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Thin Polymer-Layers Decorated and Structure Adjustable Crystal of Nanoparticles

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Abstract

A flatterned polymer chains decorated crystal of nanoparticles (NPs) is observed for polymer-NP mixtures confined between two parallel substrates. In order to minimize the entropy lost, polymer chains instead of NPs aggregate at the substrate surfaces when the number of NPs is high enough to have the conformation of chains significantly disturbed. Increasing NP concentration to be much higher than that of polymer chains leads to ordered arrangement of NPs in the central region, which are sandwiched between two thin layers of polymer chains. A scaling model regarding polymer chains as consisting of packed correlation blobs is provided in clarifying the physics mechanism back the formation of thin polymer layer and the crystallization of NPs. The order structure of the crystallized NPs is shown to be switchable through adjusting the bulk concentrations of polymer chains and NPs.

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Studies on polymer-NP mixtures are of general interests in polymer physics and material science [1–5]. Mixing polymer chains with NPs is opening a pathway for engineering flexible composites that exhibit advantageous electrical, optical, and mechanical properties [6–11]. In order to control the macroscopic performance of polymer-NP mixtures, their corresponding microscopic phase behaviors are widely explored. As part of renewed interests in nanocomposites, researchers also have been trying to design new functional materials which combine the desirable properties of NPs and polymer. However, the mechanisms by which NPs interacting with a polymer matrix is still not fully understood [12]. The absence of a general structure-property relationship is one hurdle to the broader use of polymer-NP composites in constructing functional nanomaterials [13]. Establishing the relationship requires a better understanding of the cooperative interactions between flexible polymer chains and nanoscale particles. In general, systems of polymer-NP composites involve various entropic and enthalpic effects. Clarifying the interacting mechanism between different elements of polymer-NP composites is always difficult in experiments and theories, owing to the subtle effect of nanoparticles on the local conformation change of polymer segments. More insights into the physics of polymer nanocomposites can be gained by computational studies to isolate the individual interactions based on simplified models [14]. It assists us in acquiring desired nanomaterials with specified characteristics.

For samples of polymer-NP mixtures on a substrate or confined between two parallel walls, previous theory and experimental works have mostly shown that NPs prefer to aggregate on the surface due to the polymer induced depletion attraction between NP-substrate and among NPs [15–20]. NPs and the substrate surface give a minimum restriction on the local conformation of polymer segments after phase separation between polymer chains in the central region and NPs at the substrate surfaces. In this case, the order pattern of crystallized NPs is solely decided by the geometric structure of the substrate surface. And the crystallization of NPs, started from the substrate surface, can be hindered by amorphous polymer chains in bulk. In order to prevent the direct surface contact between crystallized NPs and the substrate, there are methods of grafting polymer brushes onto the substrate surface or introducing enthalpic attraction between NPs and polymer units [21–26]. As a side effect, however, the order structure of NPs formed on bare substrate surface is eliminated simultaneously when the surface is covered by polymer chains. In this communication, after a large scale of molecular dynamics (MD) simulations, we show an interesting phenomenon of crystallized NPs sandwiched between two thin-polymer-layers. The well ordered arrangement of NPs, decorated by close-packed two dimensional polymer layers with

