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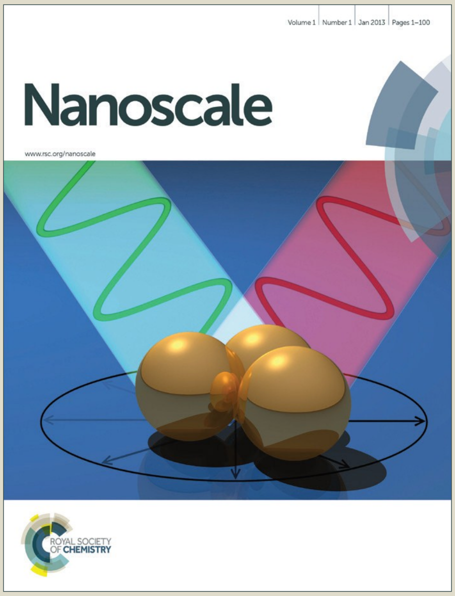

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Theoretical Study of Dispersion-to-Aggregation of Nanoparticles in Adsorbing Polymers from Molecular Dynamics Simulation

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The properties of polymer-nanoparticle (NP) mixtures significantly depend on the dispersion of the NPs. Using molecular dynamics simulations, we demonstrate that, in the presence of polymer-NP attraction, the dispersion of NPs in semidilute and concentrated polymers can be stabilized by increasing the polymer concentration. A lower polymer concentration facilitates the aggregation of NPs bridged by polymer chains, as well as a further increase of the polymer-NP attraction. Evaluating the binding of NPs through shared polymer segments in an adsorption blob, we derive a linear relation between the polymer concentration and the polymer-NP attraction at the phase boundary between dispersed and aggregated NPs. Our theoretical findings are directly relevant for the understanding and control of many self-assembly processes that use either dispersion or aggregation of NPs to yield desired materials.

Polymer-nanoparticle (NP) mixtures, combining the functionality of NPs with the processability of polymers, constitute a new class of nanomaterials exhibiting tunable and novel physical properties [1]. Significant improvements of electrical, optical, and/or mechanical characteristics have been achieved for polymer-based materials by adding NPs into polymers [2–5]. However, a major obstacle in practical applications of nanomaterials made of polymer-NP mixtures is the fabrication of stabilized dispersions of NPs in polymers. A homogenous distribution of NPs is a prerequisite for the full realization of the beneficial effects of the NPs to achieve the optimal performance of corresponding nanomaterials [6]. It is well known that a good dispersion of NPs in polymers is intrinsically difficult to achieve, owing to the unfavorable entropic interactions between polymers and NPs. The entropy gain for polymers associated with the aggregation of NPs usually triggers a phase separation between both components[7]. In order to enhance the dispersibilty of functional NPs in polymers, one promising approach is to introduce an enthalpic polymer-NP attraction. Dispersion of NPs is achieved by promoting favorable interactions, i.e. an approximately vanishing or negative Flory interaction parameter between polymers and the NP surfaces. However, a significant increase of the polymer-NP attraction may result in an aggregation of NPs that are bridged by polymer chains[8]. We conclude and verify in this communication that the phase change of dispersion-to-aggregation of NPs in adsorbing polymers is tunable through changing the polymer concentration, as well as the polymer-NP attraction.

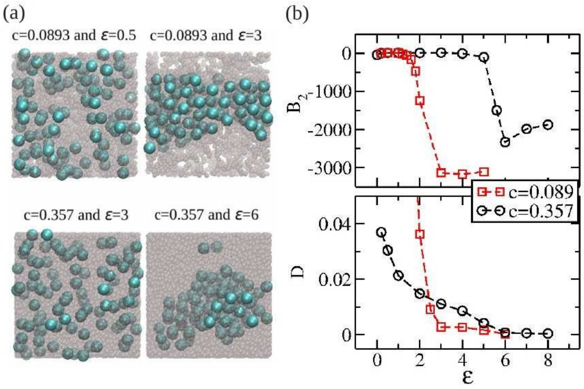

FIG. 1. (color online). (a) Snapshots of equilibrium phases of polymer-NP mixtures at different monomer-NP attractions and polymer concentrations; (b) Second virial coefficient B_2 (upper part) and diffusion coefficient D (lower part) of NPs, as a function of monomer-NP attraction strength, for two different polymer concentrations. Polymer chain length: $N = 64$.

