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Extremely asymmetric phase diagram of homopolymer-monotethered nanoparticles: Competition between chain conformational entropy and particle steric interaction

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The phase behaviors of homopolymer-monotethered nanoparticles (HMNs) in melt are investigated via a theoretical method combining self-consistent field theory for polymers and density functional theory for hard spheres. An extremely asymmetric phase diagram is observed: (i) microphases are only possible for the volume fraction of the tethered polymer \( f_A > 0.35 \); (ii) in addition to lamellar phase, the system can only self-assemble into various morphologies with a polymer-rich matrix, including gyroid phase, cylindrical phase, and spherical phase. In the frame of this theory, the critical point for HMNs’ microphase separation is significantly lower than that of linear diblock copolymers. Furthermore, the characteristic length of microphase-separated structures of HMNs is much smaller than that of linear diblock copolymers with the same molecular weight. Our calculation results on morphologies and characteristic length agree well with recent simulations and experimental observations. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4975023]

I. INTRODUCTION

Self-assembly of polymer-nanoparticle amphiphiles has attracted increasing interest due to their capacity of forming various morphologies. Among them, the homopolymer-monotethered nanoparticles (HMNs) and the copolymer-monotethered nanoparticles have been synthesized via diverse preparation approaches for studying their morphology and microstructures. A wide variety of feasible candidate nanoparticles with diverse shapes provide an opening platform for engineering versatile functional materials with tailor-made properties derived from the nanoparticles, possessing potential applications in the fields of electronic devices, photonic devices, biosensors, and energy storage.

Recently, Cheng’s group has precisely synthesized a series of this class of tadpole-shaped molecules based on molecular nanoparticles, and extensively investigated their self-assembly behaviors in melt, solution, and thin films. Molecular nanoparticles possessing unique features of persistent shape and volume with well-defined chemical structures and surface functionalities, such as spherical fullerene (C_{60}) and cubic polyhedral oligomeric silsesquioxane (POSS), are used as the building block for the heads of the “tadpoles”\(^{1}\): The primary tail chains are usually flexible polystyrene (PS) or poly(ethylene oxide) (PEO). When the polymer tails are hydrophobic and the nanoparticles are hydrophilic, the tadpole-shaped HMNs behave as “giant surfactants”, which self-assemble into small vesicles and cylinders in solvents as small-molecule surfactants do. On the other hand, in melts and in thin films, the tadpole-shape molecules self-assemble into diverse sub-10-nm ordered nanostructures including lamellae, gyroids, cylinders, and spheres, which is reminiscent of the phase separation of block copolymer melts.

Although HMNs exhibit abundant morphologies analogous to small-molecule surfactants and to diblock copolymers, obvious difference arising from fundamental molecular architecture persists. A HMN is different from a small-molecule surfactant due to the large conformational entropy of its long, flexible tail. It is also different from a diblock copolymer owing to the rigid volume exclusion of the nanoparticle. The equilibrium morphologies of HMN systems depend on the delicate balance among several terms of the free energy, including the conformational entropy of the polymers, the translational entropy and steric interaction of the nanoparticles, and the enthalpic interaction between the polymers and nanoparticles. Unfortunately, it is hard to completely study the thermodynamical behaviors of HMN systems experimentally due to the difficulty in their precise synthesis. On the theoretical side, limited approaches on HMN are available in the literature at the moment, including a coarse-grained theoretical study using the microscopic polymer reference interaction site model (PRISM) theory, and a few particle-based simulations employing dissipative particle dynamics (DPD) and Brownian dynamics (BD).

They proved several aspects to be crucial to the self-assembly morphology of the system in melt and in solution, such as the geometry of nanoparticles, the topology of tethers, and the composition of polymers. However, until now there is still lack of a complete phase diagram to show the phase separation behaviors of HMN melts. Furthermore, from the theoretical point of view, it helps to understand HMN systems via comparison with diblock copolymer systems.

Based on our previous research on the phase separation behaviors of diblock copolymer brushes grafted on nanoparticles, we investigate the phase behaviors of HMN melts in...
this work, employing a theoretical method combining the self-consistent field theory (SCFT) for polymers and the density functional theory (DFT) for nanoparticles. Since the time when it was first developed by Thompson et al., this method has successfully described the morphologies and phase diagrams of polymer/nanoparticle mixtures and polymer-tethered nanoparticles. For HMN systems, Lee et al. preliminarily studied the lamellar and the cylindrical morphologies in melt in two dimensions, and only discussed the specific case with the volume fraction of the nanoparticles fixed at 0.45. Because this method has a great advantage in giving precise free energy at the mean-field level and predicting the phase diagram without prior assumption of the structure, we consider it worth taking a straightforward step to work out the full phase-separation diagram of HMN melts. And we consider it worth taking a straightforward step to work out the full phase-separation diagram of HMN melts except for liquid state of hard spheres. Note that there are various DFT models suitable for various shapes of nanoparticles. Therefore, in principle, this theoretical method has profound application prospects in particle/polymer systems by choosing proper DFT for the particle-particle interactions.

The remainder of the paper is organized as follows. We first outline the theoretical model we used in Section II. In Section III, we present the phase diagram of HMN systems and discuss the physical properties of the microphase separation including the density profiles, the characteristic lengths, and the free energy. Finally, we summarize the main results in Section IV.