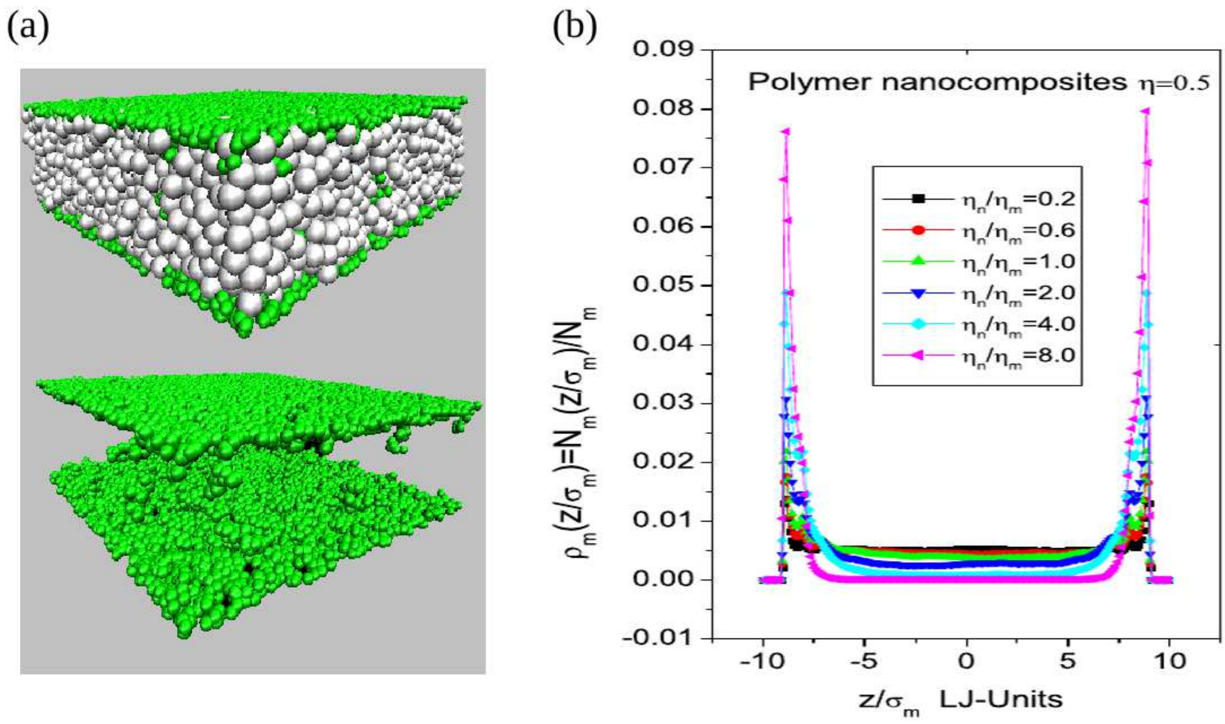

FIG. 1: (a) Snapshot of equilibrated polymer-NP mixtures. Monomers and NPs are displayed in green and white spheres, respectively, $R_\eta = 5$. (b) Density profiles of monomers along the direction perpendicular to the substrate surface at different values of R_η. Here $\sigma_n = 2\sigma_m$, $\eta = 0.5$, and $L_c = 20$.

thickness as large as one monomer size, appears when all contained polymer chains are squeezed out of the central region owing to entropic effects. At a fixed concentration of NPs, the crystal structure of NPs can be eliminated/changed simply by increasing/decreasing the concentration of polymer chains.

In the simulations, the polymer chains were modeled as bead-spring chains without explicit twisting or bending potential. Each chain is composed of $Lc = 20$ Lennard-Jones (LJ) spheres with mass m and diameter σ_m, connected by anharmonic springs governed by a finite extensible nonlinear elastic (FENE) potential [27, 28]. In the mixture we studied, the beads represent spherical Kuhn monomers, and NPs are sphere particles with diameter $\sigma_p = 2\sigma_m$. Note that, in the present paper, we are interested in the structure and behavior of mixtures of particles and polymer chains in the so-called protein limit, in which case the (nanoscale) particle size is comparable to the diameter of single monomer. We use parameters ρ_m and ρ_p to denote the bulk number densities of monomers and NPs, respectively. The volume fraction of monomers $\eta_m = \frac{\pi}{6}\rho_m{\sigma_m}^3$, that of NPs $\eta_p = \frac{\pi}{6}\rho_p{\sigma_p}^3$, and the total volume fraction $\eta = \eta_m + \eta_p$. The ratio of relative values between the concentrations of polymer chains and NPs is defined as $R_\eta = \eta_p/\eta_m$. In the calculations, we use a modified Lennard-Jones (LJ) potential, cut at the minimum and subsequently shifted up to horizontal axis to eliminate any attractive potential, to represent the monomer-monomer, monomer-NP, and NP-NP interactions [29]. All the pair interactions involved are hard-sphere like repulsion. Thereby, the whole system is in athermal case, and its corresponding equilibrium phase behavior has no temperature dependence. In addition, a cut and shifted LJ potential was implemented for the two substrates with positions at $z = -10$ and $z = 10$ to deliver a strong repulsive short-range interaction, which prevents the monomers and NPs from passing through the substrates. The boundary conditions in both x and y directions are periodic, The simulations are carried out using the open source LAMMPS molecular dynamic package. The equation of motion for the displacement of a monomer or NP is given by the Langevin equation [30]:

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = -\nabla U_i - \zeta \frac{d\mathbf{r}_i}{dt} + \mathbf{F}_i\,, \tag{1}$$

where $m_i = 1$ for monomers and $m_i = (\frac{\sigma_{NP}}{\sigma M})^3$ for NPs, $\mathbf{r}_i$ is the position of the ith particle, and U_i is the total conservative potential energy acting on the ith particle. The quantity $\mathbf{F}_i$ is a random external force without drift and a second moment proportional to the temperature and the friction constant ζ. In our simulations, the temperature $T = 1$, a time-step $\Delta t = 0.001\tau_{LJ}$, and the friction coefficient $\zeta = \tau_{LJ}^{-1}$ were implemented.

