Hierarchical and synergistic self-assembly in composites of model wormlike micellar-polymers and nanoparticles results in nanostructures with diverse morphologies

Shaikh Mubeena and Apratim Chatterji

1 Department of Physics, IISER-Pune, Dr. Homi Bhabha Road, Pune-411008, India
2 Center for Energy Science, IISER-Pune, Dr. Homi Bhabha Road, Pune-411008, India

Received 5 August 2018 and Received in final form 26 February 2019
Published online: 18 April 2019
© EDP Sciences / Societ`a Italiana di Fisica / Springer-Verlag GmbH Germany, part of Springer Nature, 2019

Abstract. Using Monte Carlo simulations, we investigate the self-assembly of model nanoparticles inside a matrix of model equilibrium polymers (or matrix of wormlike micelles) as a function of the polymeric matrix density and the excluded volume parameter between polymers and nanoparticles. In this paper, we show morphological transitions in the system architecture via synergistic self-assembly of nanoparticles and the equilibrium polymers. In a synergistic self-assembly, the resulting morphology of the system is a result of the interaction between the nanoparticles and the polymers and corresponding re-organization of both the assemblies. This is different from the polymer templating method. We report the morphological transition of nanoparticle aggregates from percolating network-like structures to non-percolating clusters as a result of the change in the excluded volume parameter between nanoparticles and polymeric chains. Corresponding to the change in the self-assembled structures of nanoparticles, the matrix of equilibrium polymers also simultaneously shows a transition from a dispersed state to a percolating network-like structure formed by the clusters of polymeric chains. We show that the shape anisotropy of the nanoparticle clusters formed is governed by the polymeric density resulting in rod-like, sheet-like or other anisotropic nanoclusters. It is also shown that the pore shape and the pore size of the porous network of nanoparticles can be changed by changing the minimum approaching distance between nanoparticles and polymers. We provide a theoretical understanding of why various nanostructures with very different morphologies are obtained.

1 Introduction

Nanoparticle assembly inside a polymeric matrix is a powerful route to form hybrid materials with the desired material strength (or alternatively different magnetic, optical and electronic properties) by a suitable choice of system parameters [1–6]. The synergistic interaction between nanoparticles and the polymeric matrix gives rise to a variety of hybrid systems and nanostructures having a wide range of applications like in cosmetics [7–10], food [11, 12], pharmacy [13, 14], novel functional materials [15, 16], ultraviolet lasers [17], hybrid nanodiodes [18–20], DNA templated electronic junctions [21, 22], quantum dots and thin wires [23].

The investigation of nanoparticle assembly inside a polymeric matrix is important for the fabrication of complex nanodevices as well as is of fundamental interest to explore the equilibrium and non-equilibrium phase behaviour of the system [24–26]. The colloid-polymer mixtures have been widely studied theoretically and experimentally and an equilibrium phase diagram is predicted using the Asakura-Oosawa model [24–27] for their varying size ratios and volume fractions. Experimental studies confirmed the predicted equilibrium colloid-polymer phase diagram [25, 28, 29] and also observed non-equilibrium phase behaviour [30]. An increase in the polymer density in the colloid-polymer system leads to its demixing into two or more phases [31]. In a deeply quenched system, the colloid rich phase may get kinetically arrested (on reaching the volume fraction \( \approx 0.57-0.59 \)) during the phase separation process, suppressing the demixing and producing a non-equilibrium gel state [31]. For non-adsorbing colloid-polymer mixtures with the polymer to colloid size...
ratio of $\approx 0.08$, these non-equilibrium gel phases are observed for colloid volume fraction $\leq 0.3$ above a threshold of polymer concentration $[32]$. This limiting value of colloid volume fraction depends on polymer concentration. Above this threshold polymer concentration, these non-equilibrium phases show a period of latency (observation period over which the morphology is maintained) before sedimentation of colloids under gravity. The latency period increases with increase in the polymer concentration and may lead to “freezing of structures” at sufficiently high concentrations $[32]$. Experimental studies have reported a variety of non-equilibrium phases including clusters, gels and glasses $[33]$. These non-equilibrium states are a challenge for theoretical studies and form an active area of research.

The discovery of the mesoporous material MCM-41 by Mobil Oil Corporation $[34]$ widely popularised the method of assembling nanostructures inside polymeric matrices and thus gave rise to the “bottom-up” approach which revolutionised the whole industry of nanofabrication $[35–42]$. Polymeric and other supramolecular matrices have long been explored as templates for fabricating nanostructures due to low cost and ease of tailoring nanomaterials with the desired properties. Later, realising the importance of synergistic interactions between nanoparticles (NPs) and the matrix, a myriad of synergistically assembled nanocomposites have also been generated. The NPs can be incorporated in a matrix by both in situ $[43,44]$ or ex situ $[45]$ methods. However, due to high surface interactions between NPs, it is difficult to disperse NPs inside the matrix. Therefore, in situ method is preferably used to produce a homogeneously dispersed NP-matrix composite. Nanorods $[46–48]$, nanowires and nanobelts $[49]$, nanocombs and nanobrushes $[50–52]$, nanosheets $[53,54]$, nanoporous $[55]$ and mesoporous structures $[56]$, nanotubes, spherical and complex morphological nanostructures have been reported in the literature. However, to exploit NP properties for nanodevice fabrication, the control over their morphological structures is still a big challenge to the researchers.

Generally, the (thermotropic) polymeric matrices have a value of elastic constants of the order of $\approx 10 \text{pN} [57]$. But there exists a class of polymers known as lyotropic polymers, WLMs at mesoscopic length scales make the wormlike micellar matrix different from a thermotropic polymeric matrix. In this paper, we study the hierarchical self-organization of NPs in a model of a self-assembling polymeric matrix that mimics the characteristic behaviour of a wormlike micellar matrix. Our generic model of self-assembling polymers represents the class of polymers known as equilibrium polymers, WLMs at mesoscopic length scales are just an example of equilibrium polymers $[EP]$. Equilibrium polymers are those whose bond energies are of the order of the thermal energies $k_B T$, and thereby chains can break or rejoin due to thermal fluctuations. This paper focuses on the transformation in the nanostructure morphology with the change in the polymeric matrix density and the excluded volume parameter (EVP) between nanoparticles and polymers.

We study the effect of the addition of NPs with diameters $\approx$ to the diameter of equilibrium polymer (EP) chains on the polymeric self-assembly. The presence of NPs affects the polymer self-assembly which in turn affects the NP self-organization. The parameters which are systematically varied in our investigations are 1) the number of monomers (which self-assemble to build the polymers) in a simulation box of fixed size, and 2) the minimum distance of approach between NPs and the matrix polymers (the quantitative estimate of EVP: Excluded Volume Parameter). We show that for a low value of EVP, a uniformly mixed state of polymers and NPs is observed for all the densities of equilibrium polymers considered here. An increase in the value of the EVP leads to the formation of clusters of polymeric chains which joins to form a percolating network-like structure intertwined with a percolating network of NPs. The network of nanoparticles breaks into non-percolating clusters of NPs at some higher value of the EVP. We are able to present these morphological transformations in a diagram. In the literature, there exist reports of a sudden decrease in the measured conductivity of polymer-nanocomposites $[63,64]$. This decrease in the conductivity is attributed to the transition of NPs from non-percolating to percolating state on a decrease in NP volume fraction $[63,64]$. In an attempt to explain these morphological transformations, we propose that these morphological transitions are due to the competition between the two repulsive interactions; the one between nanoparticles and the polymeric matrix and the repulsion between polymeric chains themselves. We try to explain the transitions by analyzing the behaviour of the total excluded volume in the system. We thus present how the system parameters can be used to tailor the mesoporous nanostructures formed in the system. This has a potential to optimize the shape and size of nanostructures obtained by in situ methods and thereby improve the design and performance of fuel cells and batteries (especially Li-ion batteries), drug delivery, optoelectronic devices and other device properties which depend on the nanostructure morphology.

The following section presents the potentials used to model NPs and equilibrium polymeric matrix and gives the details of the computational method. In sect. 3, we briefly summarize our results which were published previously. In sect. 4, we present our new results which are
are shown as spheres in fig. 1(a)) which interact with the presented by a chain of beads (called monomers here which are shown as spheres in fig. 1(a)) which interact with the given potentials to form equilibrium polymers (EP, e.g., wormlike micelles) without branches. Every single bead or a monomer in the model is representative of an effective volume of a group of amphiphilic molecules. Thus, the WLMs are modelled at a mesoscopic scale ignoring all the interactions between WLMs. In this model, WLMs are represented by Chatterji and Pandit [65, 66] and also developed and analyzed in [67]. In this model, WLMs are representative of effective volume of a group of amphiphilic molecules. Thus, the WLMs are modelled at a mesoscopic scale ignoring all the chemical details. The diameter of a monomer σ is taken as the unit of length in the system. The potential is the combination of three terms V₂, V₃ and V₄.

- We have a two-body Lennard-Jones (L-J) potential modified with an exponential term:

\[
V_2 = \epsilon \left( \frac{\sigma}{r_2} \right)^{12} - \left( \frac{\sigma}{r_2} \right)^6 + \epsilon_1 e^{-ar_2/\sigma}; \quad \forall r_2 \leq r_c,
\]

(1)

where \( r_2 \) is the distance between two interacting monomers with \( \epsilon = 110 k_B T \) and the cutoff distance of the potential is at \( r_c = 2.5 \sigma \). The exponential term in the above potential creates a maximum at \( \approx 1.75 \sigma \) which acts as a potential barrier for two monomers approaching each other. Two monomers are defined as bonded when the distance \( r_2 \) between them becomes \( \leq \sigma_3 = 1.5 \sigma \), such that the interaction energy is negative. This is explained schematically in fig. 1(a) and the plot of the potential is also shown in fig. 1(b) (full blue line). We set \( \epsilon_1 = 1.34 \epsilon \) and \( a = 1.72 \). The values of \( \epsilon, \epsilon_1 \) and \( a \) are chosen such that the depth of the binding potential between two bonded monomers is around \( 10k_B T \), but the effective depth is reduced if a trimmer is not in a perfectly straight line; also refer to fig. 1(b).