We used a bead-spring model to simulate flexible polymer chains. The connectivity between monomers is enforced by a finite extensible nonlinear elastic (FENE) potential [9]. The NP-NP and monomer-monomer interactions were modeled as attractive contribution fully truncated Lennard-Jones (LJ) potentials [10]. In this way, athermal monomer-monomer and NP-NP interactions are simulated. In addition, a full range LJ potential was implemented for NP-monomer interaction. Thus there is an excess enthalpic energy gain ε for each monomer close to a NP. Note that ε is in unit of k_BT, where the Boltzmann constant $k_B = 1$ and the system temperature was fixed at $T = 1$. Since the pair interactions of NP-NP and monomer-monomer are athermal, increasing the NP-monomer attraction effects as decreasing the system temperature. A variation of the parameter ε then modifies the strength of the enthalpic polymer-NP interaction. The monomer diameter and NP diameter were fixed at constant, $\sigma_M = 1$ (length unit) and $\sigma_{NP} = 3\sigma_M$. σ_M corresponds to a coarse grained monomer and is of order of the Kuhn segment length. For typical synthetic polymers σ_M is of the order of $1.5 - 3$ nm, so σ_{NP} is of the order of $1.5 - 3$ nm. For example, some magnetite and gold particles can be as small as $1 - 3$ nm [11]. The equation of motion for the displacement of a particle (monomer or NP) is given by the Langevin equation [12, 13]. All simulations started from a phase in which NPs and polymers were distributed homogeneously in a cubic box with fixed size $d = 30\sigma_M$. The volume fraction $c = N_{\mathrm{Monomer}}\pi\sigma_M^3/6d^3$ was used to define the polymer concentration, N_{Monomer} being the number of monomers. The system was in the semidilute to concentrated regime, with concentrations above the overlap (about $c = 0.05$ for polymers with chain length $N = 64$) and significantly below the close packing point (about $c = 0.74$) [14]. The number of NPs was kept constant at $N_{\mathrm{NP}} = 100$. The boundary conditions in all directions are periodic. In running simulations, each system was relaxed by a simulation of 10^6 LJ-times, followed by $3 * 10^6$ LJ-times of data acquisition, during which a trajectory of 3000 conformations was stored for the subsequent data analysis. It has been tested in our simulations that the relaxation time used in the simulations is very much long enough to have the system arrived in equilibrium. The simulations were carried out using the open source LAMMPS molecular dynamics package.

In a first series of simulations, the polymer concentration was varied from $c = 0.0893$ to $c = 0.427$. Snapshots of equilibrium phases of polymer-NP mixtures at selected c and ε are shown in FIG.1a. The phase of the NPs, irrespective of whether in semi-dilute ($c = 0.0893$) or concentrated polymers ($c = 0.357$), transformed from a dispersion to an aggregation upon increasing values of the interaction parameter ε. A phase separation between NPs and polymers is clearly observable. Interestingly, the occurrence of the aggregation of NPs in adsorbing polymers can be prevented at high polymer concentrations, as illustrated by the phase transition between the states of $\varepsilon = 3$, $c = 0.0893$ and $\varepsilon = 3$, $c = 0.357$. This is in contrast to the scenario of surface-contacted aggregation of NPs in athermal polymers, which is stabilized upon increasing c [15]. Our results confirm that, along with the attraction strength ε, the polymer concentration c is a key factor in governing the phase behavior of polymer-NP mixtures in the presence of monomer-NP attraction.

The second virial coefficient of the NPs, B_2, obtained from the radial distribution function, $g(r)$,