The polymer induced depletion attraction exists among NPs when they are homogeneously mixing with athermal polymers in bulk [31–33]. It can lead to a de-mixing transition between polymer chains and NPs at high polymer concentrations. The presence of the substrates can significantly alter the equilibrium phases that have been developed in bulk polymer-NP mixtures [16–20]. Our MD simulations show that controlling the competition of different kinds of entropies is a possible way in leading to the desired phase behaviors of NPs mixing with athermal polymer chains confined between two hard substrates. As shown in the part.(a) of FIG.1, phase separation between NPs and polymer chains is clearly observed. Polymer chains are squeezed out of the central region largely occupied by NPs and further form two layers on the substrate surfaces. Note that in all the simulations, polymer chains with concentration very much higher than the critical overlap value[33], are in concentrated regime. In this case, the correlation range among monomers is about two times large of the monomer size for the bead-spring model adopted here[31]. Interactions between different monomers with separation larger than one correlation length ξ are screened from each other by the surrounding other monomers. The concentrated polymer matrix on length scales larger than ξ behaves as a melt of chains made of correlation blobs, and the polymer conformation is a random walk of correlation blobs [34]. The total entropy of the whole system is largely decided by the local conformation change inside each independent correlation blob. Changing the polymer chain length mainly alters the number of correlation blobs being contained for each single polymer chain. This gives a very limited effect on the final structure of the whole system since independent correlation blobs are statistically identical and uncorrelated. Therefore, the equilibrium phase behavior of the corresponding system has no dependences on polymer chain length and distance d between the two substrates, once $Lc >> \xi$ and $d >> \xi$. This can be verified directly by performing simulations for separated systems at two different polymer chain lengths. The equilibrium phase of the considered system is supposed to be fully entropy dominated because all direct interactions involved in the simulations are hard sphere-like. The observation of the sandwich structure of NPs inbetween thin layers composed of polymer chains is opposite to a general understanding of athermal polymer-NP mixtures on substrate or under confinement. Normally polymer chains prefer to stay separated from the substrate surfaces in order to maximizing their conformational entropy. It implies that there is subtle interplay between different entropic effects in managing the equilibrium phase of NPs.

It is well-known that seggregation of NPs onto the substrate surfaces is always the main phenomenon having been observed in experiments and simulations when the bulk concentration of NPs is very much smaller than that of polymer chains. The entropic depletion attraction between NPs and the substrate surfaces is dominated in this case. However, the interacting mechanism can be apparently changed after increasing the percentage of NPs in the polymer-NP mixtures to be very high. The polymer chains can be completely stretched in bulk when NPs are full of the whole system, which results in size increase of individual polymer chains and the lost of their conformation entropy. The equilibrium phase behavior of NPs is thereby not managed merely by the depletion effect. It can be seen in the part.(b) of FIG.1, that the aggregation of polymer chains on the substrates is even stronger as increasing the bulk concentration of NPs while the bulk concentration of polymer chains is correspondingly reduced. Here, we fix the total volume fraction occupied by polymer chains and NPs at a constant value of $\eta = 0.5$. In cases of the relative ratio between the concentrations of NPs and polymer chains being very large, for instance $\eta_n/\eta_m = 8$, all NPs are prevented from direct surface contact with the substrates. It indicates that the entropic depletion attraction is completely eliminated, otherwise polymer chains are repelled from the substrate surfaces and replaced by NPs.