- To model the semiflexibility of chains, we use a three-body potential \( V_3 \):

\[
V_3 = \epsilon_3 \left( 1 - \frac{r_2}{\sigma_3} \right)^2 \left( 1 - \frac{r_3}{\sigma_3} \right)^2 \sin^2(\theta); \quad \forall r_2, r_3 \leq \sigma_3.
\]

Here \( r_2 \) and \( r_3 \) are the distances of the two monomers A and B (see fig. 1(a)) from the central monomer (in pink) which forms a triplet with an angle \( \theta \) subtended by \( r_2 \) and \( r_3 \). Here \( \epsilon_3 = 6075k_B T \). The prefactors to \( \sin^2(\theta) \) are necessary to ensure that the potential and force go smoothly to zero at the cutoff distance \( \sigma_3 = 1.5 \sigma \) for \( V_3 \). This three-body potential modeling semiflexibility acts only if a monomer has two bonded neighbors at distances \( \leq \sigma_3 \). Figure 1(b) shows the

2 Model and method

2.1 Modeling micelles (Equilibrium Polymers)

The model we use is a modified version of a previous model presented by Chatterji and Pandit [65, 66] and also developed and analyzed in [67]. In this model, WLMs are represented by a chain of beads (called monomers here which are shown as spheres in fig. 1(a)) which interact with the given potentials to form equilibrium polymers (EP, e.g., wormlike micelles) without branches. Every single bead or a monomer in the model is representative of an effective volume of a group of amphiphilic molecules. Thus, the WLMs are modelled at a mesoscopic scale ignoring all the chemical details. The diameter of a monomer σ is taken as the unit of length in the system. The potential is the combination of three terms V₂, V₃ and V₄.

- We have a two-body Lennard-Jones (L-J) potential modified with an exponential term:

\[
V_2 = \epsilon \left( \frac{\sigma}{r_2} \right)^{12} - \left( \frac{\sigma}{r_2} \right)^6 + \epsilon_1 e^{-ar_2/\sigma}; \quad \forall r_2 \leq r_c,
\]

(1)

where \( r_2 \) is the distance between two interacting monomers with \( \epsilon = 110 k_B T \) and the cutoff distance of the potential is at \( r_c = 2.5 \sigma \). The exponential term in the above potential creates a maximum at \( \approx 1.75 \sigma \) which acts as a potential barrier for two monomers approaching each other. Two monomers are defined as bonded when the distance \( r_2 \) between them becomes \( \leq \sigma_3 = 1.5 \sigma \), such that the interaction energy is negative. This is explained schematically in fig. 1(a) and the plot of the potential is also shown in fig. 1(b) (full blue line). We set \( \epsilon_1 = 1.34 \epsilon \) and \( a = 1.72 \). The values of \( \epsilon, \epsilon_1 \) and \( a \) are chosen such that the depth of the binding potential between two bonded monomers is around \( 10k_B T \), but the effective depth is reduced if a trimmer is not in a perfectly straight line; also refer to fig. 1(b).

- To model the semiflexibility of chains, we use a three-body potential \( V_3 \):

\[
V_3 = \epsilon_3 \left( 1 - \frac{r_2}{\sigma_3} \right)^2 \left( 1 - \frac{r_3}{\sigma_3} \right)^2 \sin^2(\theta); \quad \forall r_2, r_3 \leq \sigma_3.
\]

Here \( r_2 \) and \( r_3 \) are the distances of the two monomers A and B (see fig. 1(a)) from the central monomer (in pink) which forms a triplet with an angle \( \theta \) subtended by \( r_2 \) and \( r_3 \). Here \( \epsilon_3 = 6075k_B T \). The prefactors to \( \sin^2(\theta) \) are necessary to ensure that the potential and force go smoothly to zero at the cutoff distance \( \sigma_3 = 1.5 \sigma \) for \( V_3 \). This three-body potential modeling semiflexibility acts only if a monomer has two bonded neighbors at distances \( \leq \sigma_3 \). Figure 1(b) shows the
plots of $V_2 + V_3$ for a fixed value of $r_3 = \sigma$ and different values of $r_2$ and $\theta$. This potential penalizes angles $< 180^\circ$. Configurations with $\theta = 0^\circ$ are prevented by excluded volume interactions of the monomers. The value of $\epsilon_3$ is chosen such that the semiflexibility energy is significant (comparable to $k_B T$), even when either $r_2 \rightarrow \sigma_3$ or $r_3 \rightarrow \sigma_3$.

- Monomers interacting with potentials $V_2$ and $V_3$ self-assemble to form linear polymeric chains with branches. A fourth monomer can get bonded to a monomer which already has two bonded neighbours to form a branch. To avoid branching, it is necessary to repel any monomer which can potentially form a branch. Therefore, we introduce a four-body potential term which is a shifted Lennard-Jones repulsive potential $V_4$ which repels any branching monomer at distances $\approx \sigma_4$, where $\sigma_4 = 1.75 \sigma > \sigma_3$. The explicit form of the potential $V_4$ is

$$V_4 = \epsilon_4 \left(1 - \frac{r_2}{\sigma_4}\right)^2 \left(1 - \frac{r_3}{\sigma_4}\right)^2 \times V_{LJ}(\sigma_4, r_4); \quad \forall r_4 \leq 2^{1/6} \sigma_4.$$  \hspace{1cm} (3)

Here $r_2$ and $r_3$ are the distances of the two monomers from central monomer (in pink) which forms a triplet, while $r_4$ is the distance of the fourth monomer which tries to approach the central monomer which already has two bonds, as shown in fig. 1(a). We set the cutoff distance for this potential to be $2^{1/6} \sigma_4$ with a large value of $\epsilon_4 = 2.53 \times 10^5 k_B T$. This potential is non-zero only if both $r_2, r_3 < \sigma_3$ and $r_4 < 2^{1/6} \sigma_4$. The value of $\epsilon_4$ is kept large enough to ensure enough repulsion in case $(1 - \frac{r_2}{\sigma_4})^2 \ll 1$ and/or $(1 - \frac{r_3}{\sigma_4})^2 \ll 1$. These terms are necessary to ensure that if $r_2$ or $r_3$ become $\geq \sigma_3$, $V_4$ and the corresponding force goes smoothly to zero at the cutoff of $\sigma_3$.

All the three potentials are summarised in fig. 1(a). In this figure, the red spheres denote the micellar monomers having size $\sigma$. These monomers are acted upon by the two-body potential $V_2$ having a cutoff range $r_c$. The potential is shown in fig. 1(b) indicated by the legend $\tan^2 \theta = 0$ (triangle-blue line). A three-body potential $V_3$ is acting on a triplet with a central monomer bonded by two other monomers at distances $r_2$ and $r_3$ (bonded monomers are joined by dashed lines). The vectors $\vec{r}_2$ and $\vec{r}_3$ subtend an angle $\theta$ at the central monomer and the potential $V_3$ has a cutoff distance of $\sigma_3$ (fig. 1(b)).

### 2.2 Modeling nanoparticles

To explore the self-organization of NPs inside a worm-like micellar matrix (or EP matrix), we need to introduce a suitable model for NPs. The NP-NP interactions are modelled by a Lennard-Jones potential for particles of diameter $\sigma_n$:

$$V_{2n} = \epsilon_n \left[ \left(\frac{\sigma_n}{r_n}\right)^{12} - \left(\frac{\sigma_n}{r_n}\right)^6 \right] + V_0, \quad \forall r_n \leq r_{cn},$$  \hspace{1cm} (4)

where $r_n$ is the distance between the centres of two interacting NPs. The value of $\epsilon_n$ is kept fixed at $11 k_B T$. The potential $V_{2n}$ is suitably shifted by the constant $V_0$, such that it smoothly goes to zero at the cutoff distance $r_{cn} = 2 \sigma_n$. The interaction between NPs and micellar monomers at a distance $r$ is modelled by a repulsive WCA (Weeks-Chandler-Anderson) potential given by

$$V_{4n} = \epsilon_{4n} \left[ \left(\frac{\sigma_{4n}}{r_n}\right)^{12} - \left(\frac{\sigma_{4n}}{r_n}\right)^6 \right] + V_1, \quad \forall r_n \leq 2^{1/6} \sigma_{4n},$$  \hspace{1cm} (5)

which is suitably shifted by $V_1$. The prefactor of the above potential is $\epsilon_{4n}$, it is chosen to be $\epsilon_{4n} = 30 k_B T$. The value of $\sigma_{4n}$ here defines the minimum approaching distance between a NP and a monomer. Therefore, it is used as a measure of the EVP between micelles and NPs. Since the monomers and NPs of diameters $\sigma$ and $\sigma_n$ are considered to be nearly impenetrable, the EVP cannot be less than $\sigma/2 + \sigma/2$. Thus, there exists a lower bound for the variable $\sigma_{4n}$ and it can only have values $\sigma_{4n} \geq \sigma/2 + \sigma_n/2$. This is explained in fig. 2(a). In summary, the model has a fixed value of monomer diameter $\sigma$ and NP diameter $\sigma_n$ ($= 1.5 \sigma$). However, the minimum approaching distance between them, $\sigma_{4n}$, is used as a variable parameter, see fig. 2(a), (b). The other parameter we vary is the monomer diameter $\sigma_n$.

![Fig. 2.](image_url)
number density $\rho_m$. All the other values are kept constant. The polymeric matrix thus modelled is equally applicable for a wormlike micellar matrix or any other equilibrium polymeric matrix.

### 2.3 Method

To study the system behaviour, we randomly place model monomers and NPs with a fixed volume fraction in a box of size $V = 30 \times 30 \times 60 \sigma^3$ with periodic boundary conditions where the unit of energy is set by choosing $k_B T = 1$. We used the Monte Carlo method (Metropolis algorithm) to displace the position of particles and evolve the system towards equilibrium. For a high-density regime, the Monte Carlo (MC) moves seemed to be inefficient to equilibrate the system. Therefore, the system is first allowed to equilibrate for $10^4$ iterations with a few (100–200) NPs inside so that monomers can self-assemble in the form of chains in the presence of NP seeds. One Monte Carlo step (MCS) consists of attempting $N_m + N_{np}$ displacements, where $N_m$, $N_{np}$ are the number of monomers and NPs in the simulation box at that step. The particles to be displaced are chosen at random, so in 1 MCS, on an average, all the particles present in the system get an attempt to make a displacement.

Once the chains are formed in the presence of seeded NPs in $10^4$ MCS then, a semi-grand-canonical Monte Carlo (s-GCMC) scheme is switched on for the rest of the iterations. According to this scheme, every 50 MCS, only the s-GCMC scheme is switched on for the rest of the iterations. This led to a large number of NPs ($\approx 10^4$ or more) in the simulation box and shorter runs. Larger values of $\sigma_{in}$ results in higher values of EVP and fewer NPs in the box. After the number of NPs in the simulation box gets relatively stabilized, the acceptance rate of the s-GCMC attempts to introduce particles was $\approx 5\%$, with a slightly lower acceptance rate of attempts to remove NPs from the simulation box. This resulted in a net 0.1% (per 300 attempts) increase in the number of particles in the box. For higher values of $\sigma_{in}$, the rate of acceptance of s-GCMC attempts is 10–20% and also reaches to 30% in the case of $\sigma_{in} = 3.5\sigma$. Similarly, the acceptance rate of attempts to remove NPs also remains approximately the same as the acceptance rate to introduce particles, though slightly lower in value. This results in the net addition of NPs. The rate of NP addition decreases with an increase in $\sigma_{in}$.