II. THEORETICAL MODEL

We consider an incompressible melt system filled with $n$ tadpole-shaped homopolymer-monotethered nanoparticles in volume $V$. Each molecule consists of a flexible homopolymer chain A monomethylered on a spherical nanoparticle P of radius $R$, namely a HMN molecule, as shown in Fig. 1. We set the statistical segment length $a$ to be the length unit, and define $\rho_0^{-1} = 1$ as the segment volume of its flexible tail. The HMN molecule has the molecular volume $Nf_A^{-1}$, where $N$ is the degree of polymerization of a fictive, linear chain with the same volume of the HMN molecule. We define $f_A$ as the volume fraction of the tethered homopolymer. The volume of the homopolymer and the nanoparticle is $f_A N f_0^{-1}$ and $(1 - f_A) N f_0^{-1}$, respectively. To specify the configurations, each molecule is parameterized by a variable $s$, which starts from zero at the free end of the chain, and increases linearly along the homopolymer chain till $s = f_A$ at the junction of the polymer and the particle. The polymer conformation of the $\alpha$th molecule is represented by a space curve, $\mathbf{r}_\alpha(s)$. Then, the position of the center of the $\alpha$th particle is written as $\mathbf{R}_\alpha = \mathbf{r}_\alpha(f_A) + \mathbf{Rn}_\alpha$, where the unit vector $\mathbf{n}_\alpha$ is the direction between the junction and the center of the spherical particle of the $\alpha$th molecule. The partition function for the system is given by

$$Z = \frac{1}{n!} \int \prod_{\alpha=1}^{n} \mathcal{D}r_\alpha \prod_{\alpha=1}^{n} \mathcal{D}\mathbf{n}_\alpha \delta \left[ 1 - \Phi_A(r) - \Phi_P(r) \right] \times \exp \left\{ - \frac{3}{2N\rho_0^2} \sum_{\alpha=1}^{n} \int_0^{f_\alpha} ds \left[ \frac{dr_\alpha(s)}{ds} \right]^2 \right. $$

$$\left. - \chi \rho_0 \int dr \Phi_A(r) \Phi_P(r) \right\},$$

where $\delta$ is the Dirac delta function to ensure the incompressibility of system. And the interfacial energy between the polymer-rich domains and the particle-rich domains is phenomenologically described by the Flory-Huggins parameter $\chi$. The concentration operators of the polymer and the nanoparticle at a given position $\mathbf{r}$ are

$$\Phi_A(\mathbf{r}) = \frac{N}{\rho_0} \sum_{\alpha=1}^{n} \int_0^{f_\alpha} ds \delta (\mathbf{r} - \mathbf{r}_\alpha(s)),$$

$$\Phi_P(\mathbf{r}) = \frac{1}{v_R} \int_{|\mathbf{r}|<\mathbf{r}} d\mathbf{r}' \rho_P(\mathbf{r}') + \mathbf{r},$$

respectively, where

$$\rho_P(\mathbf{r}) = \frac{N}{\rho_0} \sum_{\alpha=1}^{n} \delta (\mathbf{r} - \mathbf{r}_\alpha(f_A) - \mathbf{Rn}_\alpha),$$

is the distribution operator for the center of the spherical particle. $v_R = 4\pi R^3/3$ is the volume of one spherical particle, and the volume fraction of the particle

$$f_P = \frac{v_R \rho_0}{N} = \frac{4\pi}{3} \rho_0^2 R_0^3 N^{1/2} = 1 - f_A,$$

where $R_0 \equiv a N^{1/2}$ is the root-mean-squared end-to-end distance of a fictive, linear chain of polymerization $N \equiv \alpha f_0^{-1}$. In accordance with the derived procedure of SCFT, the partition function is rewritten by introducing the field $W_i (i = A, P)$ as

$$Z = \int \mathcal{D}\Phi_A(\mathbf{r}) \mathcal{D}\rho_P(\mathbf{r}) \mathcal{D}W_A(\mathbf{r}) \mathcal{D}W_P(\mathbf{r}) \mathcal{D}\Xi(\mathbf{r}) \frac{Q^0}{n!} \times \exp \left\{ - \frac{\rho_0}{N} \int d\mathbf{r} \left[ \chi N \Phi_A(\mathbf{r}) \Phi_P(\mathbf{r}) - W_A(\mathbf{r}) \Phi_A(\mathbf{r}) - W_P(\mathbf{r}) \rho_P(\mathbf{r}) - \Xi(\mathbf{r}) (1 - \Phi_A(\mathbf{r}) - \Phi_P(\mathbf{r})) \right] \right\}.$$
where the partition function for a single HMN molecule \( Q \) is given by
\[
Q = \int d\mathbf{n}_r \int d\mathbf{r}_a \exp \left\{ -\frac{3}{2Nk_B^2} \int_0^{l_A} ds \left[ \frac{d\varphi_\rho(t)}{ds} \right]^2 \right\} \times \exp \left\{ -\int_0^{l_A} ds W_A (\mathbf{r}_a (s)) - W_P (\mathbf{r}_a(f_A) + \mathbf{Rn}_a) \right\}.
\] (7)