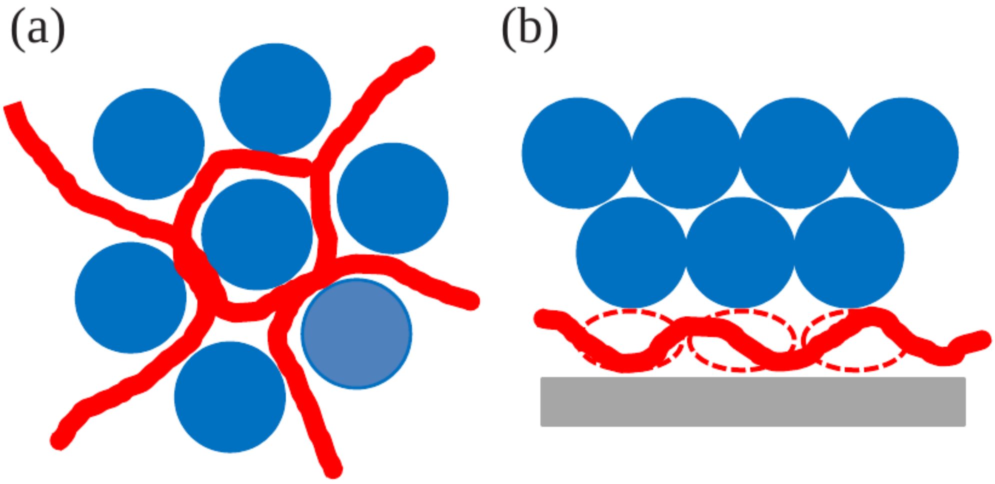

FIG. 2: (a) Sketch of polymer chains being streched by homogeneously mixed NPs in the central region; (b) Sketch of thin polymer layer inbetween substrate and crystallized NPs. The NP is shown in blue, polymer chain is red, substrate is gray, while correlation blobs are dashed contours.

In a previous study on pure polymer chains under confinement, we already knew that the range of the depletion region between the substrate surfaces and the most approaching mass center of polymer chains, contracts with increasing the polymer concentration [20, 35]. It completely disappears when the bulk polymer concentration is larger than a certain value, which is varied depending on the polymeric degree of chains. In such cases, those polymer chains touched on the substrates flatten against the substrate surfaces. The polymer chains are squeezed into two-dimensional thin layers with their surfaces parallel to the substrates, as being compressed in the perpendicular direction by increasing the bulk concentration of polymer chains. The hard surface of the substrates gives no restriction on the value of radius gyration, in parallel dimensions, of the flattened polymer chains. It means that the polymer chains flattened against the substrate surfaces sacrifice their conformation in perpendicular direction in order to maximizing their conformations in parallel dimensions. In addition, polymer chains in the central region are screened from the disturbance of the hard surfaces by the thin layers of the flattened polymer chains. In this way, the total conformational entropy of the whole system is at its maximum.

Based on the understanding of the ”sacrifice mechanism”, we specified that polymer chains in polymer-NP mixtures being squeezed out of the central region is also ascribed to a competition of entropic effects, in analogy to pure polymer chains at high concentrations confined between two hard substrates. Polymer chains at low concentrations are not enough to intrigue depletion attraction among large number of NPs in leading to the aggregation of NPs onto the substrates or in bulk. However, aiming to avoid the stretching of polymer chains which happens due to the extensive existence of NPs, polymer chains are phase separated with NPs. A scaling theory understanding of athermal polymer-NP mixture is to regard polymer chains surrounding NPs as consisting of densely packed correlation blobs[31–33]. The conformation of each correlation blob in three dimensions can be disturbed by NPs mixed homogeneously with polymer chains. As sketched in FIG.2(a), polymer chains are completely stretched in this case. In order to lower the conformation entropy lost, correlation blobs have to be squeezed out of the region occupied by NPs. After phase separation with NPs, for polymer chains adopting two dimensional configuration as thin layers at the substrate surfaces, their corresponding correlation blobs in dimensions parallel to the substrate surfaces are unrestricted by the substrates and NPs in the central region, even though they are under squeezing in the perpendicular direction, see FIG.2(b). In this way, the total conformational entropy of whole polymer chains is enlarged and the free energy is correspondingly lowered, compared to the case of polymer chains being completely stretched by NPs in the central region.