For each $\rho_m$, a much longer run ($4 \times 10^6$ iterations) was given to check if there is any change in the morphology of the system due to thermal fluctuations. Representative data is shown in the Electronic Supplementary Material (ESM) and establish that morphologies do not change with MCS. In addition to check the robustness of the morphologies obtained, canonical MC simulations were performed (without the addition and removal of NPs), with a similar number of NPs as towards the end of the s-GCMC simulations starting from random initial positions of particles. Again these show the same morphologies as obtained from s-GCMC simulations. The system is found to maintain its morphology across all 10 independent runs, longer runs and MC runs in canonical ensemble, and representative snapshots can be found in sect. III of the ESM.

### 3 Previous results

In our previous communication [67], we developed the model potentials described here, and showed that monomers interacting with the potentials self-assemble to form long cylindrical chains akin to WLMs. These polymeric chains show an exponential distribution of chain length, thus, confirming the characteristic behaviour of an equilibrium polymer (or wormlike micellar) matrix [61]. The self-assembled polymers at low densities were observed to be in a disordered (isotropic) state with relatively small chains. With an increase in the monomer number density, the short chains or monomers start joining up to form longer chains. These chains then start getting parallel to neighbouring chains, and the system shows a transition to a nematic state at a high value of density. We observe an isotropic to nematic first-order transition at monomer number density $\rho_m \approx 0.13 \sigma^{-3} - 0.14 \sigma^{-3}$.

The behaviour of the mixture of the model NPs and equilibrium polymeric chains was investigated at a high monomer number density $\rho_m = 0.126 \sigma^{-3}$ with the change in $\sigma_{in}$. The kinetically arrested assembly of NPs shows a transition from a system spanning percolating network-like structure to non-percolating clusters with an increase
in EVP ($\sigma_{4n}$). The clusters of NPs were observed to be having rod-like structures. The absolute value of $\mu$ and $\epsilon_n$ values used were much higher in our previous work compared to the present work, this led to very dense systems which remained kinetically trapped in glassy metastable states.

4 Present investigation

In this paper, the self-assembly of the equilibrium polymeric chains + NP system is investigated as a function of the $\sigma_{4n}$ (EVP) for different values of $\rho_m$. The variation is $\rho_m$ leads to a much richer range of observed morphologies. Throughout the paper, the diameter of NPs $\sigma_n$, $\sigma_4$ and $\mu$ are kept fixed at 1.5$\sigma$, 1.75$\sigma$ and $-8k_BT$, respectively, unless otherwise mentioned. All the distances mentioned here refer to the centre-to-centre distances of the particles involved. To investigate the behaviour of NPs and worm-like micellar system, four different values of the number of monomers $N_m$ are considered viz. $N_m = 2000$, 4000, 5000 and 6800 corresponding to the monomer number densities $\rho_m = 0.037\sigma^{-3}$, $0.074\sigma^{-3}$, $0.093\sigma^{-3}$ and $0.126\sigma^{-3}$, respectively. In the absence of nanoparticles, the highest number density of $\rho_m = 0.126\sigma^{-3}$ with $\sigma_4 = 1.75\sigma$, corresponds to self-assembled long chains at densities close to the isotropic-nematic transition densities [67]. At lower densities of $\rho_m$, the system (without NPs) is in the disordered isotropic phase with very short chains and most are monomers and dimers. However, in the presence of NPs, the effective density of monomers becomes relatively high enough for them to self-assemble into long chains. The chemical potential $\mu$ of NPs is chosen such that the box gets relatively packed with NPs and the NP aggregates in turn increase the effective monomer density.

4.1 Calculation of effective volume of monomers: $V_m^{eff}$

We realize that the system behaviour can be better characterized by considering the total effective excluded volume of cylindrical polymer chains due to the repulsive interactions $V_4$ and $V_{4n}$ instead of only considering the volume fraction of spherical monomers with diameter $\sigma$. The calculation of the effective volume of WLMs is explained in fig. 2. The figure shows that any two micellar chains (red spheres) at a distance of the cutoff distance $(2^{1/6}\sigma_4)$ (range of the repulsive interaction $(V_4)$) from each other are considered as non-overlapping cylinders of diameter $\sigma_4$ (shaded cylinders). Correspondingly, the effective volume of the monomer in the chain is defined to be $v_1 = \pi(\sigma_4/2)^2\sigma$. If a monomer and NP interact via $V_{4n}$ (i.e., distance between the 2 particles $<2^{1/6}\sigma_{4n}$), then the monomer is considered to be a sphere of radius $(\sigma_{4n} - \sigma_n/2)$, and the effective volume of the monomer is $v_2 = 4\pi/3(\sigma_{4n} - \sigma_n/2)^3$. Any monomer that is not involved in any of the repulsive interactions $V_4$ and $V_{4n}$ has the volume $v_3 = 4\pi/3 \times (\sigma/2)^3$.

To calculate this effective volume using a suitable algorithm, we first identify and label the monomers which are part of a chain. All monomers within a distance of 1.5$\sigma$ (cutoff distance for $V_4$) from each other are considered as bonded and thus form part of a chain. We do not observe branching in the chains. In the second step, all the chains that are involved in the repulsive interactions with other chains or nanoparticles are identified and the effective volume of micelles is calculated according to the scheme discussed above and illustrated in fig. 2. If a monomer interacts with a monomer of a neighbouring chain as well as a NP simultaneously, then, the higher of the two values of effective volume ($v_1$ or $v_2$) is considered. Thus for such monomers, the volume may get slightly overestimated when $(\sigma_{4n} - \sigma_n) > \sigma_4$. However, this overestimation does not change the interpretation of results. The effective volume fraction of micelles, thus calculated, depicts the actual excluded volume fraction because of the repulsive potentials $V_4$ and $V_{4n}$. This actual excluded volume is higher than the volume fraction of monomers $(\rho_m/3\pi(\sigma/2)^3)$. If there are $n_1$ monomers interacting with other monomers with potential $V_4$, $n_2$ monomers having repulsive interaction $V_{4n}$ with a nanoparticle and $n_3$ monomers out of the range of the potentials $V_4$ and $V_{4n}$ then, $n_1v_1 + n_2v_2 + n_3v_3$ depicts the effective volume of micelles.

This effective volume of monomers is not only dependent upon the value of $\sigma_4$ and $\sigma_{4n}$ but also on the arrangement of the constituent particles.

4.2 Systems with $(\sigma_{4n})_{min} = 1.25\sigma$: formation of a dispersed state of polymeric chains

To study the effect of change of micellar density, the system is simulated with different values of $\rho_m$ at $\sigma_{4n} = 1.25\sigma$ which is the minimum allowed value of $\sigma_{4n}$; see fig. 2. Figure 3 shows the evolution of the average energy of the constituent particles $(\langle E \rangle)$ and the NP volume fraction $V_n/V$ with MCS, for two different values of monomer number densities. The NP volume $V_n$ is given by $V_n = N_{np}/3\pi\sigma_n^2$, where $N_{np}$ is the number of NPs in the simulation box. The panels for $\langle E \rangle$ and $V_n/V$ show data for multiple runs generated from 10 independent runs; these overlap and look indistinguishable from each other. Therefore, magnified parts of the graphs are shown in the insets of (a) and (c). The insets clearly show different graphs for different independent runs indicated by different colours. All the graphs show a jump on switching to the s-GCMC scheme at $10^5$ MCSs, indicating an increase in the number of NPs in the box. The insets show the energy fluctuations and the gradual increase in the number of NPs with MCS.

All the independent runs for each $\rho_m$ produce similar configurations after $(2$ to $4) \times 10^5$ iterations and the energy and NP volume fraction graphs converge to the same value. After approximately $2 \times 10^5$ iterations, the system morphology remains relatively unchanged for the length of the runs varying from $4 \times 10^5$ to $4 \times 10^6$ of iterations. Once no further change in the polymer-NP morphology is observed, we show the representative snapshots for each value of monomer number densities $\rho_m$ in fig. 4. The monomers and the NPs are shown separately in the upper row and the lower row, respectively. All the snapshots in
Fig. 3. Panels (a), (b) show the plots of average energy per particle (both monomers and NPs) for two different values of monomer number density $\rho_m$. Panels (c), (d) show the nanoparticle volume fraction $V_n/V$ versus MCSs, $V_n$ is the volume of NPs and $V$ is the volume of simulation box. The parameter $\sigma_{4n}$ is kept fixed at $1.25\sigma$. Each panel shows multiple graphs generated from 10 independent runs initialized with different initial configurations which can be clearly seen in the magnified parts of the graphs shown in the inset of (a) and (c). The system is evolved with MC steps for a first $10^5$ iterations and then subjected to the semi–grand-canonical MC (s-GCMC) scheme on nanoparticles. The data show a sudden jump in their values when we switch on the s-GCMC.

Fig. 4. The upper row of snapshots shows snapshots of only the equilibrium polymers (micellar chains) and the lower row shows only the nanoparticles of the NP+polymer system. Different snapshots are for different values of monomer number densities: (a) and (e) is for $\rho_m = 0.037\sigma^{-3}$, (b) and (f) is for $\rho_m = 0.074\sigma^{-3}$, (c) and (g) is for $\rho_m = 0.093\sigma^{-3}$ and (d) and (h) is for $\rho_m = 0.126\sigma^{-3}$. The values of $\sigma_n$ and $\sigma_{4n}$ are kept fixed at $1.5\sigma$ and $1.25\sigma$, respectively. All the snapshots show that the nanoparticle-monomer system are in uniformly mixed state and clustering of micellar chains is not observed. All the figures have a gradient in their colour varying from red to blue to identify and distinguish between the particles which are near the front plane (red) and the ones which are closer to the back of the box (blue).

An increase in the nematic ordering of polymeric chains and their chain length can be recognized from the figures as a result of the increase in $\rho_m$ in fig. 4. The snapshot in fig. 4(a) shows smaller chains in a disordered state and the chain length and order increases for figs. 4(b) and 4(c) and finally the system forms a nematic state with longer and aligned chains in fig. 4(d). All the systems shown in the figure may show different polymer arrangements, but for all the micellar densities a uniformly mixed state of polymeric chains and NPs is observed.

All the independent runs discussed till now had the systems initialized in a state where the positions of both
the monomers and 200–300 seed nanoparticles are randomly chosen. To ensure that our conclusions are not dependent on initial conditions, we gave additional runs initialized with all monomers on one side and all the NPs on the other side of the box. It is observed that for \( \rho_m = -8k_BT \), the system evolves to form a mixed state in part of the box (see figs. S1 and S2 in the ESM). However, a phase separated state is observed for \( \mu_n = 4k_BT \) and \( \rho_m = 0.126\sigma^{-3} \).