$$B_2 = -2\pi \int_0^{\infty} [(g(r) - 1]r^2 dr \ , \tag{1}$$

is an indicator of the tendency of NPs to aggregate or to disperse. Note that many-body interactions affect the radial distribution function substantially when NPs are starting to aggregate, which further reduces the pairwise evaluated B_2 coefficient. On the other hand, many-body effects are negligible for NPs that are dispersed in the polymer matrix at sufficiently low concentration. Therefore, the value of B_2 according to Eq.1 can in fact indicate the onset of a phase transition between the dispersed state, at which B_2 is close to zero, and the aggregated state, toward which it rapidly assumes negative values. In FIG.1b we display B_2 as a function of ε at two different polymer concentrations $c = 0.089$ and $c = 0.357$. As is shown in the figure, there exsit a range of polymer-NP attraction strengths, $2.5 < \varepsilon < 5.5$, inside which NPs are aggregated (in the semi-dilute regime, $c = 0.0893$), but dispersed in the concentrated regime ($c = 0.357$). In this range of ε, the NPs display a larger diffusion coefficient D at higher polymer concentrations, as shown in the lower part of FIG.1b. The value of D was computed from the three-dimensional mean-square displacement of the NPs, which is proportional to t during time interval of t,

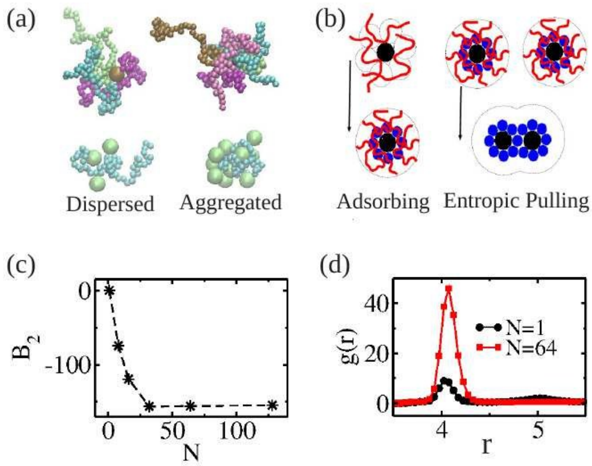

FIG. 2. (color online). (a) Snapshots of polymers surrounding one NP (upper parts), and NPs bridged by a single polymer chain (lower parts) with NPs in a dispersed state ($\varepsilon = 0.5$, left) and an aggregated state ($\varepsilon = 3$, right), at $c = 0.0893$; (b) Sketches of adsorption blobs onto one NP surface (left part), and the 'entropic pulling' induced between NPs (right part). The NP is shown in black, polymer is red, correlation blobs are gray and dashed circles (the larger gray and dashed contours represent correlated ranges surrounding each NP), while adsorption blobs are blue; (c) Second virial coefficient as a function of polymer chain length at constant polymer concentration, $c = 0.357$, and fixed monomer-NP attraction, $\varepsilon = 5$; (d) Radial distribution functions of NPs in the matrices of polymer chains $N = 64$ and unconnected monomers $N = 1$, here $c = 0.357$ and $\varepsilon = 6$.

$$< [r(t) - r(0)]^2 >= 6Dt \ . \tag{2}$$

This result can be explained as follows: In the case of low concentration c, NPs aggregate into clusters with size much larger than the polymer mesh-size. Thereby, the aggregated NPs remain trapped in polymers and can not move much even for a very long timesteps. However, at high polymer concentrations, the dispersed NPs can diffuse inside the mesh of polymers, since the NP size does not exceed much the mesh-size. In this way, we can make difference between the dispersed and aggregated states using the measured value of the averaged diffusion coefficient of the NPs, which is larger than zero for the first case and is almost zero for the second case.

In FIG.2a, we have visualized the local conformations adopted by polymer segments in the vicinity of NPs that are dispersed and aggregated, respectively. One structural feature of the aggregation of NPs in adsorbing polymers is that the entire surface of each NP is covered with monomers. Simultaneously, those polymer chains that are sandwiched between NPs have nearly all of their monomers adsorbed on the surfaces of the aggregated NPs. Whenever the NPs are homogeneously dispersed in the polymers, the number of direct surface contacts between monomers and NPs for each polymer chain is significantly lowered, and the NPs are largely unsheltered by monomers. The results imply that the phase change of dispersion-to-aggregation of NPs is accompanied by a local conformation change of the polymer segments at the surface of NPs. Therefore, the role of correlation effect between monomers has to be considered to clarify the differences between the states in which the NPs are either dispersed or aggregated.