Moreover, we take into account the excluded volume interaction between the spherical particles by DFT introduced by Tarazona.\(^{38}\) Finally, the free energy of a single HMN molecule obtained from the mean-field approximation as well as the additional steric term is written as
\[
\frac{F}{nk_BT} = -\ln \left( \frac{Q}{V} \right) + \frac{1}{V} \int d\mathbf{r} [\chi N\varphi_A (\mathbf{r}) \varphi_P (\mathbf{r}) - w_A (\mathbf{r}) \varphi_A (\mathbf{r}) - w_P (\mathbf{r}) \rho_P (\mathbf{r}) - \xi (\mathbf{r}) (1 - \varphi_A (\mathbf{r}) - \varphi_P (\mathbf{r})) + \rho_P (\mathbf{r}) \psi_H (\varphi_P (\mathbf{r}))].
\] (8)

Here \( \varphi_A (\mathbf{r}), \varphi_P (\mathbf{r}) \) are the local volume density fractions of the homopolymer A and the particle P, respectively. \( w_A (\mathbf{r}), w_P (\mathbf{r}) \) are the fields which contribute to the polymers and the particles, respectively. \( \xi (\mathbf{r}) \) is the Lagrange multiplier to ensure the incompressibility condition. \( T \) is the temperature and \( k_B \) is the Boltzmann constant. The last term in the integral of Eq. (8) describes the steric energy of particles, which follows the example suggested by Lee et al.\(^{35}\) The steric term \( \psi_H \) is given by
\[
\psi_H (\varphi_P) = \frac{4\bar{\varphi}_P - 3 \varphi_P^2}{(1 - \varphi_P^2)}.
\] (9)

Note that the steric term we employed here was deduced only for the liquid state of hard spheres. Therefore, it is improper for solid states.

The free energy in Eq. (8) can be decomposed into three parts: the interfacial energy \( (U) \), the entropy contribution \( (-TS) \), and the steric interaction energy \( (F_{\text{steric}}) \),
\[
\frac{U}{nk_BT} = \frac{1}{V} \int d\mathbf{r} \chi N\varphi_A (\mathbf{r}) \varphi_P (\mathbf{r}),
\] (10)
\[
-\frac{TS}{nk_BT} = -\ln \left( \frac{Q}{V} \right) + \frac{1}{V} \int d\mathbf{r} [\chi N\varphi_A (\mathbf{r}) - w_A (\mathbf{r}) \varphi_A (\mathbf{r}) - w_P (\mathbf{r}) \rho_P (\mathbf{r}) - \xi (\mathbf{r}) (1 - \varphi_A (\mathbf{r}) - \varphi_P (\mathbf{r}))],
\] (11)
\[
F_{\text{steric}} = \frac{1}{V} \int d\mathbf{r} \rho_P (\mathbf{r}) \psi_H (\varphi_P (\mathbf{r})).
\] (12)

Furthermore, a special case of the free energy in Eq. (8) is that for the uniform disordered phase, where it reduces to
\[
\frac{F_{\text{uniform}}}{nk_BT} = \chi N\bar{f}_A f_P + \frac{(4\bar{f}_P - 3 \bar{f}_P^2)}{(1 - \bar{f}_P)^2},
\] (13)
where the first and the second terms on the right side are the interfacial energy and the steric interaction energy, respectively.

The local particle volume fraction \( \varphi_P (\mathbf{r}) \) and the weighted nonlocal volume fraction \( \bar{\varphi}_P (\mathbf{r}) \) are given as
\[
\varphi_P (\mathbf{r}) = \frac{1 - f_A}{v_R} \int_{|r'|<R} d\mathbf{r'} \rho_P (\mathbf{r'} + \mathbf{r}),
\] (14)
\[
\bar{\varphi}_P (\mathbf{r}) = \frac{1 - f_A}{v_{2R}} \int_{|r'|<2R} d\mathbf{r'} \rho_P (\mathbf{r'} + \mathbf{r}).
\] (15)

The partition function for a single HMN molecule \( Q \) can be rewritten as
\[
Q = \int d\mathbf{q} (\mathbf{r}, s) q^+ (\mathbf{r}, s),
\] (16)
where \( q(\mathbf{r}, s) \) and \( q^+ (\mathbf{r}, s) \) are the forward and backward propagators of the polymer chain, respectively, which are the probabilities of finding the segment \( s \) at position \( \mathbf{r} \). They satisfy the modified diffusion equations
\[
\frac{\partial q (\mathbf{r}, s)}{\partial s} = \frac{N q^2}{6} \nabla^2 q (\mathbf{r}, s) - w_A (\mathbf{r}) q (\mathbf{r}, s),
\] (17)
\[
\frac{\partial q^+ (\mathbf{r}, s)}{\partial s} = \frac{N q^2}{6} \nabla^2 q^+ (\mathbf{r}, s) + w_A (\mathbf{r}) q^+ (\mathbf{r}, s).
\] (18)

The initial condition of Eq. (17) is \( q(\mathbf{r},0) = 1 \), and that of Eq. (18) is \( q^+ (\mathbf{r},0) = \int d\mathbf{n} \exp [-w_P (\mathbf{r} + \mathbf{Rn})] \).