All the results from ten independent runs (and the data shown in figs. S1, S2 in the ESM) indicate that the mixed state of NP and micellar chains could be the thermodynamically preferred state of the system for the value of \( \mu_n = -8k_BT \). The systems considered here are quite dense and show very slow changes in the number of nanoparticles and energy values even after very long runs (see fig. S2 in the ESM). Therefore, we assume that the structures discussed (see fig. 4) are most probably in a phase which is close to equilibrium state of the system, though the system is relaxing slowly to equilibrium. Here we remind the reader that, because of the inherently non-equilibrium nature of the simulation where we periodically expose the system to a particle-bath, we can only claim that the system can be close to the equilibrium state. The rest of the paper considers the systems initialized with a randomly mixed state of micelles and NPs and investigates the effect of the change in \( \sigma_{4n} \) for each value of \( \rho_m \).

4.3 Systems with \( \sigma_{4n} > 1.25\sigma \): polymer and NP clusters with different morphologies

We next investigate the effect of the change in the value of \( \sigma_{4n} \) for different monomer densities by varying \( \rho_m \) and \( \sigma_{4n} \). The results from these runs were further substantiated with ten independent runs for each value of \( \rho_m \) and \( \sigma_{4n} \). The average energy of the system for ten independent runs for two different values of \( \sigma_{4n} = 2.5\sigma \) and \( 2\sigma \) is shown in fig. 5 for values of densities (a) \( 0.037\sigma^{-3} \), (b) \( 0.074\sigma^{-3} \), (c) \( 0.093\sigma^{-3} \) and (d) \( 0.126\sigma^{-3} \). The system is evolved with Monte Carlo steps without s-GCMC for the first \( 10^5 \) iterations and then the s-GCMC scheme is switched on which is marked by a rapid lowering in the energy values in fig. 5. In each figure, each visible line shows multiple lines overlapping each other, generated by 10 independent runs. Here, we emphasise again that all the systems are initialized with random positions of monomers and 100–200 seed NPs. This method of initialization is reminiscent of the in situ method of preparation of nanoparticles inside the matrix of polymers, where the NPs start nucleating out from a chemical solution on suitable addition of a reactant (s-GCMC).

After evolving the system for \( \approx 10^6 \) iterations, the representative snapshots for four different values of \( \rho_m = 0.037\sigma^{-3} , 0.074\sigma^{-3} , 0.093\sigma^{-3} \) and \( 0.126\sigma^{-3} \) are shown in figs. 6, 7, 8 and 9, respectively. For each NP+micelles system, the monomers and NPs are shown separately in the upper and lower rows, respectively, in figs. 6, 7, 8 and 9. Each figure shows the snapshots for four different values of \( \sigma_{4n} \) which keeps increasing as one goes from (a) to (d), or alternatively from (e) to (h). Snapshots (a) to (d) show monomers (in red), and (e) to (h) show NPs (in blue). Only for snapshots of NPs in figs. 6, 7(a) and (e), there exists a gradient in colour (varying from red to blue along one of the lengths of the simulation box) from the front plane to the rear plane. This helps to identify particles lying in different planes and thereby clearly see the pores in NP aggregates. These pores are occupied by monomers.

In each of the figures, one can see in the leftmost snapshot (snapshots (a) and (e), which are for a lower value of \( \sigma_{4n} \)) a network-like structure of micellar chains or NPs which spans the system. An increase in the value of \( \sigma_{4n} \) leads to a decrease in number of nanoparticles, thus, gradually breaking the network of NPs as shown in figs. 7(g), 8(f), (g) and 9(f). With further increase in \( \sigma_{4n} \), these networks break into non-percolating clusters as shown for \( \sigma_{4n} = 3.25\sigma, 3\sigma \) and \( 2.25\sigma \) in figs. 7(h), 8(h) and 9(g), respectively. We do not observe the breaking of networks into individual NP clusters for \( \rho_m = 0.037\sigma^{-3} \) in fig. 6 for the range of values of \( \sigma_{4n} \) considered here. Therefore, with an increase in \( \rho_m \), the value of \( \sigma_{4n} \), at which the network breaks into non-percolating clusters gets shifted to a lower value of \( \sigma_{4n} \). From the snapshots 7(h), 8(h) and 9(g), it can be clearly seen that different densities

---

**Fig. 5.** Plots of average potential energy \( \langle E \rangle \) per particle (monomer and NP) of the system for different values of monomer number densities (a) \( \rho_m = 0.037\sigma^{-3} \), (b) \( 0.074\sigma^{-3} \), (c) \( 0.093\sigma^{-3} \) and (d) \( 0.126\sigma^{-3} \). Each panel shows the energy graphs for two different values of \( \sigma_{4n} = 2\sigma \) and \( 2.5\sigma \). For each value of \( \sigma_{4n} \), there are ten graphs overlapping each other and converging to the same values. The canonical Monte Carlo scheme (without s-GCMC) is applied for the first \( 10^5 \) iterations. Then the s-GCMC scheme is switched on which leads to a further decrease in the energy values indicated by jumps in the values of \( \langle E \rangle \) in each graph.
Fig. 6. The snapshots for NPs and monomers from the NP + WLM system for the lowest value of monomer number density \( \rho_m = 0.037\sigma^{-3} \). The snapshots in the upper row show only the monomers while only the NPs are shown in the lower row. The snapshots from (a) to (d) (and correspondingly from (e) to (h)) are for \( \sigma_4n = 2.0\sigma, 2.5\sigma, 3\sigma \) and \( 3.5\sigma \), respectively. There is a gradient in colour along one of the shorter axis of the box for the snapshots (e) to (h), to help the reader differentiate the particles present near the front plane from those at the rear. All the snapshots indicate the formation of the network-like structure of aggregates of nanoparticles and micellar chains inter-penetrating each other.

Fig. 7. The snapshots of NPs and monomers from the NP + WLM system for the value of monomer number density \( \rho_m = 0.074\sigma^{-3} \). The snapshots in the upper row show only the monomers while, the lower row only shows the NPs. Snapshots from (a) to (d) (or correspondingly from (e) to (h)) are for \( \sigma_4n = 1.75\sigma, 2.25\sigma, 2.75\sigma \) and \( 3.25\sigma \), respectively. The snapshots (a) and (e) have a gradient in colour varying from red to blue along one of the shorter axis of the simulation box to help the reader differentiate the particles at the front plane and those closer to the rear. Snapshots (e), (f), and (g) are forming network-like structures of nanoparticles, while the nanoparticle network breaks down into non-percolating clusters in (h) by forming individual sheetlike nanostructures.
Fig. 8. The snapshots of NPs and monomers from the NP + micellar-polymer system for the value of number density of monomers $\rho_m = 0.093\sigma^{-3}$. Snapshots in the upper row show only micellar monomers (red) while the snapshots in the lower row only show nanoparticles (blue). Snapshots from (a) to (d) (or correspondingly from (e) to (h)) are for $\sigma_{4n} = 1.75\sigma$, $2.25\sigma$, $2.5\sigma$ and $3\sigma$, respectively. With the increase in the value of $\sigma_{4n}$ from left to right, the snapshots of nanoparticles show that the network gradually breaks and form individual sheet-like clusters for a high value of $\sigma_{4n}$, as shown in the snapshot (h).

Fig. 9. The snapshots of NPs and monomers from the NP + micellar-polymer system for monomer number density $\rho_m = 0.126\sigma^{-3}$. The snapshots in the upper row show only micellar monomers while, only the NPs are shown in the lower row. Snapshots (a) to (d) (or (e) to (h)) correspond to $\sigma_{4n} = 1.75\sigma$, $2\sigma$, $2.25\sigma$ and $2.5\sigma$, respectively. With increase in the value of $\sigma_{4n}$, the figure shows the nanoparticle networks in (e) and (f) breaking into individual rod-like nanostructures as shown in the snapshots (g) and (h).
It shows the density correlation function for monomers along the $x$, $y$, and $z$-axes of the box for $\sigma_m = 1.5\sigma$. The function is calculated using the expression

$$G(x_i, x'_i) = \frac{\langle \rho(x_i) - \rho(x'_i) \rangle \langle \rho(x_i) - \rho(x'_i) \rangle}{\langle \rho(x_i) - \rho(x'_i) \rangle^2},$$  

(6)

where $\rho(x_i)$ is the density of the monomers in cubic box of size $\sigma^3$ at $x$, at a particular $y$-$z$ plane. The angular brackets in the numerator correspond to averages taken at different $y$-$z$ planes, as well as over different microstates from independent runs. The term $\langle \rho(x_i) \rangle$ is the mean density of monomers in the simulation box. The term in the denominator normalizes the function from 1 to $-1$. The different symbols indicate the different values of micellar densities in fig. 10. The plots for different $\rho_m$ overlap each other and are indistinguishable from each other. They have the same spatial period for all densities and along different axes. This indicates the periodic nature of the network-like structures in all three directions.

For the lowest density of micelles considered here, i.e. $\rho_m = 0.037\sigma^{-3}$, the morphological changes from a network of NPs to sheets to rod-like structures is not observed for $\sigma_m > 1.25\sigma$. The effect of an increase in the value of $\sigma_m$ is observed to decrease the number density of NPs without changing the periodicity of the networks. The plot of density correlation function for all the values of $\sigma_m$ considered for $\rho_m = 0.037\sigma^{-3}$, has the same periodicity as shown by the plots in fig. 10. To confirm this, fig. 10 shows graphs for $\rho_m = 0.037\sigma^{-3}$ for two different values of $\sigma_m = 1.5\sigma$ (circle-black symbols) and $3\sigma$ (star-orange symbols). Also refer to the snapshots in fig. 6.

Furthermore, the snapshots of NPs in fig. 6 show that as $\sigma_m$ increases, the pore size (occupied by EPs) increases and the wall thickness (or the thickness of the NP-network) is seen to decrease. Thus, increase in $\sigma_m$ affects the porosity of the network. We define porosity as the volume fraction of the void inside the NP network. The porosity is calculated by subtracting the NP volume fraction from 1. Figure 11 shows the variation of porosity versus $\sigma_m$ quantifying the observed behaviour of the porosity with the increase in $\sigma_m$. For a given value of $\sigma_m$, an increase in micellar density decreases the available volume for NPs. Therefore, fig. 11 also shows an increase in porosity with the increase in $\rho_m$ at fixed $\sigma_m$. The non-linear behaviour of the plot for $\rho_m = 0.123\sigma^{-3}$ is related to the drop in the number of NPs which can get introduced in the box as one increases $\sigma_m$. Experimentally, the NP porous structure can be obtained by dissolving away the polymeric matrix.