The scaling theory of NPs in athermal polymers [16–19] is based on the idea that the polymers which surround the NPs can be regarded as consisting of densely packed correlation blobs. In order to maximize the conformational entropy of the whole polymers, correlation blobs are squeezed out of the narrow gap between different NPs once they approach each other [15], generating the entropic depletion attraction between the NPs. For each correlation blob being squeezed out, the system free energy lowers about one kT [14]. The squeeze-out of correlation blobs can be prevented by introducing an attraction between polymers and NPs. However, when gradually increasing the attraction, a certain threshold value can be reached above which the conformational entropy contribution of polymer segments within a correlation blob is no longer high enough to offset the enthalpy gain from the polymer-NP attraction. In this case, those correlation blobs at the surfaces of NPs are adsorbed and separate into adsorption blobs. The adsorption blob size ξ_{ads} is always smaller than the correlation blob ξ, provided that adsorption blobs exist[16–19]. The local conformational change of polymer segments in correlation blobs under adsorption, labeled 'adsorbing', is shown in FIG.2b. Based on this scaling concept, we now develop a model to describe the phase transition of NPs between dispersion and aggregation. We assume that the formation of stable adsorption blobs around NPs is the prerequisite for triggering the occurrence of the aggregation of NPs. The whole entropy penalty for the polymers that are adsorbed onto NPs is expected to be reduced if NPs share single layers of adsorption blobs, sandwiched between them. In this way, a lower number of polymer segments is trapped inside the adsorption blobs, and the overall conformational entropy of the system is therefore increased. As sketched in FIG.2b, we claim an entropic force pulling NPs together, thus inducing the aggregation. Note that the 'entropic pulling' discussed here should be distinguished from the well-known 'entropic depletion attraction' induced between NPs in athermal polymers: while both share the same principle of maximizing the total conformational entropy of polymers, the 'entropic depletion attraction' acts to reduce the forbidden volume between NPs by pushing the NPs together. By contrast, for the case of aggregation, polymer segments are released out of the adsorption blobs and into correlation blobs. This difference is the reason for the unexpected behavior found in simulations, that an increasing polymer concentration stabilizes the dispersion of NPs in strongly adsorbing polymers, which is opposite to the situation of NPs in athermal polymers. The correlation blob size is smaller at higher polymer concentrations, which implies a higher number of correlation blobs surrounding the surface of each NP. Therefore, a stronger polymer-NP attraction is required in order to balance out the entropy loss of the adsorbed correlation blobs.

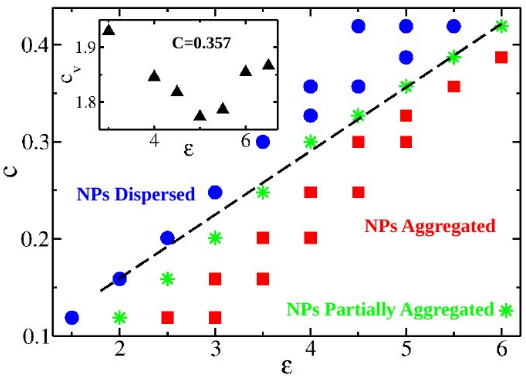

FIG. 3. (color online). $\varepsilon - c$ phase diagram derived from the simulation results. The green stars represent the partially aggregated phase, and the black dashed line is a linear fit to those green stars above $c > 0.2$, here $N = 64$. Insert: Dependence of heat capacity at constant volume on NP-monomer attraction, $c = 0.357$.

The 'entropic pulling' arises from the correlations among monomers, and therefore it diminishes when the polymer length N drops below the average number of monomers inside a correlation blob, $N < \xi^2$. A calculation of B_2, as function of N at constant c and fixed ε, is given in FIG.2c. As long as $N >> \xi^2$, the virial coefficient remains invariant, and it approaches zero once the polymer chains cease to overlap. The 'entropic pulling' does not exist in the case of unconnected monomers, i.e. $N = 1$. A direct comparision between the radial distribution functions of NPs in the matrices of polymer chains ($N = 64$) and unconnected monomers ($N = 1$) is shown in FIG.2d. Since the monomer-NP attraction and other parameters except N are identical for the two cases, the much stronger aggregation found for NPs in polymers is due to the connectivity of polymer chains.