Furthermore, \( q(\mathbf{r},s), q^+ (\mathbf{r},s) \) is proportional to the distribution function \( \rho(\mathbf{r},s) \) for the \( sth \) segment. The normalized distribution is given by
\[
\rho (\mathbf{r}, s) = \frac{V}{Q} q (\mathbf{r}, s) q^+ (\mathbf{r}, s).
\] (19)

Minimizing the free energy in Eq. (8) with respect to the fields and densities \( (\varphi_A (\mathbf{r}), \varphi_P (\mathbf{r}), w_A (\mathbf{r}), w_P (\mathbf{r}), \xi (\mathbf{r})) \), we obtain the self-consistent mean field equations,
\[
w_A (\mathbf{r}) = \chi N\varphi_P (\mathbf{r}) + \xi (\mathbf{r}),
\] (20)
\[
w_P (\mathbf{r}) = \chi N\varphi_P (\mathbf{r}) + \xi (\mathbf{r}),
\] (21)
\[
\varphi_A (\mathbf{r}) + \varphi_P (\mathbf{r}) = 1,
\] (23)
where
\[
\psi_H (\chi) = \frac{d\psi_H (\chi)}{d\chi}.
\] (25)

Here we solve the self-consistent field equations by the pseudo-spectral method.\(^{39}\) First of all, the initial value of \( \varphi_A (\mathbf{r}) \) is generated, besides, \( \rho_P (\mathbf{r}) \) is uniform and \( \xi (\mathbf{r}) \) is set to zero. Next, the local particle volume fraction \( \varphi_P (\mathbf{r}) \) and the weighted nonlocal volume fraction \( \bar{\varphi}_P (\mathbf{r}) \) are calculated from Eqs. (14) and (15), then the field potentials \( w_A (\mathbf{r}), \rho_P (\mathbf{r}) \) are obtained via Eqs. (20) and (21). The propagators \( q(\mathbf{r},s), q^+ (\mathbf{r},s) \) can be solved through diffusion equations Eqs. (17) and (18), and the single partition function \( Q \) of HMM molecules is calculated from Eq. (16). The values of \( \varphi_A (\mathbf{r}), \rho_P (\mathbf{r}), \psi_H (\chi) \) are evaluated by Eqs. (14), (22), and (23), respectively. To ensure the
incompressibility, the pressure field $\xi(\mathbf{r})$ is obtained according to Eqs. (20) and (24). Finally, the fields $w_A(\mathbf{r})$, $w_P(\mathbf{r})$, and $\xi(\mathbf{r})$ are updated by the simple mixing method. The procedure is iterated until standard deviations of the fields between two iterations are smaller than $10^{-5}$ and the incompressibility condition is achieved.

The calculations are carried out in three-dimensional $(L_x \times L_y \times L_z)$ lattices. The degree of polymerization $N$ is chosen as 1000, and the step length of chain discretization is uniformly chosen as $\Delta s = 0.01$. The spatial discretization is always smaller than $0.02R_0$ to ensure the accuracy of the free energy. Periodic boundary conditions are satisfied in all axis directions. In order to obtain equilibrium morphologies, we minimize our free energy with respect to the size of the computational box.$^{40}$

III. RESULTS AND DISCUSSION

In this study, we apply a theoretical method combining self-consistent field theory and density functional theory to investigate the phase behaviors of HMN melts. The equilibrium morphologies of the phase separation of HMN melts are determined by the complicated interplay between three parts of the free energy, i.e., the system entropy, the interfacial tension between the polymer-rich domains and the particle-rich domains, and the steric interaction between the particles. By systematically changing the volume fraction of the polymer $f_A$ and the Flory-Huggins interaction parameter $\chi$, we determine a phase diagram to exhibit the strongly asymmetric phase separation behaviors of HMN melts, as compared with the symmetric phase diagram of linear diblock copolymers.

A. Morphological phase diagram of HMN melts

In the phase diagram of HMN melts, there are four equilibrium morphologies, including the lamellar phase (L), bicontinuous gyroid phase (G), hexagonally arranged cylindrical phase (C) of the particle-rich domain, and body-centered cubic spherical phase (S) of the particle-rich domain, as shown in Fig. 2.

An intuitive explanation of the sequence of the morphologies is as follows. Since the polymers are chemically jointed on each nanoparticle, they always tend to separate the particles to avoid the strong steric interaction between the particles. If the polymer size is large enough (i.e., with large $f_A$), the particle is encapsulated by the tethered flexible polymer. Thus, S phases are analogous to the accumulation of the ”soft” particles with a hard core. When the particle size increases, encapsulating the whole particle causes too much conformational penalty. Thus, C phases are preferred when the polymers are still long enough to wrap the cylinders. Similarly, further increasing the particle size results in G and L phases.

Although HMNs exhibit the same morphology classes as linear diblock copolymers do,$^{41}$ the phase diagram of HMNs is totally asymmetric compared with that of linear diblock copolymers. Several morphologies, including G phase with small $f_A$, C phase of the polymer-rich domain, and S phase of the polymer-rich domain, (analogous to G phase with $f_A < 0.5$, C phase of B-rich domain, and S phase of B-rich domain in the phase diagram of AB linear diblock copolymers,$^{41}$ respectively) disappear from the phase diagram. Instead of that, for $0.26 < f_A < 0.35$, the phase diagram is filled with a narrow region where our calculations are not convergent, and we expect that the nanoparticles in this region are in a sphere-packing state.

