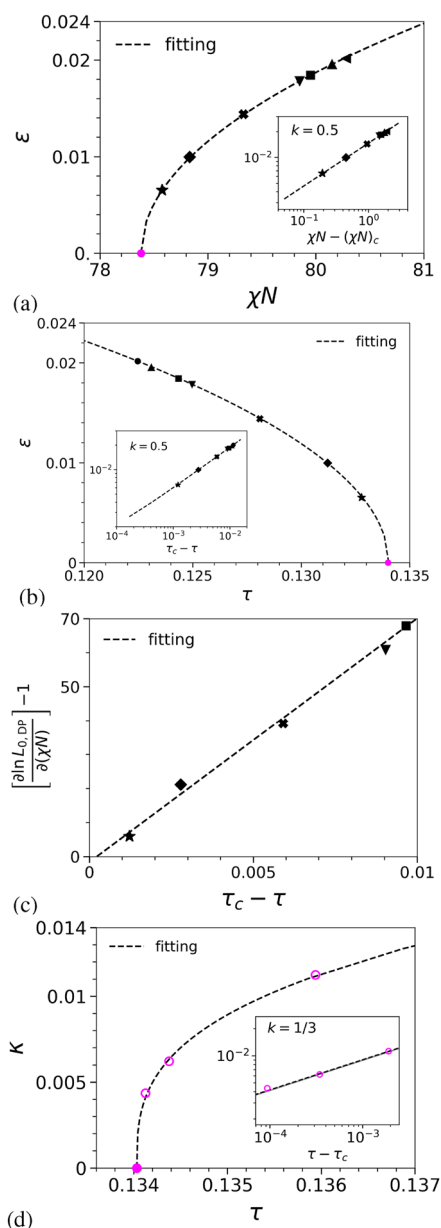


FIG. 7. Order parameter ε as a function of (a) χN and (b) τ . The fitting curves are $\varepsilon_{\text{fit}} = 0.0147[\chi N - (\chi N)_c]^{1/2}$ in (a) and $\varepsilon_{\text{fit}} = 0.1876(\tau_c - \tau)^{1/2}$ in (b). (c) The inverse derivative $[\partial \ln L_{0,\text{DP}} / \partial(\chi N)]^{-1}$ as a function of $\tau_c - \tau$. The linear fit has a slope of 7169.2 and an intercept of -1.5981 . (d) κ , evaluated along the critical isotherm $\chi N = (\chi N)_c$, as a function of τ . The fitting curve is given by $0.09(\tau - \tau_c)^{1/3}$. The markers in (a)–(c) correspond to the same $(\tau, \chi N)$ coexistence points listed in Fig. 6(d).

jump as χN is varied. At $\tau = 0.1375$, however, this jump disappears [Fig. 6(c)]. This behavior suggests the existence of a critical point at which the DP and BCC phases become indistinguishable and the discontinuity vanishes. In Fig. 6(d), pairs of data points with matching marker symbols denote the natural periods of the coexisting DP and BCC phases along the DP–BCC coexistence line, defined by $\beta f_c^{\text{DP}} = \beta f_c^{\text{BCC}}$. As τ increases along the coexistence line, the difference between the two natural periods decreases, and they converge to a common value at the critical point. Although the above results provide strong evidence for the existence of such a critical point, its exact location has yet to be determined. The following describes how we locate it.

Because the DP and BCC phases have distinct natural periods in the discontinuous transition regime, we define an order parameter,

$$\varepsilon = \ln \left(\frac{L_{0,\text{BCC}}}{L_{0,\text{DP}}} \right), \quad (3.1)$$

to quantify this difference. Because the cubic unit-cell volume is $V_0 = L_0^3$, this quantity can also be written as $\varepsilon = \frac{1}{3} \ln (V_{0,\text{BCC}}/V_{0,\text{DP}})$ and, therefore, represents the logarithmic dilation strain associated with the structural transformation. It is nonzero when the BCC and DP phases have distinct natural periods and vanishes when their natural periods merge at the critical point. In contrast to Δ , which characterizes local connectivity, ε captures the global structural difference between the two phases and, thus, serves as a natural order parameter for the BCC–DP critical behavior. Beyond the critical point, only a single $\text{Im}\bar{3}m$ state exists. We characterize its deviation from the critical state by

$$\kappa = \ln \left(\frac{L_{0,c}}{L_0} \right). \quad (3.2)$$

Here, $L_{0,c}$ is the natural period at the critical point and L_0 is the natural period of the $\text{Im}\bar{3}m$ state.