It has been shown that the correlation blob size scales as $\xi \sim c^{-1}$ for polymer chains in the concentrated regime [20], which resembles Θ-like behavior. On the other hand, the adsorption blob size scales as[16–19]

$$\xi_{ads} \sim \frac{kT}{\varepsilon - \varepsilon_{cr}} \,, \tag{3}$$

ε_{cr} being the critical value of ε above which single polymer chains are adsorbed. The transition between dispersion and aggregation of NPs takes place if $\xi \approx \xi_{ads}$. This indicates a linear relation between c and ε, as

$$c \sim \varepsilon - \varepsilon_{cr} \tag{4}$$

for the phase boundary between the dispersed and aggregated states.

Our simulations demonstrate that NPs undergo a sharp transition from a dispersed to an aggregated state upon lowering c, as well as on strengthening ε. The corresponding phase diagram is shown in FIG.3. NPs are considered as dispersed if $B_2 \approx 0$, and in aggregated state if $B_2 << -100$. Partially aggregation of NPs, implying a transition state, is observed when the value of B_2 is of the order of -100. The dispersed and aggregated distributions of NPs can also be directly observed in MD simulations by visualizing the corresponding system-snapshots. The insert of FIG.3 shows the heat capacity at constant volume, c_v, as a function of ε for one certain situation of $c = 0.357$. In this case, the dispersion-to-aggregation transition happens at $\varepsilon \approx 5$. As increasing ε, c_v decreases firstly when $\varepsilon < 5$ and then increases after $\varepsilon > 5$. The decreasing dependence of c_v on ε before the transition is because of the stronger adsorption of polymer segments onto each dispersed NP at higher ε, which lowers the total freedom degrees of the whole system. When ε is above the transition value, we know that, based on the provided "entropic pulling", increasing ε leads to more polymer segments being released from the adsorption onto aggregated NPs. Therefore, the system freedom degrees and heat capacity are increased. The phase boundary between the aggregated and the dispersed distribution of NPs can be fitted to $c \sim \varepsilon + constant$ at $c > 0.2$, according to Eq.(4). In the plot of the phase diagram shown in FIG.3, we only consider a monomer-NP attraction strength of $\varepsilon > kT$. This excludes the aggregation of NPs that is caused by the depletion attraction and occurs in the case of $\varepsilon << kT$ or in athermal polymers [14].

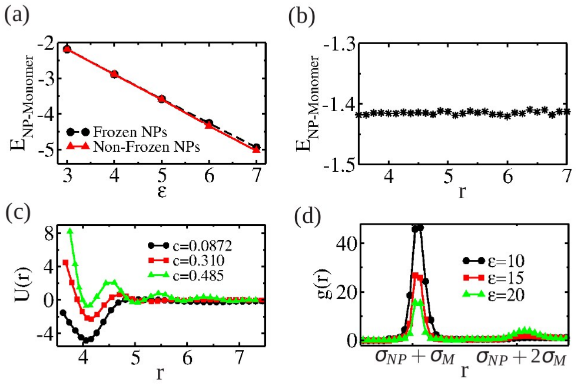

FIG. 4. (color online). (a) The sum of all monomer-NP enthalpic interactions as functions of the monomer-NP interaction parameter ε, for the situation of NPs that are dispersed and immobilized, and for the case of mobile NPs in polymers. $c = 0.357$ and $N = 64$; (b)The sum of all monomer-NP enthalpic interactions at varying separations r between two immobile NPs, r being the mass-center distance. $c = 0.310$, $N = 64$, and $\varepsilon = 5$; (c) Polymer induced potentials between a pair of NPs at different polymer concentrations. $N = 64$ and $\varepsilon = 5$; (d) Radial distribution functions of NPs in the case of strong monomer-NP attractions ($\varepsilon > 10kT$). Here $c = 0.357$, $N = 64$, σ_{NP} and σ_M being the diameters of the NP and the monomer, respectively.