FIG. 2. The phase diagram and equilibrium phase morphologies of HMN melts. The ordered phases are labeled as: L (lamellae), G (gyroids), C (hexagonally arranged cylinders), and S (body-centered cubic spheres). In the sketches on the upper row, the red-colored regions correspond to particle-rich domains, and the polymer-rich domains as the complementary region are not shown for clarity. The black dashed line marks the order-disorder transition (ODT) line. In the phase diagram, the oblique lines indicate the region of unavailable $f_A$ value. The grid represents the region where our calculations are not convergent, and we expect that the nanoparticles in this region are in a sphere-packing state.

1. Highly asymmetric phase diagram

As the most obvious difference, the phase diagram of HMN melts is highly asymmetric compared with the mirror-symmetric phase diagram of AB linear diblock copolymers.$^{41}$

The phase diagram of HMNs exhibits the sequence of phase-separation morphologies of the S phase, C phase, G phase, and L phase, if we decrease $f_A$ from 1. One may anticipate a sequence of G, C, and S phases of polymer-rich domains embedded in a particle-rich matrix with small $f_A$, which is just a straightforward conjecture via analogy with the morphologies of AB linear diblock copolymers with $f_A < 0.5$. However, these structures disappear and leave the phase diagram extremely asymmetric. We attribute this to the penalty on conformational entropy of the polymers confined in the domains with concave interfaces, such as the spheres and cylinders. This is analogous to the behavior of rod-coil systems in which the flexible chains prefer to stay on the convex of the rod-coil interface, and consequently a non-lamellar phase only exists in the coil-rich matrix.$^{42–44}$ However, the G and C phases of polymer-rich domain embedded in the particle-rich matrix emerge if one introduces concave interfaces at the molecular
architecture level, such as by adding the number of heads of a single molecule.\textsuperscript{15,45}

For $f_A > 0.5$ in the phase diagram of HMNs, the region for each phase is also very different from the corresponding phase region in the phase diagram of linear diblock copolymers. For example, with $\chi N = 40$, the stable regions of L, G, C, and S phases of linear diblock copolymers are $0.337 < f_A < 0.663$, $0.663 < f_A < 0.682$, $0.682 < f_A < 0.834$, and $0.834 < f_A < 0.879$, respectively.\textsuperscript{41} As to the phase diagram of HMNs, they are $0.35 < f_A < 0.53$ for L phase, $0.53 < f_A < 0.58$ for G phase, $0.58 < f_A < 0.73$ for C phase, and $0.73 < f_A < 0.76$ for S phase. As shown above, except for an obvious decreasing for the L phase region, G, C, and S phases have nearly the same region width as those of diblock copolymers, while all the phase boundaries shift to lower $f_A$ with an amplitude approximately 0.1. This phenomenon is reminiscent of the phase behaviors of conformationally asymmetric block copolymers and rod-coil systems, where the phase boundaries shift towards lower composition of the “soft” component.\textsuperscript{33,44,46} This is because flexible chains prefer to stay on the convex part of an interface, which has already been mentioned in the previous paragraph.

We have to note that the phase diagram of microphase separation behaviors of HMN melts may be incomplete due to the limitation of our computational ability. We also tried other morphologies besides the ones shown in the phase diagram, e.g., the perforated lamellae (PL). We find that the PL phase, morphologies besides the ones shown in the phase diagram, the limitation of our computational ability. We also tried other previous paragraph.

As shown in Fig. 2, the order-disorder transition (ODT) line, and plot it as a dashed line in the phase diagram in Fig. 2 in order to emphasize the inaccuracy and the potential disputations. Moreover, the inaccuracy does not influence the qualitative properties of the phase diagram.

As shown in Fig. 2, the order-disorder transition (ODT) line of HMNs is shifted much lower $\chi N$ than that of diblock copolymers. The minimal value of $\chi N$ on the ODT is 10.495 at $f_A = 0.5$ for linear diblock copolymers,\textsuperscript{41} while it is approximately 1.7 at $f_A = 0.35$ for HMNs calculated by the SCFT/DFT method. We qualitatively interpret such an extraordinarily low ODT as follows. Entropic forces always push the system into the disordered state, while chemical incompatibility separates different species. Evidently, the nanoparticle of a HMN has much less conformational entropy than the corresponding block of a diblock copolymer molecule with the same molecular volume. The shorter polymer chain results in the less conformational entropy of HMNs in the disordered state. Consequently, HMNs remain ordered for much lower $\chi N$ than diblock copolymers when $f_A$ is small. When $f_A = 0.5$, ODT appears at $\chi N = 12.5$, which is a little higher than linear diblock copolymers. This is because the steric interaction between the particles resists phase separation.

The large decrease of ODT in the small $f_A$ region is reminiscent of a similar phenomenon in rod-coil diblock copolymer
melts, that the lowest ODT value is below $\chi N = 5$,\textsuperscript{43,50} far lower than that for coil-coil diblock copolymer melts.