In figs. 6, 7, 8 and 9, we observe the clustering of NPs and micellar chains into different morphologies for values of $\sigma_m \geq 1.5\sigma$, whereas fig. 4 shows that for $\sigma_m = 1.25\sigma$ (the minimum possible value of $\sigma_m$), we obtain a uniformly mixed state of self-assembled micellar chains and NPs. To get an insight into the spatial arrangement of micellar chains, we calculate the pair correlation function $g(r)$ of monomers corresponding to the snapshots shown in figs. 4, 6, 7, 8 and 9. The plots in fig. 12 correspond to $g(r)$ for the snapshots shown in fig. 4 while the plots...
The value of \( \sigma \) different values of micellar densities. It can be seen that the a porous network of NPs. The different symbols indicate the presents the volume fraction of the void (occupied by EPs) inside a porous network of NPs. The different symbols indicate the different values of micellar densities. It can be seen that the porosity of the networks increases with either increase in the value of \( \sigma_n \) or increase in monomer number density \( \rho_m \).

This is consistent with the observation that all micellar chains in fig. 4 are found to exist with NPs in between. With a NP of size 1.5\( \sigma \) between two monomer chains, the monomer chains have no possibility to remain within the range of \( \sigma_m \). Thus, it confirms the observation that for \( \sigma_n = 1.25\sigma \), clustering of micellar chains is not observed and a uniformly mixed state of EPs and NPs is formed.

In contrast to the plots in fig. 12, there appears a peak around 1.75\( \sigma \) in figs. 13(a), (b), (c) and (d). Except for the plots in fig. 13(a), we observe that the peak height decreases with the increase in the value of \( \sigma_n \), and finally vanishes for a sufficiently high value of \( \sigma_n \). The appearance of a peak around 1.75\( \sigma \) is consistent with the observed clustering of WLMs as seen in figs. 6, 7, 8 and 9. As the value of \( \sigma_n \) increases, the NP network gradually starts breaking and hence giving more space for micellar chains to be relatively further away from each other. This explains the decrease in the peak height around 1.75\( \sigma \) with the increase in \( \sigma_n \). When the NP network breaks to the extent that most of the micellar chains get enough volume to be at a distance \( r > 1.75\sigma \), this peak disappears. The value of \( \sigma_n \) at which this happens can be seen to be decreasing with increase in \( \rho_m \), viz. 3\( \sigma \) and 2.25\( \sigma \) for \( \rho_m = 0.093\sigma^{-3} \) and 1.126\( \sigma^{-3} \), respectively.

However, for \( \rho_m = 0.037\sigma^{-3} \) (see fig. 13(a)) the peaks are present around 1.75\( \sigma \) for all the values of \( \sigma_n \). This is because, with an increase in \( \sigma_n \), the network-like structure does not show any tendency to break, see fig. 6. Therefore, for all values of \( \sigma_n \), the WLMs show the clustering of chains that is reflected in the peaks of \( g(r) \) at \( r \approx 1.75\sigma \) for all the values of \( \sigma_n \).

For \( \rho_m = 0.037\sigma^{-3} \), only the network-like structures are observed for the range of values of \( \sigma_n \) considered here, barring \( \sigma_n = 1.25\sigma \). To ensure that the network architecture observed in the snapshots in fig. 6 is not an artefact of the small box size, these structures were reproduced in a larger box size of 60 \( \times \) 60 \( \times \) 60\( \sigma \) for all values of \( \sigma_n \) considered for \( \rho_m = 0.037\sigma^{-3} \). A representative snapshot for \( \sigma_n = 2.5\sigma \) and \( \rho_m = 0.037\sigma^{-3} \) is shown in fig. 14(a). The figure shows that the snapshot has a statistically similar network of micellar chains as in the smaller box size shown in fig. 6. Figure 14(b) shows a magnified image of one of the junctions of the network.

As seen in the snapshots of figs. 7(h), 8(h) and 9(g), (h), the anisotropy of the NP clusters depends on the micellar density. Moreover, the nanoparticle clusters that link together to form a percolating network as in figs. 6(e), 7(e), 8(e) and 9(e) also differ in their anisotropy. Since the morphology of NP-clusters also affects the arrangement of chains and vice versa, the arrangement of micellar chains (pores) can be used to indirectly interpret the anisotropy of the NP structures. The distribution of angle between micellar chains \( P(\theta) \) is analyzed and the plots are shown in fig. 15 for all values of \( \rho_m \). It is calculated by

\[
P(\theta) = \frac{N(\theta)}{\sum \theta N(\theta)},
\]

where \( N(\theta) \) is the total number of pair of chains at an angle \( \theta \). The angle \( \theta \) between two chains is calculated by

\[
\theta = \arccos\left(\frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{|\mathbf{r}_1||\mathbf{r}_2|}\right)
\]
indicates that the distance between adjacent monomer chains. The appearance of a peak around 1.75σ of σm = 0.037σ−3 for the lowest value of monomer number density ρm = 0.037σ−3 for simulations performed in a larger box size of 60 × 60 × 60σ3. This monomer-network is similar to the monomer-network structures obtained in a smaller box size of 30 × 30 × 30σ3 as shown in fig. 6. A magnified image of one of the network junctions is shown in (b). Irrespective of the value of σ4m, all the network structures obtained for ρm = 0.037σ−3 produce statistically similar monomeric network structures (with the same periodicity).

using the largest eigenvectors of the corresponding gyration tensors G of the chains as follows:

\[ \theta = \cos^{-1} \frac{\vec{e}_1 \cdot \vec{e}_2}{|\vec{e}_1||\vec{e}_2|}, \]

where \( \vec{e}_1 \) and \( \vec{e}_2 \) are the largest eigenvectors of G.

The distribution \( P(\theta) \) is normalized for different values of σ4m by dividing it by the number of all possible combinations of the pair of chains. Each plot in fig. 15 shows the distribution of angles between micellar chains for different values of σ4m as indicated in the figures. For ρm = 0.037σ−3, a high value of the distribution around 90° is seen for all values of σ4m. This shows the perpendicular arrangement of micellar chains at the network junction, as can be seen in fig. 14(b). The density correlation plots in fig. 10 and quantitatively similar distribution function for angles in fig. 15(a) for ρm = 0.037σ−3 confirm the periodic architecture of EP networks for all σ4m values, as seen in fig. 6. The distribution plots for the monomer densities ρm = 0.074σ−3 and 0.093σ−3 in figs. 15(b) and (c) show that, after a particular value of σ4m, there appear two peaks around 10° and 90° indicating a preference for a parallel and a perpendicular arrangement of micellar chains, respectively. These are the densities where NPs form sheet-like structures. The parallel arrangement indicates that the chains within an aligned micellar domain form sheet-like structures, see figs. 7 and 8. As a consequence, the NP-clusters also have a sheet-like morphology. The peak around 90° in the distribution plot corresponds to the perpendicular arrangement of these sheet-like domains of aligned micellar chains. We find the formation of sheet-like domains to be unexpected and interesting and the reason for the formation of such structures is explained later in the text.

Finally for the highest micellar density considered ρm = 0.126σ−3, for σ4m ≥ 2σ4, there appears a high peak around 10°. Here, the presence of peaks only around 10° is indicative of the nematic ordering of micellar chains and correspondingly we observe the rod-like structure of NPs. The height of the peaks at 90° gradually reduces from (b) to (d) and resulting in only peaks for parallel arrangement in (d). This is indicative of the change in the anisotropy of NP clusters. This can be confirmed by calculating the shape anisotropy \( S_{AN} \) of NP clusters using the following formula:

\[ S_{AN} = 1 - 3\frac{\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3}{(\lambda_1 + \lambda_2 + \lambda_3)^2}, \]

where \( \lambda_1, \lambda_2, \lambda_3 \) are the eigen-values of the gyration tensor of the NP cluster. Using the above formula, the average shape anisotropy of the nanoparticle clusters shown in snapshots of figs. 7(h), 8(h) and 9(h) is calculated to be 0.165, 0.211 and 0.414, respectively. This shows that the shape anisotropy of the NP clusters increases with the increase in micellar density and the shape of the NP clusters varies from sheet-like to rod-like structures.
clusters. The nanoparticles aggregate when the nanoparticle network breaks into non-percolating clusters. The number of NPs in the system and hence affects the number of monomer-NP contacts. Hence, the effect of the transition function for all micellar densities (see fig. 10 and the discussion of the effective volume of micelles. In the presence of a large number of NPs (in case of a system spanning network of NPs), monomers are more densely packed. This is also confirmed from the height of the peaks of $\sigma_{4n}$, respectively. Each panel shows graphs for different values of $\sigma_{4n}$. The distribution of angles subtended between pairs of micellar chains at different values of monomer densities, $\rho_m = (a) 0.037\sigma^{-3}$, (b) 0.074$\sigma^{-3}$, (c) 0.093$\sigma^{-3}$ and (d) 0.126$\sigma^{-3}$, respectively. Each panel shows graphs for different values of $\sigma_{4n}$. For the lowest micellar density (a), a peak at 90° angle is shown, hence confirming that many of the polymers lie to each other, as seen in the snapshots of fig. 14(b). Plots in (b) and (d) show two peaks: one around 10° and the other around 90°. The peak around 10° corresponds to the formation of aligned domains of micellar chains which result in sheet-like structures, while the peak around 90° shows that the sheet-like domains lie perpendicular to each other. Panel (d) shows a peak for a parallel arrangement of micellar chains only, which indicates the formation of rod-shaped aggregates of nanoparticles.

![Fig. 15](image1)

**Fig. 15.** The distribution of angles subtended between pairs of micellar chains at different values of monomer densities, $\rho_m = (a) 0.037\sigma^{-3}$, (b) 0.074$\sigma^{-3}$, (c) 0.093$\sigma^{-3}$ and (d) 0.126$\sigma^{-3}$, respectively. Each panel shows graphs for different values of $\sigma_{4n}$. For the lowest micellar density (a), a peak at 90° angle is shown, hence confirming that many of the polymers lie to each other, as seen in the snapshots of fig. 14(b). Plots in (b) and (d) show two peaks: one around 10° and the other around 90°. The peak around 10° corresponds to the formation of aligned domains of micellar chains which result in sheet-like structures, while the peak around 90° shows that the sheet-like domains lie perpendicular to each other. Panel (d) shows a peak for a parallel arrangement of micellar chains only, which indicates the formation of rod-shaped aggregates of nanoparticles.

![Fig. 16](image2)

**Fig. 16.** Panel (a) shows the variation in the average length $\langle L \rangle$ of micellar chains with $\sigma_{4n}$, where $L$ is the number of monomers in a particular chain. Panel (b) shows the plot for number of nanoclusters ($N_c$) in the system. The quantity $\langle L \rangle$ shows a decrease in its value at a higher value of $\sigma_{4n}$ where nanoparticle network breaks into non-percolating clusters. The quantity $\langle N_c \rangle$ shows a jump from its value of 1 to a larger value when the nanoparticle network breaks into non-percolating clusters. The nanoparticle aggregates with $\langle N_c \rangle = 1$ span the length of the simulation box as seen in the snapshots and also confirmed by calculating the largest eigenvalue of the gyration tensor for these aggregates.