In order to clarify the role that the enthalpic effect is playing in contributing to the phase transition to the dispersion-to-aggregation of NPs, enthalpies derived from direct monomer-NP attractions are computed at different attraction strengths and compared for two systems: (a) NPs are dispersed and artificially 'frozen' (immobilized) inside the polxmer matrix, and (b) NPs are mobile and allowed to assume conformations of low free energies. As can be seen in FIG.4a, the enthalpy difference between the two systems develops gradually and becomes discernable as the monomer-NP attraction strengthens. However, the difference remains small even at $\varepsilon = 7$, already far above the value required for a transition from dispersion to aggregation of the latter system. In FIG.4b, a calculation of the sum of all monomer-NP enthalpic attractions for two NPs in the polymers shows that the enthalpy does not vary with the separation of the NPs. In this calculation, corresponding to each point plotted in the figure, the distance between the two NPs was predefined and fixed. Independent simulations were run for all points at various separations between the NPs. Moreover, direct measurements of the polymer induced effective potential between pairs of NPs have been done under different polymer concentrations, with the results shown in FIG.4c. Details of the procedures of force calculation can be found in our previous work [10]. Based on these calculations, we conclude that there is no significant enthalpic contribution to the free energy changes when the state of NPs transforms between dispersed and aggregated phases in the presence of monomer-NP attraction. It implies that the effective attraction between NPs arises mainly from entropic effects, which are related with changes in the conformational entropy of polymer chains in equilibrium with the NPs.

In FIG.4c, we show that the depth of the primary minimum of the potential of mean force between NPs which is responsible for the aggregation of NPs, becomes shallower with increasing polymer concentration. The weakened attraction supports the observation that an increase of the polymer concentration stabilizes the dispersion of NPs in the presence of strong monomer-NP attraction. In addition, a second minimum in the potential curve is visible at a further separation between NPs. Its appearance is due to an extended entropic depletion attraction induced between monomer-coated NPs [10]. As seen in FIG.4d, an evaluation of the radial distribution function of NPs indicates that, in addition to the main state of the aggregation which involves one layer of monomers sandwiched between NPs, there exists a meta-stable state at very high polymer-NP attractions, in which the sandwiched monomers are not enthalpically interacting with different NPs simultaneously, i.e. monomers are not shared by different NPs. Interestingly, the aggregation of polymer-dressed NPs (and hence with two layers of monomers sandwiched between the NPs) is competing with the aggregation (with a single layer of monomers sandwiched between NPs), once the NP-monomer attraction increases. Our simulations also confirm that upon increasing monomer-NP attractions to extremly large values about $\varepsilon > 10kT$, the adsorption blob consists of a single monomer only, and each NP is irreveribly covered by a single layer of monomers. In this (nearly unrealistic) case, the size of NPs increases to about $\sigma_{NP} + 2\sigma_M$, and the extended depletion attraction starts to govern the equilibrium phase of the dressed NPs.

In summary, our MD simulations show that an increase of the polymer concentration counteracts the aggregation of NPs caused by enthalpic monomer-NP interactions, which thereby, contrary to expectation, stabilizes the dispersion and accelerates the NPs' diffusion. The conclusion appears to corroborate an experimental study investigating the phase structure of NPs in adsorbing polymers [22]. The transition between the dispersed and aggregated states is consistent with the adsorption crossover of polymer segments onto NPs. A nearly linear relation between polymer concentration and the monomer-NP attraction strength has been derived, based on scaling theory, yielding $c \sim \varepsilon + Constant$ for the regimes considered here. Direct computations show that the dispersion-to-aggregation transition of the NPs in adsorbing polymers cannot be related to any significant changes in enthalpy. The occurrence of the aggregation can be understood as an increase in entropy through shared adsorption blobs among different NPs, an effect we may refer to as the 'entropic pulling' effect. Our finding of the controllable dispersion-to-aggregation of NPs in polymeric hosts which is applicable to macroscopic processing provides new opportunities to fabilicate nanoscale structure predefined materials. Furthermore, our developed scaling model offers physics insights into the microscopic behaviors of polymer-NP mixtures, which would be also interesting for understanding the delivery of nanomedcine in biopolymers[21, 23].