Here we have to emphasize that the Flory-Huggins parameter $\chi$ denotes the strength of the interfacial tension between the polymer-rich regions and the particle-rich regions, which includes (but is more than) the chemical incompatibility between the nanoparticles and the polymers. This is quite different from the diblock copolymer melts where the Flory-Huggins parameter is usually interpreted as the chemical incompatibility.

For the spherical phases under strong-segregation limit, the origin of $\chi_{AP}$ is analogous to that of a flexible diblock copolymer system. However, under the uniform limit, since the incompressibility cannot exclude the polymers from the interiors of the particles, the free energy of the disordered state is controversial. On one hand, the conformational entropy is obviously overestimated under the uniform limit. On the other hand, the phenomenological interfacial tension is under suspicion whether it compensates adequately the overestimation of the conformational entropy, because we cannot distinguish different contributions from the effective parameter $\chi_{AP}$. Therefore, the ODT estimation under the framework of SCFT/DFT is inaccurate.

Although the free energy of the disordered state is not accurate, the deviation is still acceptable. Under the uniform limit, the free energy of HMNs melt is Eq. (13),

$$F_{\text{uniform}} = N \chi_{AP} f_P + \frac{(4f_P - 3f_{\text{c}}^2)}{(1 - f_P)^2},$$

where the first and the second terms are the interfacial energy and the steric interaction energy, respectively. Both terms approach zero with decreasing $f_P$. When the particle size is significantly smaller than the polymers, the expression is more accurate. Under the small particle limit, the free energy above degenerates to the free energy of an isotropic polymer melt. When $f_A$ and $f_P$ are comparable, although the conformational entropy might be overestimated, the dominant part of the free energy is the steric interaction term, which increases fast with increasing $f_P$.

Concerning the ODT, we admit that the ODT calculated here is not accurate. But the acceptable inaccuracy does not change the qualitative properties of the phase diagram. As a simple examination, we could estimate the free energy of the disordered state by taking only the free energy of the nanoparticle liquid,

$$F' = \frac{(4f_P - 3f_{\text{c}}^2)}{(1 - f_P)^2}.$$  

Obviously, this estimation totally neglects the contribution of the interfacial energy and the conformational entropy of the polymers. Thus, it must be lower than the accurate free energy of the corresponding disordered melt of HMNs (which is not accessible by our present SCFT/DFT method). Comparing $F'$ with the free energy of lamellae phases with $f_A = 0.4$ and various $\chi N$, we obtain the phase transition point at $\chi N = 5.8$, which is slightly higher than $\chi N = 3.0$ on the ODT line in the phase diagram in Fig. 2 and is still far lower than the minimal value $\chi N = 10.495$ on the ODT for linear diblock copolymers.

Our phase diagram agrees well with the experimental observations of the self-assembly of polystyrene monothethered polyisilesquioxane functionalized by a hydrophilic group (DPOSS-PS$_n$) in the bulk.\textsuperscript{15} With the volume fraction of polystyrene increasing, the assembled structures of DPOSS-PS$_n$ change from the L phase, to G phase, to C phase, and to the S phase, which shows the same phase transition sequence as in our phase diagram. The absence of G, C, and S phases with larger particle size than in the L phase in the experiments supports our conclusion that the phase diagram of HMN is extremely asymmetric. The differences on the location of each phase region between our phase diagram and the experimental results are attributed to several possible reasons, such as the hydrogen bonding interaction, the dipole-dipole interaction, the effective segment size, and the effective interaction parameter $\chi$.

Moreover, according to the experimental observations of the molecular nanoparticles monothethered by a diblock copolymer chain,\textsuperscript{19,20} the nanoparticles lead to the phase separation of originally disordered diblock copolymers having their block lengths much shorter than the limiting value for the phase separation in the precursors. We understand this as a side proof supporting our conclusion that the critical point for HMNs’ microphase separation is significantly lower than that of linear diblock copolymers.

On the theoretical side, Iacovella et al. performed BD simulation to study the equilibrium morphologies formed by HMNs in a solvent good for the nanospheres but poor for the tethers.\textsuperscript{27} They demonstrated that large nanoparticles favor curved morphologies and small nanoparticles favor lamellar sheets. At a glance, this seems to be opposite to our results in the melt. However, if we define the positive direction of the curved interface as the direction pointing from the particle side towards the polymer side, in both of our calculations and their simulations, smaller nanoparticles always prefer the interface with larger curvatures. Indeed, in their simulations the hydrophilic, large particles stay at the interface of negative curvature and the small ones stay at the zero-curvature interface, forming lamellar sheets.

**B. Density distributions of particles and tethered polymers**

In order to elucidate the details of the self-assembled structures, especially the spatial distribution of the nanoparticles, we plot the one-dimensional density profiles along a certain axis in three dimensions, including the density fraction of the tethered polymers $\varphi_A$, the density fraction of the particles $\varphi_P$, the distribution function of the centers of the nanoparticles $\rho_{\text{center}}$, and the distribution function of the grafting points $\rho_{\text{graft}}$. The density profiles of L phase with $\chi N = 40$ and $f_A = 0.5$, the C phase with $\chi N = 40$ and $f_A = 0.65$, and the S phase with $f_A = 0.74$ and $\chi N = 40$ are shown in Figs. 3(b), 4(b), and 5(b), respectively.