### 4.5 Understanding the morphological changes

The purpose of the introduction of the parameter $\sigma_{4n}$ is to control the minimum approaching distance between micelles and NPs, but it also influences the arrangement and the number of NPs in the system and hence affects the effective volume of micelles. An increase in the value of $\sigma_{4n}$ indicates an increase in the effective volume of micelles. We remind the reader that the effective volume of micelles also gets modified by the density of NPs present in the system as well as their organization and number of monomer-NP contacts. Hence, the effect of the transformation from network-like structure to non-percolating clusters with increase in $\sigma_{4n}$ can be understood in terms of change in the effective volume of micelles.

From the experimental perspective, different values of $\sigma_4$ would correspond to WLMs of different chemical compositions such that they have different diameters. Here, it is kept constant ($\sigma_4 = 1.75\sigma$). Now, with a given value of $\sigma_4$ and $\rho_m$, the parameter $\sigma_{4n}$ effectively determines the space available for the incoming NPs in the simulation box. Experimentally, in the micelle-NP mixture (with fixed value of $\sigma_4$), the effective range of repulsion between WLMs and NPs can be tuned by changing the value of $\sigma_{4n}$, and thereby controlling the effective volume available to NPs. That, in turn, will determine the morphology of NP mesostructures formed in the presence of a background micellar matrix.

A characteristic quantity that changes with the density of monomers is the average length of monomer chains. The average chain length of WLMs $\langle L \rangle$, increases with increase in the value of monomer density. In the presence of a large number of NPs (in case of a system spanning network of NPs), monomers are more densely packed. This is also confirmed from the height of the peaks of $g(r)$ in fig. 13. Therefore, the effect of the change of NP morphology from network to non-percolating clusters within the increase in $\sigma_{4n}$ is expected to be seen in the value of $\langle L \rangle$. We first discuss the behaviour of $\langle L \rangle$ with an increase in $\sigma_{4n}$, as it will help us quantitatively better appreciate the behaviour of the effective volume fraction of micelles.

The behaviour of $\langle L \rangle$ for different values of $\rho_m$ is shown in fig. 16(a). At $\sigma_{4n} = 1.25\sigma$, the average length increases with an increase in $\rho_m$. This is also consistent with the snapshots shown in fig. 4. On increase in the value of $\sigma_{4n}$ from 1.25$\sigma$ to 1.5$\sigma$, this trend is reversed. This is due to the fact that, on increase of $\sigma_{4n} = 1.25\sigma$ to 1.5$\sigma$, the NPs and the WLMs undergo a change in their arrangement from (a) dispersed phase to (b) network-like structure of aggregates of NPs and WLMs, respectively. This transition is such that the network-like structure of WLMs has the same period for the density-density correlation function for all micellar densities (see fig. 10 and the corresponding snapshots in figs. 6, 7(a), 8(a) and 9(a)). At $\sigma_{4n} = 1.5\sigma$, the WLMs with a high $\rho_m$ are more “crushed” (have smaller chains) compared to the systems with lower $\rho_m$. Therefore, denser micellar systems have lower $\langle L \rangle$ for this particular value of $\sigma_{4n}$.
With increase in the value of $\sigma_{4n}$ to values greater than $1.5\sigma$, the NP networks start breaking into non-percolating clusters. Due to the presence of higher number of monomer-NP contacts in the systems with higher $\rho_m$, the effect of the increase in the value of $\sigma_{4n}$ on effective volume of WLMs is also greater. Therefore, for the same increase in the value of $\sigma_{4n}$, the relative decrease in the number of NPs is greater at a higher value of $\rho_m$. Hence, the percolating nanoparticle network is “more easily broken” at a higher $\rho_m$. Hence, for $\sigma_{4n} > 1.5\sigma$ the $\langle L \rangle$ increases with $\rho_m$ at fixed $\sigma_{4n}$, as was discussed previously for the $\sigma_{4n} = 1.25\sigma$ system. In fig. 16(b), we identify and plot the number of NP-clusters $N_c$ in the simulation box. When $N_c > 1$, we can identify the value of $\sigma_{4n}$ at which the percolating cluster of NPs breaks down into smaller clusters at each value of $\rho_m$.

The effective volume of WLMs ($V_{m_{eff}}$) depends on the combination of the value of $\sigma_{4n}$, the NP number density and more importantly, the number of contacts with NP and monomers. Therefore, at a higher value of $\sigma_{4n}$ (i.e. $> 2.5\sigma$, when the introduction of NPs inside the system becomes relatively difficult), the effective micellar volume decreases and hence a decrease in $\langle L \rangle$ can be seen. This decrease in the average length is an indication of the breaking of NP network. This decrease starts at $\sigma_{4n} = 2.25\sigma$, $3.25\sigma$ and $3.5\sigma$ for $\rho_m = 0.126\sigma^{-3}$, $0.093\sigma^{-3}$ and $0.074\sigma^{-3}$, respectively. In conclusion, the behaviour of $\langle L \rangle$ clearly indicates the existence of two points of structural changes. The first one is for the change from dispersed state to clustering of micellar chains (from $\sigma_{4n} = 1.25\sigma$ to $\sigma_{4n} = 1.5\sigma$), and the other is for the breaking of NP network into non-percolating clusters at a higher value of $\sigma_{4n}$.

Since the changes in behaviour $\langle L \rangle$ indicates a corresponding change in $V_{m_{eff}}$, a decrease in the value of $V_{m_{eff}}$ is expected around the point of transformations. To confirm these observations, the behaviour of the volume fractions of the constituent particles and the average energies of NPs and monomers are examined, and the plots are shown in figs. 17 and 18, respectively.

Figure 17 shows (a) the plot of the effective monomer volume fraction $V_{m_{eff}}/V$ (b) NP volume fraction $V_m/V$ and (c) the ratio of effective volume fraction of monomers to monomers volume fraction $V_{m_{eff}}/V_m$. Change in the value of $\sigma_{4n}$ from $1.25\sigma$ to $1.5\sigma$ corresponds to the formation of clusters of micellar chains from a dispersed state as discussed before. These clusters of micellar chains join to form a system spanning network-like structure, and this shows up as a small peak in the value of $V_{m_{eff}}$ at $\sigma_{4n} = 1.5\sigma$. With further increase in $\sigma_{4n}$, the $V_{m_{eff}}$ increases at first but then starts to decrease after a certain value of $\sigma_{4n}$ (e.g., for $> 2.25\sigma$ for $\rho_m = 0.126\sigma^{-3}$) for the three highest values of $\rho_m$. The decrease in the value of the effective volume fraction of monomers corresponds to the transition from the network-like morphology of NPs to non-percolating clusters. This change in NP-morphology is not observed for the lowest density of micelles for the values of $\sigma_{4n}$ considered here. Hence, for this case, the quantity $V_{m_{eff}}/V$ keeps on increasing for $\rho_m = 0.037\sigma^{-3}$.

In fig. 17(b), the NP volume fraction decreases with an increase in $\sigma_{4n}$ as introducing NP in the system becomes increasingly difficult with an increase of $V_{m_{eff}}$.

The ratio of the effective volume fraction of monomers to their actual volume fraction $V_m$ (see fig. 17(c)) shows the extent of the effect of $\sigma_4$ and $\sigma_{4n}$ on the effective volume fraction of micelles. Its behaviour is similar to the behaviour of $V_{m_{eff}}/V$. The behaviour of the ratio $V_{m_{eff}}/V_m$ also incorporates the role of the arrangement of constituent particles and hence the morphology of the system. A high value of $V_{m_{eff}}/V_m$ indicates the presence of a large number of interacting monomer-NP pairs and this can lead to a clustering of WLMs in the midst of NP-clusters. When ($V_{m_{eff}}/V_m$) $\approx$ 1, a dispersed state of WLMs is shown at $\sigma_{4n} = 1.25\sigma$ since $\sigma_{4n}$ is comparable to $1.25\sigma$. At higher values of $\sigma_{4n}$, the presence of relatively few NPs in the WLM matrix leads to ($V_{m_{eff}}/V_m$) $\approx$ 1.
The monomers with number densities $\rho_m$ (see legends). The lines showing variation in the PE of monomers and PE of nanoparticles intersect at some intermediate value of $\sigma_m$. The point of intersection is shown by dashed vertical lines. The change from micellar densities decreases when $\rho_m = 0.037\sigma^{-3}$ and $\rho_m = 0.093\sigma^{-3}$. On the other hand, for $\rho_m = 0.074\sigma^{-3}$ and $\rho_m = 0.093\sigma^{-3}$, the quantity $\langle E_m \rangle$ decreases when $\sigma_m$ changes from 1.25$\sigma$ to 1.5$\sigma$. The monomers with number densities $\rho_m = 0.126\sigma^{-3}$ and $\rho_m = 0.093\sigma^{-3}$ are “crushed” between nanoparticle clusters. They form smaller chains compared to the systems with number densities $\rho_m = 0.037\sigma^{-3}$ and $\rho_m = 0.074\sigma^{-3}$ (see fig. 16). The existence of smaller chains in the box increases the values of both $V_2$ and $V_4$ for $\rho_m = 0.126\sigma^{-3}$ and $\rho_m = 0.093\sigma^{-3}$. Hence, the energy of monomers $\langle E_m \rangle$ shows an increase in its value for $\rho_m = 0.126\sigma^{-3}$ and $\rho_m = 0.093\sigma^{-3}$ but decreases for $\rho_m = 0.037\sigma^{-3}$ and $\rho_m = 0.074\sigma^{-3}$, for the same change in value of $\sigma_m$ from 1.25$\sigma$ to 1.5$\sigma$. For the same change in $\sigma_m$ (from 1.25$\sigma$ to 1.5$\sigma$), the energy of NPs $\langle E_n \rangle$ show a decrease in their value. This decrease in nanoparticle energy is a result of an increase in the packing of (attractive) nanoparticles due to an increase in $\sigma_m$.

With further increase in $\sigma_m$, $\langle E_m \rangle$ decreases while $\langle E_n \rangle$ shows an increase. This decrease in $\langle E_m \rangle$ is due to the increase in the effective volume fraction of monomers, which in turn results in an increased chain length. However, $\langle E_n \rangle$ again shows an increase after $\sigma_m = 2\sigma$, $\sigma_m = 3\sigma$ and $\sigma_m = 3.25\sigma$ for $\rho_m = 0.126\sigma^{-3}$, $\rho_m = 0.093\sigma^{-3}$ and $\rho_m = 0.074\sigma^{-3}$, respectively. This increase in the value of $\langle E_n \rangle$ corresponds to the breaking of the nanoparticle network into non-percolating clusters that results in the decrease in micellar chain length (see figs. 16 and 17(a)). Thus the dependence of the average monomer energy on $\rho_m$ changes for the change in $\sigma_m$ from 1.25$\sigma$ to 1.5$\sigma$; this is a consequence of the change from the dispersed state of chains of monomers to the network-like structure.