The precise location of the critical point is difficult to determine directly from the numerical SCFT solutions. Because SCFT is a mean-field theory, the order parameter is expected to vanish with the mean-field exponent $\beta_{\text{MF}} = 1/2$. We, therefore, fit ε along the coexistence line to the square-root forms $\varepsilon \propto [\chi N - (\chi N)_c]^{1/2}$ and $\varepsilon \propto (\tau_c - \tau)^{1/2}$, as shown in Figs. 7(a) and 7(b), respectively. These fits yield the critical point at $(\tau_c, (\chi N)_c) = (0.134\,032, 78.3835)$, as shown by the magenta points in Figs. 6(d), 7(a), and 7(b).

With the critical point thus determined, the remaining mean-field exponents can be obtained. Figure 7(c) shows that the inverse response $[\partial \ln L_{0,\text{DP}} / \partial(\chi N)]^{-1}$ approaches zero linearly as $\tau \rightarrow \tau_c$, where $L_{0,\text{DP}}$ is the natural period of the DP phase. The derivative is evaluated numerically using a central-difference scheme with a step size of $\Delta(\chi N) = 0.001$. The slight displacement of the fitted zero crossing from $\tau_c - \tau = 0$ is attributed to the numerical error introduced by the finite-difference approximation. The corresponding response, therefore, diverges with the mean-field exponent $\gamma_{\text{MF}} = 1$. This divergence reflects the increasing sensitivity of the natural period to changes in χN near the critical point, as also shown in Figs. 6(a)–6(c). Along the critical isotherm ($\chi N = (\chi N)_c$), Fig. 7(d) gives $\kappa \propto (\tau - \tau_c)^{1/3}$, corresponding to the critical-isotherm exponent $\delta_{\text{MF}} = 3$. These scaling relations demonstrate that the BCC–DP transition is consistent with the mean-field universality class.

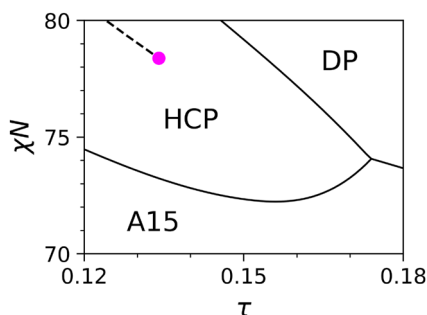


FIG. 8. SCFT phase diagram of the A-g-B CSBCP melts in the τ - χN plane at $f_A = 0.52$. The magenta solid circle represents the critical point at $(\tau, \chi N) = (0.134\,032, 78.3835)$.

Figure 8 shows another phase diagram in the τ - χN plane at $f_A = 0.52$ with the BCC–DP critical point (shown in magenta). The dashed line denotes the DP–BCC coexistence line. Both the coexistence line and the critical point lie within the thermodynamically stable HCP region, indicating that the BCC–DP critical behavior is hidden by the stable HCP phase.

IV. CONCLUSION

In summary, we have used SCFT to investigate the formation of the DP network and the transition between the DP and BCC phases in A-g-B CSBCP melts. We find that the A-g-B CSBCP melts can form a thermodynamically stable DP network. The stability of the DP phase arises primarily from the ability of the comb-shaped chain architecture to adopt different conformations.