In order to verify our argumentations, here we use ν, the ratio of monomers within areas of $-9.125 \leq z \leq -7.125$ and $7.125 \leq z \leq 9.125$ over the total number of monomers in the system, to define the probability of monomers being squeezed onto the substrates after system is at its equilibrium state. We consider three different situations of $\eta = 0.4$, 0.5, and 0.6, respectively. For each situation, we fix the value of η, and increase R_η gradually. As can be seen in the FIG.3 that the probability of monomers inside the two layers is increased after adding more NPs in the system. η and R_η are the two key factors in controlling the value of ν, i.e. the aggregation degree of polymer chains onto the substrates. Polymer chains can be completely squeezed out of the central region when the system is in its concentrated cases of $\eta = 0.5$ and $\eta = 0.6$, simultaneously the value of η has to be very large, e.g. $R_\eta > 6$. The conformation of polymer chains is significantly limited by the appearance of large number NPs in which case the free space left for the distribution of polymer segments is extremely low. The total entropy lost for the whole polymer chains is minimized in the phase transition of polymer chains from three dimensional coils to two dimensional thin layers flattened against the substrates. It intrigues the phase separation between polymer chains and NPs. In the present case, the entropic effect taking responsibility for the happening of de-mixing is competing with the depletion attraction existed between NPs, which is dominated at low R_η.

A calculation of the density profiles of NPs along the direction perpendicular to the substrate

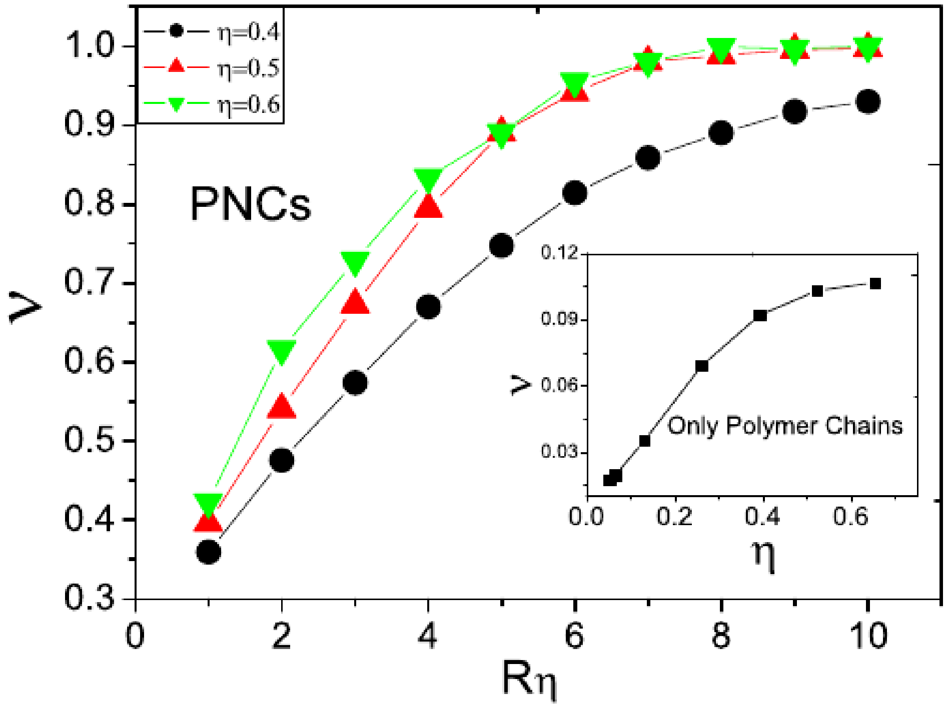

FIG. 3: Averaged probability ν of monomers being squeezed onto the surfaces of walls as function of R_η at different η. The insert shows ν as function of η in pure polymers case. Here $\sigma_n = 2\sigma_m$ and $L_c = 20$.

surfaces shows that, as seen in FIG.4a, the distribution of NPs is at higher order as increasing the bulk concentration of NPs. A perfect layering structure of NPs can be apparently observed over the full range of the system at high values of η and R_η. Note that, in such cases, the polymer chains have been fully squeezed out of the central region occupied by crystallized NPs, and compressed into single thin-layer on each surface of the substrates. The two-dimensional thin layer of polymer chains is normally in amorphous phase due to the connectivity of polymer chains and the correlation between polymer segments, which thereby gives a hindrance to the crystallization of NPs. In FIG.4b the calculation of structure factor of NPs, in dimensions parallel to the substrate surfaces, shows that the order of arrangement of NPs is enhanced by increasing η. The perfect crystal of NPs appears simultaneously with the formation of thin polymer layers at high η and R_η. The crystal structure of NPs sandwiched between two thin polymer layers has not been disturbed by the direct surface contact between polymer chains and NPs. In forming crystal of NPs, the total volume occupied by NPs in central region is contracted and, oppositely, the space for distributing thin polymer layer at each surface of the substrate is increased. In this way, the conformation entropy lost of polymer chains is reduced owing to the extension of squeezed correlation blobs in