Moreover, the transition from the nanoparticle network to non-percolating clusters is also indicated by an increase in $\langle E_n \rangle$ for higher values of $\sigma_m > 1.5\sigma$. In fig. 18 the points of intersection of both the energies are shown by vertical lines (dashed). As the NP network gradually breaks with the increase in the value of $\sigma_m$, the NP energy increases and the energy of monomers decreases. At a value of $\sigma_m$, just higher than the point of intersection of these two energy plots, the nanoparticle network breaks into individual clusters. With the decrease in micellar density $\rho_m$, the point of intersection of the two energies gets shifted to higher values of $\sigma_m$. Correspondingly, with the lowering of $\rho_m$, the value of $\sigma_m$ at which the NP network breaks into non-percolating clusters also gets shifted to higher values of $\sigma_m$.

All these observations can be well explained in a plot of the effective micellar volume fraction $V_m = \langle V_m \rangle$ versus the NP volume fraction which is shown in fig. 19(a). The orange dashed vertical line divides the parameter space into two regions; the region to the right of the line is where NP (and polymer) network morphologies are observed. The region on the left of the line marks the parameters for which the NPs form non-percolating clusters. The rightmost point for each case of micellar density (the maximum value of NP volume fraction for each $\rho_m$) belongs to the system which has WLMs dispersed in between NPs.
the regions having the points showing uniformly dispersed and network-like structures of WLMs are not well separated and they overlap. If we replot this graph with the variable along the Y-axis replaced by \( V_m^{\text{eff}}/V_m \), then the regions with the dispersed and the network of clusters of micellar chains can also be clearly distinguished and both the morphological transformations can be marked on the diagram. This is shown in fig. 19(b).

In fig. 19(b), the parameter space is divided into 4 regions: 1, 2, 3, and 4. The points in region-1 are for \( \sigma_{4n} = 1.25\sigma \) which form a dispersed state WLMs. These points are joined by a (thin, green) horizontal line intersecting the Y-axis at \( \approx 1 \). Region-2 shows the systems with network-like morphologies of both NPs and WLMs. Region-3 represent the systems forming non-percolating clusters of NPs between the clusters of WLMs. Finally, the region-4 depicts the systems with non-percolating clusters of nanoparticles in the background matrix of non-clustered WLMs. Each colour corresponds to a particular micellar density \( \rho_m \), consistent with the legend color of fig. 19(a). For a particular value of \( \rho_m \), the different morphologies of the system are indicated by the different symbol patterns.

At \( \sigma_{4n} = 1.25\sigma \) and for all the values of \( \rho_m \), the value of the ratio \( V_m^{\text{eff}}/V_m \), remains \( \approx 1 \). All such points are joined by a thin green horizontal line at \( V_m^{\text{eff}}/V_m \approx 1 \) intersecting the Y-axis at \( \approx 1 \) at the bottom right corner of fig. 19(b). An increase in the value of \( \sigma_{4n} \) from 1.25\( \sigma \) to 1.5\( \sigma \) results in the onset of formation of clusters of micellar chains and a percolating network of NPs. All such points are indicated by the corresponding symbol marked “Network”: these morphologies span over a large parameter space in the graph. All the symbols that represent the percolating network of NPs and the corresponding WLM-clusters are located above a value of \( V_m^{\text{eff}}/V_m \approx 2 \): this is marked by a dashed horizontal line.

At higher values of \( \sigma_{4n} \) (depending on \( \rho_m \)), the NP networks break to form non-percolating clusters (marked “Clusters”). This corresponds to a decrease in the value of the effective volume of micelles and all such points are shown by the corresponding symbol for non-percolating clusters of NPs. Depending on the value of \( \rho_m \), the morphology of these non-percolating clusters changes from sheets to rodlike structures and are suitably labelled by arrows. For all the values of \( \rho_m \), the change from network-like morphology to non-percolating clusters of NPs is observed to occur at a value of NP volume fraction \( \approx 0.08 \); this is shown by a dashed orange vertical line.

All the observations discussed in this paper for the NP-micellar system can be understood by examining the behaviour of the average potential energies (PE) involved in the system. The plots of these potential energies \( E_2, E_3, E_{2n}, E_4, E_{4n} \) are shown in figs. 20(a), (b), (c), (d) and (e) due to the potentials \( V_2, V_3, V_{2n}, V_4 \) and \( V_{4n} \), respectively. All the PE values are averaged over 10 independent runs with \( (1-2) \times 10^6 \) iterations in each run. The error bars are too small to be visible. Moreover, these potential energies are normalized by dividing them with the number of the interacting particles that are relevant for the concerned potential.

A lower value of \( E_2 \) is indicative of a higher value of \( \langle L \rangle \). The behaviour of \( E_2 \) in fig. 20(a) shows an increase for a change of \( \sigma_{4n} = 1.25\sigma \) to 1.5\( \sigma \) at both \( \rho_m = 0.126\sigma^{-3} \) and \( \rho_m = 0.093\sigma^{-3} \), indicating scission of chains. At other values of \( \rho_m \), \( E_2 \) decreases with increase in \( \sigma_{4n} \), indicating a corresponding increase in \( \langle L \rangle \). However, with further increase in \( \sigma_{4n} \), \( E_2 \) shows an upturn (except for \( \rho_m = 0.037\sigma^{-3} \)). This occurs at \( \sigma_{4n} = 2.25\sigma \) for \( \rho_m = 0.126\sigma^{-3} \); at \( \sigma_{4n} = 3.25\sigma \) for \( \rho_m = 0.093\sigma^{-3} \), and at \( 0.074\sigma^{-3} \) for the highest \( \rho_m \). Thus, it is consistent with the behaviour of the average length of WLM chains shown in fig. 16. Analyzing fig. 20(b), longer chains give rise to a large number of bonded triplets along a chain resulting in a higher value of \( E_3 \). Therefore, the decrease in the value of \( E_3 \) for change of \( \sigma_{4n} = 1.25\sigma \) to 1.5\( \sigma \) for \( \rho_m = 0.126\sigma^{-3} \) and \( \rho_m = 0.093\sigma^{-3} \) is indicative of the formation of smaller chains at 1.5\( \sigma \), consistent with previous analysis. Moreover, with further increase in the value of \( \sigma_{4n} \), \( E_3 \) shows relatively higher values indicating the presence of longer chains.

The PE of interacting NPs \( E_{2n} \), shown in fig. 20(c), also shows a decrease at 1.5\( \sigma \) indicating an increase in the packing of nanoparticles in spite of the decrease in its number density. It then shows an increase in its value at a higher value of \( \sigma_{4n} \), due to a decrease in its number density. The PE \( E_4 \) in fig. 20(d), a measure of \( V_4 \) between adjacent micellar chains, shows an increase when the micellar chains transform to a network-like structure at \( \sigma_{4n} = 1.5\sigma \) from a dispersed state at \( \sigma_{4n} = 1.25\sigma \). The quantity \( E_4 \) then drops indicating that the average distance between WLMs increases as \( \sigma_{4n} \) increases. The repulsive potential \( V_{4n} \) between NPs and WLMs contributes to \( E_{4n} \) shown in fig. 20(e). The quantity \( E_{4n} \) also shows the two points...
of morphological transformations, first a decrease in $E_{4n}$ at $\sigma = 1.5\sigma$ for all values of $\rho_m$, and then an increase in $E_{4n}$ as NP-monomer contacts increase with increase in $\sigma_{4n}$, again followed by a decrease as the number of NPs decrease in the box as percolating NP-clusters break into non-percolating ones. The decrease in $E_{4n}$ at $\sigma_{4n} = 1.5\sigma$ is due to the re-organization of WLMs to form clusters: this reduces the number of monomer-NPs contacts. The values of the repulsive potential energies $E_4$ and $E_{4n}$ are of the order of $10^{-2}k_B T$, thereby, indicating that the re-arrangement of the system architecture with the increase in $\sigma_{4n}$ is to avoid the repulsive interactions within the system.

Thus, the plots of $E_4$ and $E_{4n}$ with low values ($\sim 10^{-2}k_B T$) points to the emergence of different self-assembled structures as a consequence of the system trying to decrease the interfacial interactions. The repulsive interaction potential $V_{4n}$ between NPs and WLMs will lead to a phase separated state at higher NP densities to reduce the mutual repulsion. But the presence of the steep repulsive potential $V_4$ between WLMs evokes a competition between $V_4$ and $V_{4n}$. Micellar chains, aligned in parallel such that the distance between them is $r < \sigma_4$, will lead to a higher contribution to the total PE due to steep rise in $V_4$. Therefore, reducing the combined value of $E_4$ and $E_{4n}$ not only requires a reduction of the inter-face area between WLMs and NPs but also encourages WLMs to arrange such that they are out of the range of $V_4$.

For a system with low $\rho_m$ (fig. 6), the perpendicular arrangement between micellar chains which meet at the junctions of the network (see fig. 14(b) and fig. 15) is a consequence of the requirement to reduce the repulsive interaction between them. By remaining at an angle of 90°, the possibility of the chains of monomers coming in contact with each other is very low. With an increased value of $\rho_m$ (figs. 7 and 8), the $\langle L \rangle$ of WLMs increases. Therefore, at higher monomer densities if the same structure as shown in fig. 6 is maintained, it would lead to an increased width of the WLM clusters and higher contributions from $V_4$. Hence, the WLMs align themselves in parallel and form thin sheet-like domains to reduce the number of contacts between themselves, compared to (say) hexagonally packed cluster of lines. The steep increase of $V_4$ with decrease in $r_4$ rejects the Monte Carlo steps which bring the monomers from adjacent chains just below $\sigma_4$. Hence, the values of $E_4$ remains much lower than $k_B T$.

Moreover, the arrangement of these sheetlike planes at an angle perpendicular to neighbouring domains (as noted in fig. 15(b) and (c)) also seems to be the part of the strategy to lower $V_4$ between WLMs. At even higher values of $\rho_m$ ($= 0.126\sigma^{-3}$), large system spanning sheets of WLMs will result in a energy cost in $E_{2\sigma}$, if the attractive NP become fragmented clusters at intermediate values of $\sigma_{4n}$. Therefore, in such cases, the NPs prefer to nematically arrange themselves in clusters trying to maintain a distance $r > 1.75\sigma$ from each other. In fact, for values of $\epsilon_n$ lower than what is reported in this study, we have in fact obtained parallel system-spanning layers (sheets) of WLMs and NPs.