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Theoretical Study of Dispersion-to-Aggregation of Nanoparticles in Adsorbing Polymers from Molecular Dynamics Simulation

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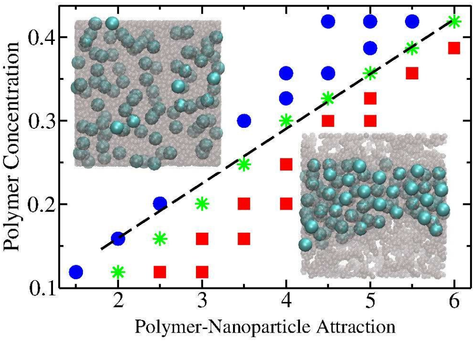

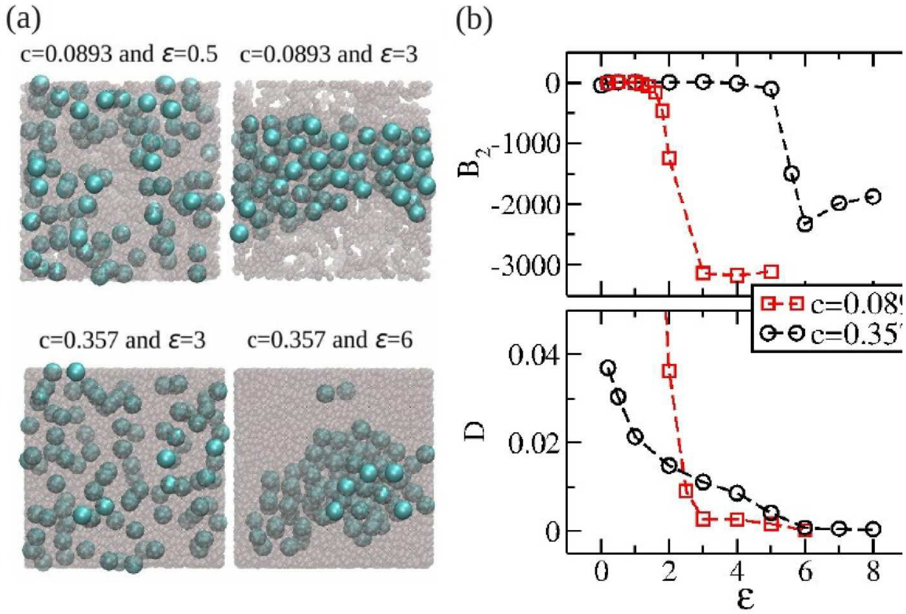

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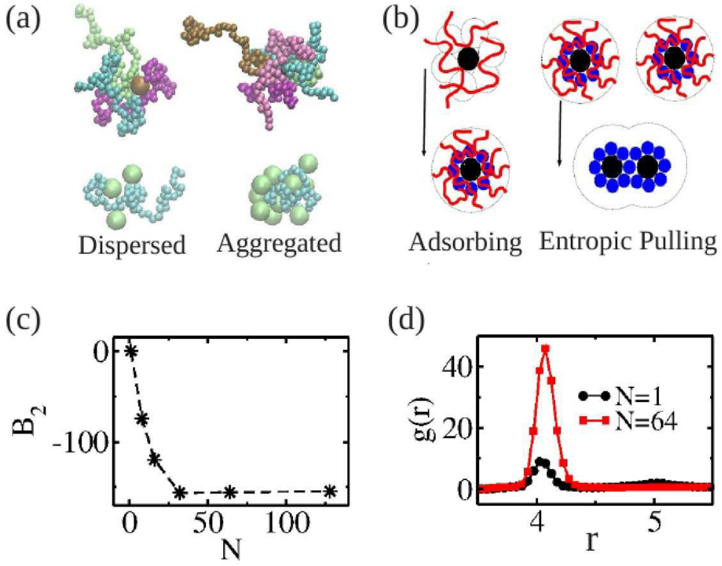