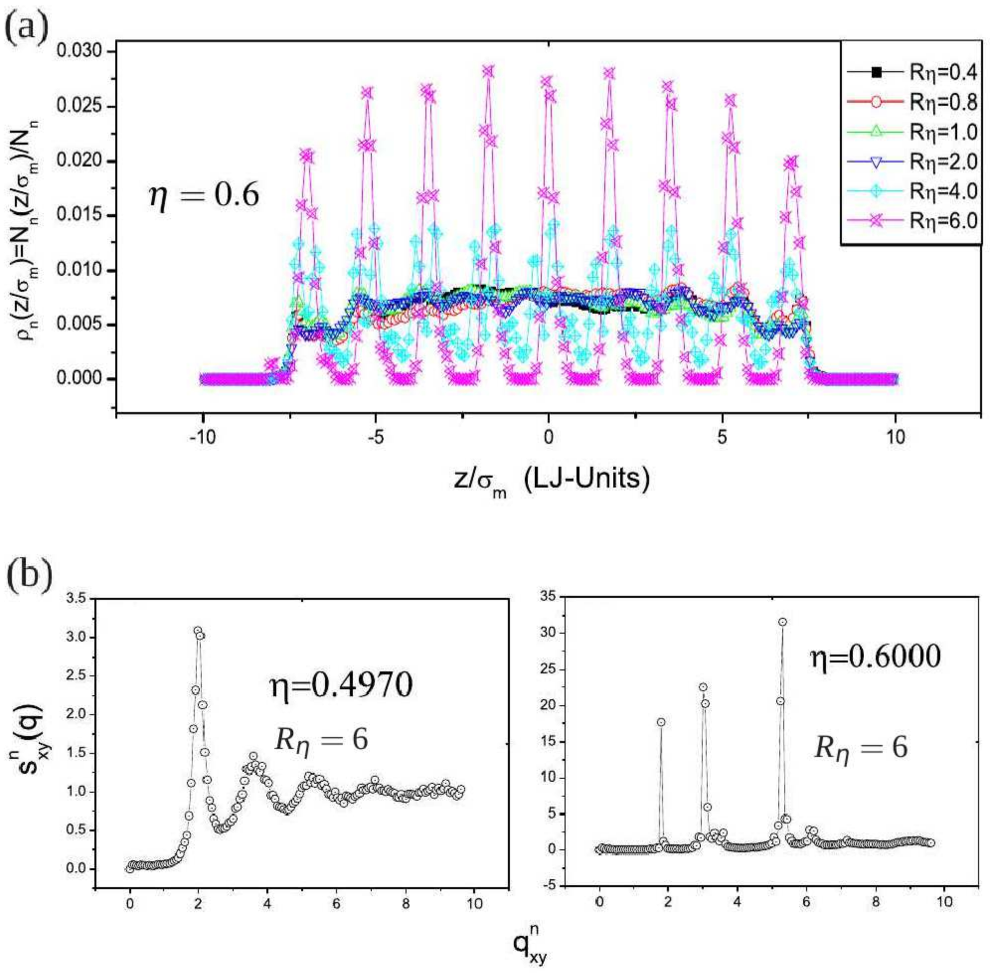

FIG. 4: (a) Density profile of NPs along the direction perpendicular to the surfaces of walls at different R_η, for the case of $\eta = 0.6$. (b) Structure factors of NPs in dimensions parallel to the surface of walls at different η, and $R_\eta = 6$. Here $\sigma_n = 2\sigma_m$ and $L_c = 20$.

perpendicular direction.

Central to discussions of NP-polymer composites is a consideration of enthalpic and entropic interactions when NPs are introduced into polymer matrix. Examples were highlighted in which enthalpic and entropic interactions were exploited to direct the placement of NPs, tailor morphologies, and thereby control the macroscopic behavior of the composite material [36]. It is exciting to consider the extent to which NPs filled polymer materials can be directed to assemble into hierarchically ordered nanocomposites [37, 38]. The observed phenomenon of polymer-decorated crystal of NPs is dominated by the competition of different entropic effects, which is thereby controllable by modifying the local structure of polymer segments at the surfaces of NPs and the