We further show that, unlike conventional OOTs, the DP–BCC transition can be continuous. Both phases have the same $\text{Im}\bar{3}m$ space group, and the DP network can be viewed as arising from the formation of struts connecting nearest-neighbor spherical domains in the BCC phase. As the A–B incompatibility increases, the shells surrounding the spherical domains swell anisotropically and progressively connect to form a network, whereas the spherical cores remain relatively unchanged. Whether the transition is continuous or discontinuous depends on the chain-architecture parameter τ . At relatively large τ , the connectivity parameter Δ varies continuously with χN . When τ falls below a threshold value, however, the connectivity parameter, the derivative of the free energy, and the natural period all exhibit discontinuous jumps, indicating a first-order transition. Thus, the DP–BCC transition behavior can be controlled by varying the relative positions of the side chains along the backbone. The first-order BCC–DP coexistence line terminates at a critical point at $(\tau_c, (\chi N)_c) = (0.134\,032, 78.3835)$. As this point is approached, the difference between the natural period of the BCC and DP phases vanishes. Beyond the critical point, only a single $\text{Im}\bar{3}m$ state remains. The associated critical exponents are $\beta = 1/2$, $\gamma = 1$, and $\delta = 3$, consistent with the scaling under the mean-field limit.

This continuous transition pathway may provide a useful strategy for designing nanonetwork materials with tunable connectivity. For example, varying χN (i.e., temperature) could enable isolated domains to progressively develop into interconnected

channels. It also provides a mechanistic framework for understanding topological defects in network structures.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) includes the initial conditions for solving the MDE to obtain the propagators (Table S1), DP morphologies and volume-fraction profiles for the A-g-B CSBCP and AB diblock copolymer (Figs. S1 and S2), vertex-density distributions for the BCC and DP phases (Figs. S3 and S4), and the free-energy data used to characterize the DP–BCC transition (Fig. S5).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Juntong He: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Xue-Hui Dong:** Conceptualization (equal); Formal analysis (equal); Investigation (supporting); Methodology (equal); Project administration (supporting); Writing – original draft (supporting); Writing – review & editing (equal). **Jiajia Zhou:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (lead); Investigation (supporting); Methodology (equal); Project administration (lead); Supervision (equal); Writing – original draft (supporting); Writing – review & editing (equal). **An-Chang Shi:** Conceptualization (equal); Formal analysis (equal); Investigation (supporting); Methodology (equal); Project administration (supporting); Supervision (supporting); Writing – original draft (supporting); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supplementary Material: Continuous and Discontinuous Transitions between Double Primitive Network and Body-Centered Cubic Spheres

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TAB S1: Propagators on the A-g-B CSBCP chain with their corresponding conjugate field type α and initial conditions.

Alt text: The table lists 22 directed chain propagators, their A or B conjugate fields, and initial conditions. Seven propagators starting at free ends have initial value one. The other initial values are products of two incident propagators evaluated at contour endpoint $s = 1$, encoding the grafted chain connectivity.