In one period of L phase, C phase, and S phase, the particle density profiles $\varphi_P$ are unimodal, and the widths of the peaks are on the scale of a single particle size. This indicates that the nanoparticles arrange in single layers in the L phase, in single cylinders in the C phase, and in one-nanoparticle-per-spherical-domain in the S phase, as illustrated by the
FIG. 3. Two periods of lamellar structure of HMNs with $\chi N = 40$ and $f_A = 0.5$. (a) A sketch illustration of morphology (left) and a color-map illustration of grafting point distribution (right). (b) Density profiles of a nanoparticle ($\phi_P$) and a tethered polymer ($\phi_A$). (c) Distribution functions of a grafting point ($\rho_{\text{graft}}$) and centers of nanoparticle ($\rho_{\text{center}}$). (b) and (c) are drawn along the arrow shown in (a).

sketches in Figs. 3(a), 4(a), and 5(a), respectively. According to the maxima and the minima of the density profiles, we conclude that the L phase has the highest degree of separation, while the S phase has the lowest degree of separation.

Although HMNs exhibit the same morphology class as linear diblock copolymers do, as we compare the density profiles of HMNs with those of linear diblock copolymers with the same $\chi N$ and $f_A$, we still find the domains of HMNs different from the domains of diblock copolymers in three aspects, as listed below.

1. The domain size of HMNs is much smaller than that of the corresponding linear diblock copolymers. As shown in Fig. 3(b), the period of L phase with $\chi N = 40$ and $f_A = 0.5$ is $0.42aN^{1/2}$, while the period of the lamellar structure of the linear diblock copolymers with the same $\chi N$ and $f_A$ is five times larger. Such a large difference on the characteristic length of domains is mainly due to the much smaller size of the spherical nanoparticle ($\sim(1 - f_A)^{1/3}N$), as compared to the effective size of a flexible coil ($\sim(1 - f_A)^{1/2}N$) of the same molecular volume. This feature is useful to generate diverse structures of HMN systems with feature size around 10 nm or smaller.

Interestingly, as shown in Fig. 6, the period of L phase $D^*/aN^{1/2}$ decreases with increasing $f_A$ when $\chi N$ is small, while it increases with $f_A$ when $\chi N$ is large enough. If we analyze $D^*$ in the unit of the particle diameter $d$, we find, with fixed $\chi N$, $D^*/d$ always increases with increasing $f_A$. It is easy to be interpreted in that the longer polymer chain always results in a larger domain size in the same morphology class, if we keep the particle size fixed. With the same $f_A$, $D^*/d$ of the same morphology class increases with increasing $\chi N$, because the interfacial energy becomes more dominant over the entropic energy and the polymer chain prefers to stretch out.

As shown in Fig. 7, the characteristic lengths of other morphologies have similar features as L phase. For one class of morphologies, the ratio $D^*/d$ always increases with increasing $f_A$ for fixed $\chi N$, due to the increasing radius of gyration of the polymer chains. However, with fixed $f_A$, $D^*/d$ of the same morphology has some fluctuations within a narrow range with increasing $\chi N$. 

FIG. 4. The cylindrical structure of HMNs with $\chi N = 40$ and $f_A = 0.65$. (a) A sketch illustration of the morphology (left) and a color-map illustration of the grafting point distribution (right). (b) The density profiles of nanospheres ($\phi_P$) and polymer ($\phi_A$). (c) The distribution functions of grafting points ($\rho_{\text{graft}}$) and centers of nanospheres ($\rho_{\text{center}}$). (b) and (c) are drawn along the arrow shown in (a).
For large $\chi N$, the width of the interfacial region between the domains of a HMN system is obviously much broader than that of a corresponding linear diblock copolymer system. For the L, G, and C phases, the spherical geometry of the nanoparticle determines the width of the interfacial region on the scale of particle radius at least, even the particles line up in ordered rows. Moreover, as shown in Fig. 3(c), the density distribution of the centers of the spherical particles, $\rho_{\text{center}}$, reaches its highest value at the center of the particle-rich layer, and a non-negligible width of the distribution persists. Specifically, the width $w_h$ of the peak of $\rho_{\text{center}}$ at half maximum is approximately one third of the diameter of the nanospheres with $\chi N = 40$ and $f_A = 0.5$. As shown in Fig. 8, $w_h/d$ decreases with increasing $\chi N$, which indicates that the nanoparticles arrange into a more ordered state to benefit the interfacial energy. However, $w_h/d$ of one class of morphologies always increases with increasing $f_A$ for fixed $\chi N$. In Fig. 9, $w_h/d$ of C and S phases has the same features as that of the L phase. The width of G phases is not considered because of the nonuniformity of the structure. The non-negligible width of the distribution of the centers of the nanoparticles indicates a liquid state of hard spheres in
the particle-rich domain. Thus the fluctuations of particle positions broaden the width of the interface between the particle-rich domains and the polymer-rich domains further.