5 Discussion and conclusion

In this paper, we examine in detail the behaviour of mixtures of attractive nanoparticle (NPs) and equilibrium polymers (EPs), e.g. wormlike micellar systems, with the variation of the monomer number density $\rho_m$ and the excluded volume parameter (EVP) between micellar chains and nanoparticles. The density of monomers which self-assemble to form equilibrium polymers affects the self organization of aggregates of NPs, which in turn affect the organization and length of the self-assembled polymeric chains. The method used to obtain these results was a suitably adapted semi-grand-canonical Monte Carlo simulation, where the mixture of nanoparticles and polymers was allowed to relax towards equilibrium for $\sim 10^6$ MCS, but was also periodically perturbed between every 50 MCS. This perturbation allowed NP-exchange by exposing the simulated system to a NP-particle-bath such that 300 attempts were made to introduce and remove nanoparticles after every 50 MCS. This also helped to effectively change the positions of NPs to very different locations. This would be important to relax the system, because given the relatively high density of particles in the system the NPs could trapped locally for long times in a glassy cage of neighbouring particles. But this MC scheme breaks the detailed balance, and makes the system essentially non-equilibrium.

One obtains a number of interesting near-equilibrium (kinetically arrested) configurations of NP morphologies, starting from a mixed phase of NPs and EPs, obtained when the size of NPs are relatively small compared to the width of micellar chains. For higher values of the EVP, the morphology of the NP aggregates changes to porous percolating connected network of NPs, where the thickness of the pores can be suitably controlled by the EVP and number density of monomers. On further increase of EVP, the NPs form disconnected aggregates with varying shape anisotropy values. The NP aggregate between clusters of semi-flexible polymeric chains, hence instead of nucleating to spherically symmetric aggregates, they develop into the anisotropic rod-like (or sheet-like) aggregates which grow parallel to the alignment of background semi-flexible micellar matrix. We establish that the anisotropy of the NP clusters is governed by the density of the equilibrium polymeric matrix.

Furthermore, the steep repulsive potential between neighbouring micellar chains, and its contribution relative to the repulsive potential between chains and NPs, can lead to the formation of the planar sheet-like arrangement of micellar chains due to self-avoidance. This in turn leads to planar sheets of NP-aggregates. Apriori, this was was an unexpected result for us. This and the other morphologies obtained are examples of the production of nanostructures via synergistic interactions of the equilibrium polymeric matrix and the NPs. The value of the volume fraction of NPs for the transformation from network-like morphology to non-percolating clusters of NPs is approximately identified as $\approx 0.08$. We summarize the different morphologies obtained in a (non-equilibrium) phase diagram with the effective volume fraction of EPs and the
volume fraction of NPs on the two axes. There have been experimental studies [68] which explore the fundamental aspects of the wormlike micelle and NP interactions, where they see “double network” of micelles and NPs. But there
the underlying interactions are expected to be different, with chains getting attached to NPs to form a network of micelles. We have considered the purely repulsive interaction between chains and NPs.

Understanding the underlying physical mechanism and energetics of the different morphologies obtained due to synergistic interactions between self-assembling polymers and attractive NPs is expected to help the experimental scientist fine-tune the relevant parameters to control the yield of different porous nanostructures with the required surface area and porosity. The micelles can be dissolved away once the NPs aggregate and self-organize to the suitable morphology. This might have significant relevance, for example, in the design of batteries materials and super-capacitors, where one needs to balance between large surface area (to increase charge storage) as well as large pores to enable quick dynamics of ions during the charging and discharging process, which affects power density. On the other hand, the NPs could also be possibly dissolved away after the self-assembled polymers are made into gels by addition of suitable additives to enable the experimentalist to obtain polymeric sponges as has been demonstrated using ice-templating techniques [69, 70]. We expect the EP-NP morphologies to be kinetically arrested phase separating states, except when the value of $\sigma_{4n} = 1.25\sigma$ when, in all likelihood, we get a thermodynamically stable mixed state.

**Experimental realization:** We use the semi-grand-canonical Monte Carlo scheme to introduce (and remove) NPs at randomly chosen positions in the box, this might seem unphysical and difficult to realize experimentally in a relatively dense polymeric matrix. However, one could possibly have a background solution in which the monomers self-assemble to form equilibrium polymers. Then, appropriate chemical reagents could be periodically added in small quantities, these could quickly diffuse through the background polymer matrix and initiate nucleation of nanoparticles out of the solution. This would then aggregate and self-organize into the suitable morphologies depending on the synergistic interactions with the background polymeric matrix. The nucleation reaction can be stopped at a suitable time, and the system quenched to low temperatures to prevent the evolution of these morphological structures into equilibrium phase separated states.

We acknowledge helpful discussions with Dr. Arijit Bhattacharya, Dr. Guruvansamy Kumaraswamy and Dr. Deepak Dhar. We thank the National Param Super Computing facility (NPSF) of C-DAC, India for use of Yuva cluster, the computer cluster in ISER-Pune, funded by DST, India, by Project No. SR/NM/NS-42/2009. We acknowledge funding and the use of a cluster bought using DST-SERB Grant No. EMR/2015/000018 to A. Chatterji. AC acknowledges funding support by DST Nanomission, India, under the Thematic Unit Program (Grant No.: SR/NM/TP-13/2016).

**Author contribution statement**

AC came up with the model potentials and suggested the investigations of the mixture of nano-particles equilibrium polymer mixtures as a function of $\sigma_{4n}$ and $\rho_{m}$. The simulations and subsequent analysis were done by SM. The first draft of the manuscript was written by SM, but AC took the manuscript to final form.

**Publisher’s Note** The EPJ Publishers remain neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**References**

1. C. Black, K. Guarini, G. Breyta, M. Coburn, R. Ruiz, R. Sandstrom, E. Silkowski, Y. Zhang, I. Vac. Sci. Technol. B: Microelectron. Nanometer Struct. Process. Meas. Phenom. **24**, 3188 (2006).
2. R. Shenhari, T.B. Norsten, V.M. Rotello, Adv. Mater. **17**, 657 (2005).
3. R.B. Thompson, V.V. Ginzburg, M.W. Matsen, A.C. Balazs, Macromolecules **35**, 1060 (2002).
4. A. Haryono, W.H. Binder, Small **2**, 600 (2006).
5. Y. Lin, A. Böker, J. He, K. Sill, H. Xiang, C. Abetz, X. Li, J. Wang, T. Emrick, S. Long et al., Nature **434**, 55 (2005).
6. B. Rosenberg, R. Tenne, Prog. Polym. Sci. **33**, 40 (2008).
7. H.A. Patel, R.S. Somani, H.C. Bajaj, R.V. Jasra, Bull. Mater. Sci. **29**, 133 (2006).
8. R.Y. Lochhead, *The role of polymers in cosmetics: Recent trends*, in *Cosmetic Nanotechnology* (ACS Publications, 2007) Chapt. 1, pp. 3–56, https://pubs.acs.org/doi/pdf/10.1021/bk-2007-0961.ch001.
9. L.M. Katz, *Nanotechnology and applications in cosmetics: General overview*, in *Cosmetic Nanotechnology* (ACS Publications, 2007) Chapt. 11, pp. 193–200, https://pubs.acs.org/doi/pdf/10.1021/bk-2007-0961.ch11.
10. S. Raj, S. Jose, U. Sumod, M. Sabitha, J. Pharm. Bioallied Sci. **4**, 186 (2012).
11. H.M. De Azeredo, Food Res. Int. **42**, 1240 (2009).
12. N. Sozer, J.L. Kokini, Trends Biotechnol. **27**, 82 (2009).
13. V. Mourio, in *Nanocomposites for Musculoskeletal Tissue Regeneration*, edited by H. Liu (Woodhead Publishing, Oxford, 2016) pp. 175–186.
14. P. Dwivedi, S.S. Narvi, R.P. Tewari, J. Appl. Biomater. Funct. Mater. **11**, 129 (2013).
15. C. Ingrosso, A. Panniello, R. Comparelli, M.L. Curri, M. Striccoli, Materials **3**, 1316 (2010).
16. M. Striccoli, M. Curri, R. Comparelli, in *Toward Functional Nanomaterials* (Springer, 2009) pp. 173–192.
17. G. Kedawat, B.K. Gupta, P. Kumar, J. Dwivedi, A. Kumar, N.K. Agrawal, S.S. Kumar, Y.K. Vijay, ACS Appl. Mater. Interfaces **6**, 8407 (2014).
18. L. Gence, V. Callegari, S. Melinte, S. Demoustier-Champagne, Y. Long, A. Dinescu, J. Duval, in *Nanowires Science and Technology* (InTech, 2010).
19. S. Park, S.-W. Chung, C.A. Mirkin, J. Am. Chem. Soc. **126**, 11772 (2004).
20. T.K. Das, S. Prusty, Polym.-Plast. Technol. Eng. **51**, 1487 (2012).
21. A. Turberfield, Phys. World **16**, 43 (2003).
22. S.H. Park, H. Yan, J.H. Reif, T.H. LaBean, G. Finkelstein, Nanotechnology **15**, S525 (2004).
23. M. Alam, A. Siddiqui, M. Husain et al., Express Polym. Lett. 7, 723 (2013).
24. H. Lekkerkerker, W.-K. Poon, P. Pusey, A. Stroobants, P. Warren, Europhys. Lett. 20, 559 (1992).
25. W. Poon, J. Phys.: Condens. Matter 14, R589 (2002).
26. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
27. A. Gast, C. Hall, W. Russel, J. Colloid Interface Sci. 96, 251 (1983).
28. H. De Hek, A. Vrij, J. Colloid Interface Sci. 84, 409 (1981).
29. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
30. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
31. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
32. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
33. A. Gast, C. Hall, W. Russel, J. Colloid Interface Sci. 96, 251 (1983).
34. H. De Hek, A. Vrij, J. Colloid Interface Sci. 84, 409 (1981).
35. G.J. Fleer, A.M. Skvortsov, R. Tunier, Macromol. Theory Simul. 16, 531 (2007).
36. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
37. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
38. A. Gast, C. Hall, W. Russel, J. Colloid Interface Sci. 96, 251 (1983).
39. H. De Hek, A. Vrij, J. Colloid Interface Sci. 84, 409 (1981).
40. G.J. Fleer, A.M. Skvortsov, R. Tunier, Macromol. Theory Simul. 16, 531 (2007).
41. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
42. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
43. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
44. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
45. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
46. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
47. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
48. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
49. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
50. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
51. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
52. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
53. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
54. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
55. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
56. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
57. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
58. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
59. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
60. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
61. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
62. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
63. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
64. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
65. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
66. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
67. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
68. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).
69. W. Poon, J. Phys.: Condens. Matter 14, R859 (2002).
70. S. Asakura, F. Oosawa, J. Chem. Phys. 22, 1255 (1954).