Propagator	α	Initial Condition
$q_{0,1}(\mathbf{r}, s)$	A	$q_{0,1}(\mathbf{r}, s = 0) = 1$
$q_{6,5}(\mathbf{r}, s)$	A	$q_{6,5}(\mathbf{r}, s = 0) = 1$
$q_{7,1}(\mathbf{r}, s)$	B	$q_{7,1}(\mathbf{r}, s = 0) = 1$
$q_{8,2}(\mathbf{r}, s)$	B	$q_{8,2}(\mathbf{r}, s = 0) = 1$
$q_{9,3}(\mathbf{r}, s)$	B	$q_{9,3}(\mathbf{r}, s = 0) = 1$
$q_{10,4}(\mathbf{r}, s)$	B	$q_{10,4}(\mathbf{r}, s = 0) = 1$
$q_{11,5}(\mathbf{r}, s)$	B	$q_{11,5}(\mathbf{r}, s = 0) = 1$
$q_{1,2}(\mathbf{r}, s)$	A	$q_{1,2}(\mathbf{r}, s = 0) = q_{0,1}(\mathbf{r}, s = 1)q_{7,1}(\mathbf{r}, s = 1)$
$q_{2,3}(\mathbf{r}, s)$	A	$q_{2,3}(\mathbf{r}, s = 0) = q_{1,2}(\mathbf{r}, s = 1)q_{8,2}(\mathbf{r}, s = 1)$
$q_{3,4}(\mathbf{r}, s)$	A	$q_{3,4}(\mathbf{r}, s = 0) = q_{2,3}(\mathbf{r}, s = 1)q_{9,3}(\mathbf{r}, s = 1)$
$q_{4,5}(\mathbf{r}, s)$	A	$q_{4,5}(\mathbf{r}, s = 0) = q_{3,4}(\mathbf{r}, s = 1)q_{10,4}(\mathbf{r}, s = 1)$
$q_{5,6}(\mathbf{r}, s)$	A	$q_{5,6}(\mathbf{r}, s = 0) = q_{4,5}(\mathbf{r}, s = 1)q_{11,5}(\mathbf{r}, s = 1)$
$q_{5,4}(\mathbf{r}, s)$	A	$q_{5,4}(\mathbf{r}, s = 0) = q_{6,5}(\mathbf{r}, s = 1)q_{11,5}(\mathbf{r}, s = 1)$
$q_{4,3}(\mathbf{r}, s)$	A	$q_{4,3}(\mathbf{r}, s = 0) = q_{5,4}(\mathbf{r}, s = 1)q_{10,4}(\mathbf{r}, s = 1)$
$q_{3,2}(\mathbf{r}, s)$	A	$q_{3,2}(\mathbf{r}, s = 0) = q_{4,3}(\mathbf{r}, s = 1)q_{9,3}(\mathbf{r}, s = 1)$
$q_{2,1}(\mathbf{r}, s)$	A	$q_{2,1}(\mathbf{r}, s = 0) = q_{3,2}(\mathbf{r}, s = 1)q_{8,2}(\mathbf{r}, s = 1)$
$q_{1,0}(\mathbf{r}, s)$	A	$q_{1,0}(\mathbf{r}, s = 0) = q_{2,1}(\mathbf{r}, s = 1)q_{7,1}(\mathbf{r}, s = 1)$
$q_{1,7}(\mathbf{r}, s)$	B	$q_{1,7}(\mathbf{r}, s = 0) = q_{0,1}(\mathbf{r}, s = 1)q_{2,1}(\mathbf{r}, s = 1)$
$q_{2,8}(\mathbf{r}, s)$	B	$q_{2,8}(\mathbf{r}, s = 0) = q_{1,2}(\mathbf{r}, s = 1)q_{3,2}(\mathbf{r}, s = 1)$
$q_{3,9}(\mathbf{r}, s)$	B	$q_{3,9}(\mathbf{r}, s = 0) = q_{2,3}(\mathbf{r}, s = 1)q_{4,3}(\mathbf{r}, s = 1)$
$q_{4,10}(\mathbf{r}, s)$	B	$q_{4,10}(\mathbf{r}, s = 0) = q_{3,4}(\mathbf{r}, s = 1)q_{5,4}(\mathbf{r}, s = 1)$
$q_{5,11}(\mathbf{r}, s)$	B	$q_{5,11}(\mathbf{r}, s = 0) = q_{4,5}(\mathbf{r}, s = 1)q_{6,5}(\mathbf{r}, s = 1)$

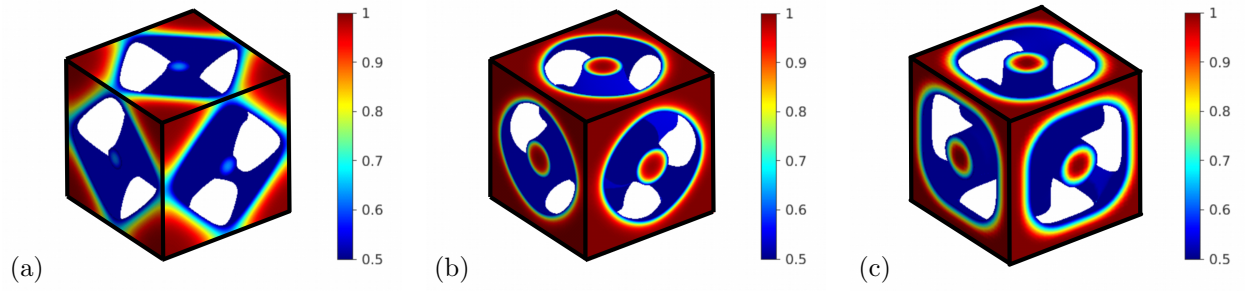


FIG S1: Volume-fraction fields of the A-segment for the DP phase formed by the *A-g-B* CSBCP at $f_A = 0.5$, $\tau = 0.16$ χN =(a)75 and (b)120 and by (c) an AB diblock copolymer at $f_A = 0.5$ and $\chi N = 40$.