(3) As shown in Figs. 3(c), 4(c), and 5(c), the probability density of the grafting points is still taking the highest value at the interface, but it is not as focused as the distribution of the junction points of diblock copolymers. Even at the center of the particle-rich domains or the center of the polymer-rich domains, the grafting point density is still more than one third of its highest value at the interface. Although there is only a little difference between the grafting-point distribution at the centers of the domains and on the interfaces, the orientational distribution is nonuniform. For example, we integrate the grafting-point distribution along the radius axis within the cell of a selected cylindrical domain, and obtain the angular distribution of the grafting points, $p(\theta)$, as shown in Fig. 10. We find the minima of $p(\theta)$ along the directions pointing towards the neighboring cylinders (i.e., $\theta = \frac{n}{5}$, $n = 0, 1, ..., 5$) and the maxima of $p(\theta)$ along the directions pointing towards the centers of the spaces between the three neighboring cylinders (i.e., $\theta = \frac{n}{5}$, $n = 0, 1, ..., 5$). This indicates that the grafting points tend to orient towards the more spacious region in the polymer-rich domains.

C. The competition of free energy

In order to understand the delicate competition between the enthalpy and entropy of the system, we decompose the free energy into three parts: (1) the interfacial energy ($U$) between the polymer-rich regions and the particle-rich regions, typically the interfacial interaction terms including the phenomenological Flory-Huggins parameter $\chi$; (2) the entropic energy ($-TS$) of the molecules in the fields $w_A(r)$ and $w_R(r)$, including the translational entropy of the molecule, the conformational entropy of the polymer, and the orientational entropy of the nanoparticle in terms of the grafting point; (3) steric interaction energy ($F_{\text{steric}}$), which is the compensation of the translational entropy due to the impenetrable head. The free energy of a single molecule as well as its components with $\chi N = 40$ is shown in Fig. 11. Due to positive $\chi N$, the interfacial energy always tends to separate the nanospheres and the polymers. Therefore, in the corresponding regions where the morphology is stable or metastable, the values of $U$ for different morphologies have the relation $U_L < U_G < U_C < U_S < U_{\text{Disordered}}$ (Fig. 11(b)). $U_L$ is extremely lower than the others, because the particles form quasi-two-dimensional liquid sheets to depress the interfacial energy. For G and C phases, the particles form quasi-one-dimensional liquid structures, and leave larger interfacial area than L phase does. However, the L phase has much larger steric interaction energy than the G and C phases (Fig. 11(d)). The larger degree of aggregation of nanoparticles results in lower domain-domain interfacial energy but at the same time stronger repulsive volume interaction.

An interesting and worth-to-mention phenomenon is that when $f_A < 0.48$ (i.e., the volume fraction of the spheres $f_P = 0.52$, which is the volume fraction of the simple cubic lattice), the L phase is still stable until we approach the limit volume fraction for the close packing of spheres. Compared with the possible lattice arrangements of HMNs, the L phase has two advantages on entropic energy. It has a higher translational entropy due to the liquid layer of spheres, and a less compressed conformation of the tail in the flat layer, as compared to the tails in the narrow and curved space between the large spheres on the lattice nodes. However, since the lamellae period $D$ is approximately the same as the particle diameter with small $\chi N$, as shown in Fig. 6, the position correlation between the particles in neighboring layers arising from local

![Figure 9](image1.png)  
**FIG. 9.** The width $w_h$ of nanosphere-center distribution of C, S phases at half maximum over the diameter of nanospheres $d$, as a function of $f_A$ for a series of $\chi N$ values. The dotted lines denote the phase transitions.

![Figure 10](image2.png)  
**FIG. 10.** (a) The two-dimensional distribution of the grafting points in the cylindrical structure with $\chi N = 40$ and $f_A = 0.65$. (b) The angular probability distribution $p(\theta)$ of the grafting points calculated in the cell of a selected cylinder, as indicated in (a).
IV. CONCLUSIONS

In conclusion, we have investigated the self-assembly behaviors of HMN melts via a theoretical method combining SCFT and DFT. An extremely asymmetric phase diagram is constructed due to the huge molecular architecture difference and topological constraints between the spherical hard nanoparticle and the flexible linear polymer tail. Despite a narrow region \(0.26 < f_A < 0.35\) of sphere-packing state of nanoparticles, the phase diagram shows a sequence of L, G, C, and S phases of particle-rich domains with increasing \(f_A\), the same as that of the corresponding linear diblock copolymers for \(f_A > 0.5\). The conformational entropic pressure of the flexible linear polymers favors their stay on a convex interface and accordingly the particles in a concave interface. Such effect not only shifts the transition line between the ordered phases towards smaller \(f_A\) but also suppresses the emergence of G, C, and S phases of polymer-rich domains, and consequently makes the phase diagram totally asymmetric. These results are not only supported by the experimental observations but also can be confirmed mutually by the asymmetric phase diagram of conformationally asymmetric block copolymers and rod-coil systems.

Moreover, systems of HMN molecules start to phase separate with much lower \(\chi N\) when \(f_A\) is small, and always have much smaller structural period than linear diblock copolymers of the same molecule size and volume fraction, because the characteristic size of a rigid sphere is much smaller than a flexible chain of the same molecule volume. The smaller period size of the ordered structures obtained in HMN melts could help to design diverse nanostructures with a characteristic length less than 10 nm.

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