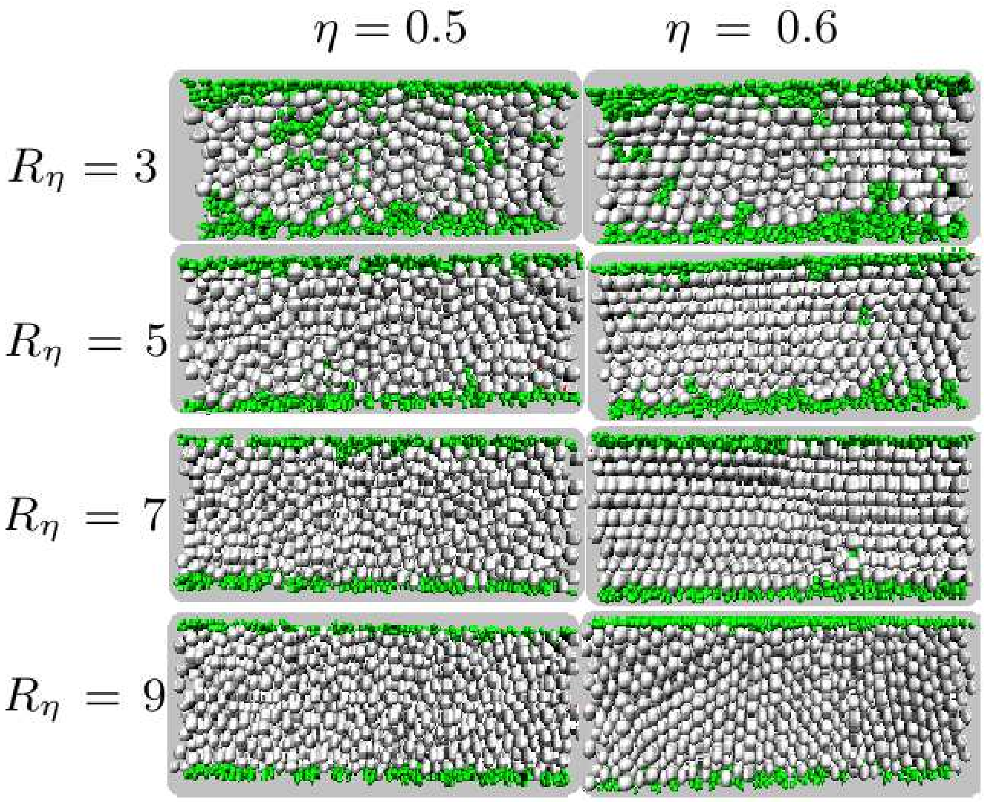

FIG. 5: Snapshots of equilibrated polymer-NP mixtures at different η and R_η. Here $\sigma_n = 2\sigma_m$, and $L_c = 20$.

substrates. Our simulations show that, as can be seen in FIG.5, the crystal structure of NPs is modified by simply changing the relative ratio R_η between the concentrations of polymer chains and NPs. NPs prefer to crystallize as layering structure at small R_η, in which cases the substrate surfaces are closely packed with polymer chains. Increasing the value of R_η to be very large, e.g $R_\eta = 9$, leads to a pyramidal structure of NPs starting from one surface of the substrates. The phase change of NPs is induced by the local conformation change of polymer chains flattened on the substrates. In the latter case, the polymer chains adopting thin layer structure inbetween the substrates and NP are not close-packed in dimensions parallel to the substrate surfaces. It leads to the patterning distribution of polymer chains on the substrate surfaces, and which thereby controls the order structure of NPs in the central region. With these in hand, NP/polymer mixtures hold promise for the fabrication of hierarchically ordered materials that have tailored structures and functionalities that span multiple length scales and dimensions.

In summary, an interesting phenomenon of flattened polymer chains decorated crystal of NPs is observed for polymer-NP mixtures confined between two substrates. The crystallization process of NPs emerges accompanied by the phase separation between NPs and polymer chains, which is clarified to be entropy dominated. The density profile studies have demonstrated that polymer chains prefer to take two dimensional thin layer conformation on the substrates, instead of being stretched by NPs in the central region, when a large number of NPs are contained in the system. The order structure of crystallized NPs is shown to be switchable by tuning the bulk concentrations of polymer chains and NPs. The construction of a complex order structures of polymer-NP mixture remains a challenge but will lead to nanoscale materials with new functionalities. Essential to meeting this challenge is establishing guidelines for discovering assembly methods that yield a desired structure. The finding of the structure tunable crystals of NPs decorated by thin-polymer-layers opens a convenient route for designing novel self-adaptive nanodevices.

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