Alt text: Three cutaway cubic views show A-segment volume fractions in double primitive networks. Colors range from blue at 0.5 to red at one. Central circular regions on the exposed faces become strongly A-rich as the graft copolymer χN increases from 75 to 120, resembling the diblock copolymer at $\chi N = 40$.

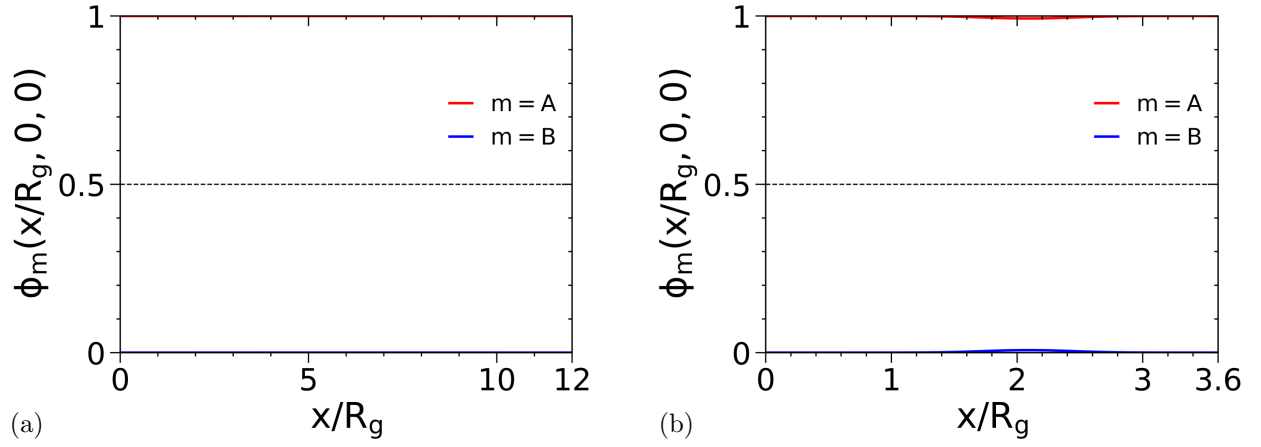


FIG S2: Volume-fraction profiles of the A- and B-segments, $\phi_m(x/R_g, 0, 0)$, along the line connecting neighboring nodal points in the DP phase formed by (a) an AB diblock copolymer at $f_A = 0.5$ and $\chi N = 40$ and (b) the A-g-B CSBCP at $f_A = 0.5$, $\tau = 0.16$, and $\chi N = 120$.

Alt text: Two line plots compare A- and B-segment volume fractions between neighboring network nodes. In the diblock copolymer, A remains near one and B near zero along the entire line. The graft copolymer shows a shallow A minimum and a complementary B maximum near $x/R_g = 2.1$; A still strongly dominates.