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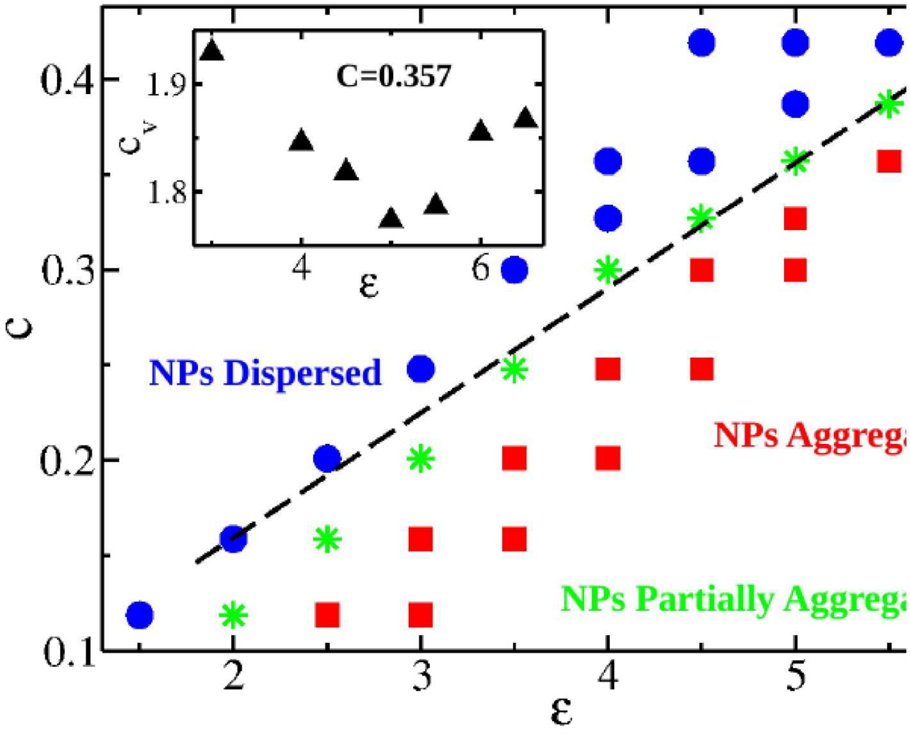

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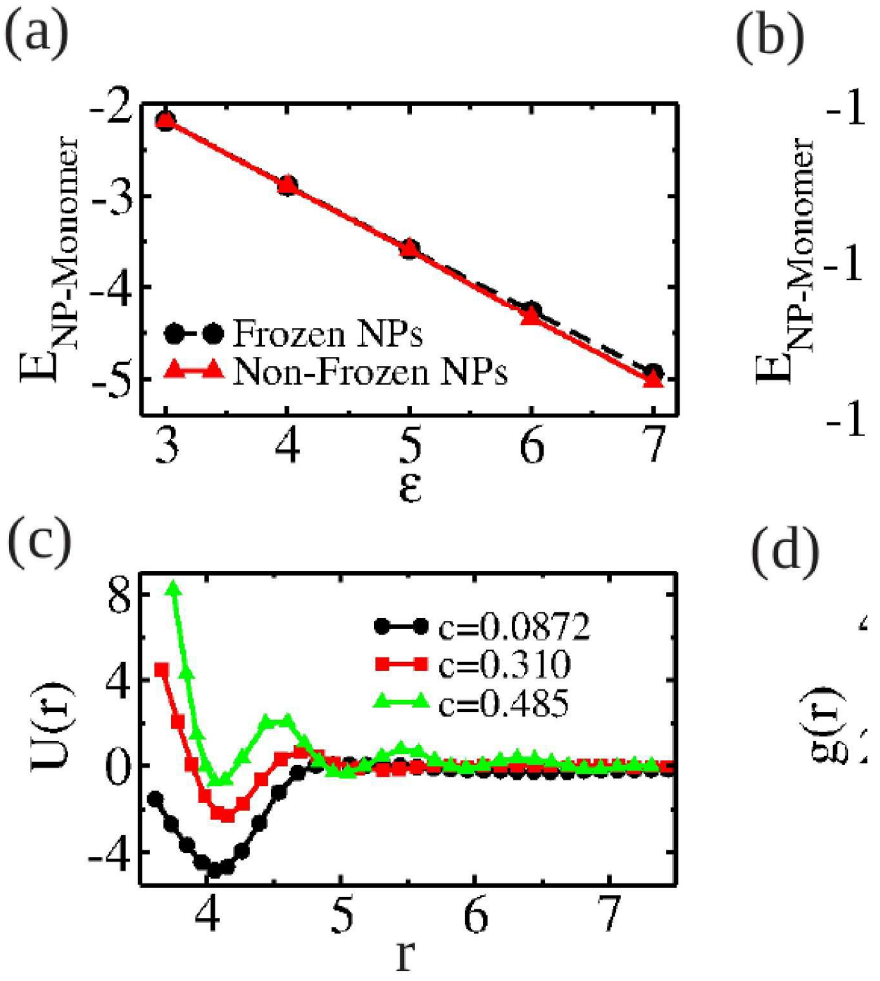

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