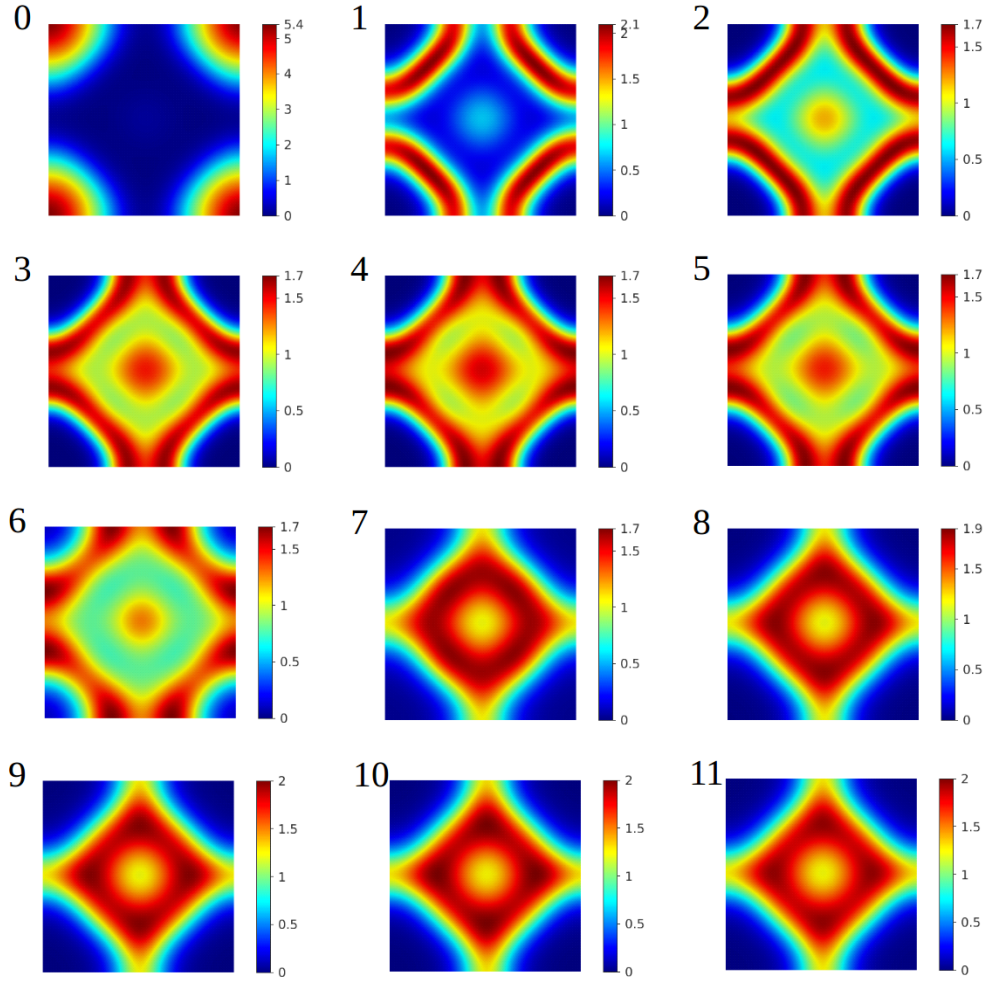


FIG S3: Density distributions, $\rho^v(\mathbf{r})$, of vertices $v = 0-11$ for the BCC phase at $\chi N = 72$, $f_A = 0.5$, and $\tau = 0.16$.

Alt text: Twelve heat maps show vertex densities in the body-centered cubic phase. Vertex 0 concentrates at the corners; vertices 1–6 show varying curved bands and central enrichment. Vertices 7–11 form broad diamond-shaped high-density bands around the center. Each panel has its own blue-to-red scale, with red indicating higher density.

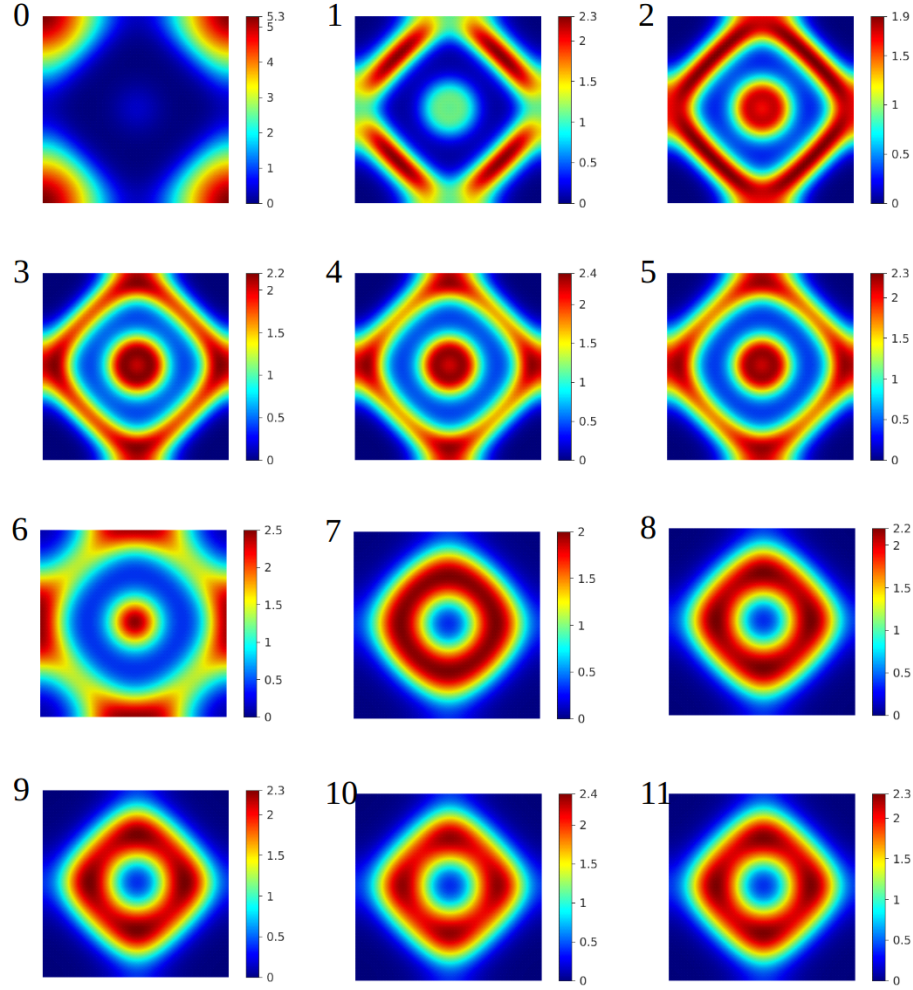


FIG S4: Density distributions, $\rho^v(\mathbf{r})$, of vertices $v = 0$ –11 for the DP phase at $\chi N = 73$, $f_A = 0.5$, and $\tau = 0.16$.

Alt text: Twelve heat maps show vertex densities in the double primitive phase. Vertex 0 concentrates at the corners. Vertices 2–6 have sharp central peaks surrounded by lower-density rings and outer bands. Vertices 7–11 form rounded diamond-shaped high-density rings around low-density centers. Separate blue-to-red scales indicate increasing density.

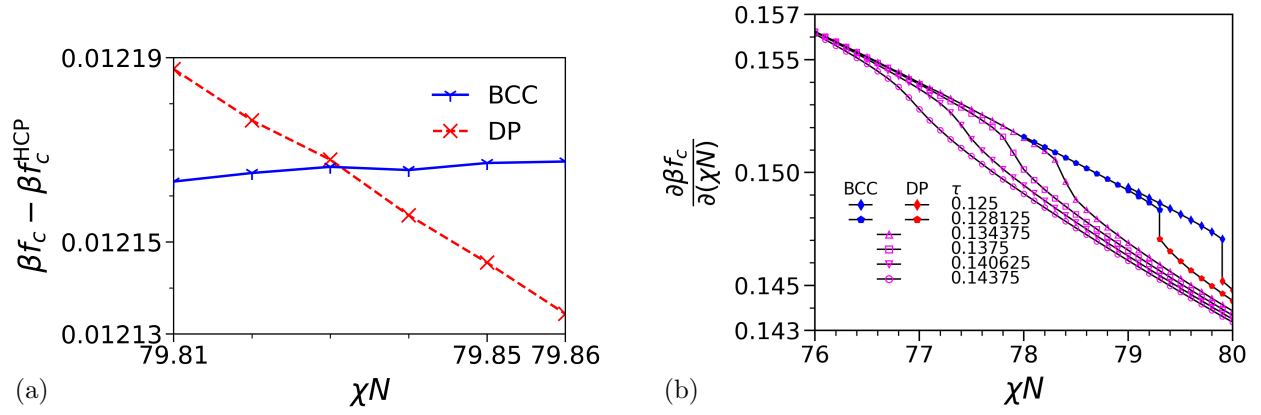


FIG S5: (a) Dimensionless Helmholtz free-energy differences relative to the HCP phase, $\beta f_c - \beta f_c^{\text{HCP}}$, as functions of χN for the BCC and DP phases at $\tau = 0.125$. (b) First derivatives of the dimensionless Helmholtz free energy per chain, $\partial(\beta f_c)/\partial(\chi N)$, as functions of χN for various values of τ at $f_A = 0.52$.

Alt text: In (a), the double primitive free-energy difference relative to hexagonal close-packed spheres decreases and crosses the nearly flat body-centered cubic curve; both differences remain positive. In (b), the free-energy derivative decreases with χN . Discontinuous drops at $\tau = 0.125$ and 0.128125 give way to continuous curves at larger τ .